CONTRIBUTIONS TO THE
MECHANISMS AND SIMULATION OF
MINERAL PROCESSING OPERATIONS

BY

JAN STEPHANUS JAKOB VAN DEVENTER

A dissertation submitted in fulfilment of the requirements for the
degree of Doctor of Engineering at the University of Stellenbosch

Promoter: Prof. L. Lorenzen

The University of Stellenbosch
August 1999
To Tiny, George and Ben

for their love and support

during the 19 years

of this research.
Declaration

I hereby certify that this dissertation is my own original work, except where specifically acknowledged in the text. Although the published papers contained in this submission have been produced in collaboration with co-workers, my own contribution has been stated explicitly in each case. Some of the research has been submitted in part as theses by co-workers, but the collection of papers in their published form have not been submitted at any other university.

J.S.J. VAN DEVENTER

27 August 1999
Abstract

This collection of 101 published papers is based on 19 years of research, mainly in South Africa and recently also in Australia. The main thrust of this work was the simulation of mineral processing operations where conventional modelling was inadequate owing to their ill-defined nature. These papers presented some of the first applications of knowledge based systems and neural networks to mineral processing problems.

A new methodology was proposed for modelling ill-defined kinetic processes by relating rates to process conditions via non-parametric methods. The kinetic and equilibrium parameters could be related to adjustment factors if reference conditions changed. These methods were applied to batch and continuous flotation, leaching and adsorption systems as well as pyrometallurgical processes. In the case of continuous process data intrinsic reaction rates could be back-calculated and then related to process conditions via a neural net. It was explained how the configuration of mineral processing circuits could be optimised by a two-stage linear programming method where the constraints were determined interactively by a knowledge based system or neural network. In the case of non-linear system constraints neural nets were shown to detect and locate gross errors efficiently in material balancing problems. Several novel hybrid neural net architectures were proposed which allowed the integration of parametric fundamental knowledge with non-parametric heuristic knowledge. Furthermore, it was shown how neural nets could be used to extract knowledge from historical process data records.

Pioneering work was conducted on the application of textural image analysis to flotation froth surfaces and ore particles on a conveyor belt. It was possible to relate image features to metallurgical performance via neural net architectures. Different types of topological maps were used to classify froth types, to track the profile of changes in process and flotation conditions, and to relate froth class to concentrate grade and recovery. Perturbations in the comminution circuit were reflected in perturbations in the froth image features and metallurgical performance. It was also shown that the spray
angle of a hydrocyclone as determined by image analysis could be used as input to a soft sensor for predicting size distribution.

A model was developed to combine transport phenomena in the froth phase with fluid flow behaviour in order to optimise mechanical cells and flotation columns. Rate constants for the various sub-processes were determined by fitting models to concentration profiles measured at industrial plants. It was shown that the behaviour of the froth phase during the flotation of sulphides, gold and uranium was affected by galvanic interaction between metallic iron and the individual mineral species. A conceptual model was developed for the flotation behaviour of free gold in the presence of refractory sulphides for different oxidative conditions and different sequences of reagent addition.

The use of diagnostic leaching to evaluate the efficiency of mineral processing operations was explained in detail. A first attempt was made to relate diagnostic leaching data to mineral liberation via semi-empirical equations and neural nets. It was explained how the liberation patterns of different types of gold ore could be distinguished by using topological maps. The mechanisms of selected sundry processes such as electrokinetic solid-liquid separation, flow splitting, induced aeration and jet reactors were also investigated.
Samevatting

Hierdie versameling van 101 publikasies is gebaseer op navorsing oor 19 jaar, hoofsaaklik in Suid-Afrika en onlangs ook in Australië. Die fokuspunt van hierdie werk is die simulasie van mineraal prosesserings operasies waar konvensionale modellering ontoereikend is vanweë swak gedefinieerdheid. Hierdie publikasies toon van die heel eerste toepassings van kennis gebaseerde stelsels en neurale netwerke op mineraal prosesserings probleme.

‘n Nuwe metodiek is voorgestel vir die modellering van swak gedefinieerde kinetiese prosesse deur die reaksie tempo’s te verbind met proses toestande via nie-parametrisie tegnieke. Die kinetiese en ekwilibrium parameters is in verband gebring met verstellingsfaktore indien die verwysingstoestande verander het. Hierdie metodes is toegepas op enkellading en kontinue flottasie, loging en adsorpsie stelsels, asook op pirometallurgiese prosesse. In die geval van kontinue proses data kon die intrinsieke reaksie snelhede terugbereken word en in verband gebring word met proses toestande via ‘n neurale net. ‘n Twee stadium lineêre programmerings metode is voorgestel vir die optimale ontwerp van mineraal prosesserings aanlegte deur die beperkings interaktief te bepaal met ‘n kennis gebaseerde stelsel of neurale netwerk. In die geval van nie-lineêre stelsel beperkings is getoon dat neurale nette effektief buitengewone foute kon uitken en opspoor in massabalans probleme. Verskeie nuwe hibriede neurale net argitektuure is voorgestel om parametrisie fundamentele kennis te integreer met nie-parametrisie heuristiese kennis. Verder is getoon hoe neurale nette gebruik kan word om kennis te ekstraheer uit historiese rekords van proses data.

Pioniers werk is gedoen om tekstuur gebaseerde beeldanalise tegnieke toe te pas op flottasie skuim oppervlaktes en erts partikels op ‘n vervoerband. Dit is moontlik om beeld kenmerke in verband te stel met metallurgiese doeltreffendheid via neurale netwerk argitektuure. Verskeie topologiese afbeeldings is gebruik om skuim tipes te klasifiseer, om die profiele van veranderings in proses en flottasie toestande te volg, asook om die skuim klas in verband te bring met herwinning en konsentraat graad. Versteurings in die
grootereduksie aanleg is afgebeeld deur ooreenkomstige versteurings in die skuim kenmerke en metallurgiese gedrag. Daar is ook getoon hoe die sproei hoek van 'n hidrosikloon soos bepaal deur beeldanalise, gebruik kan word as inset tot 'n sagte sensor om partikelgrootte verspreiding te voorspel.

'n Model is ontwikkel om oordragsverskynsels in die skuimfase te combineer met vloeiapatrone om sodoende meganiese flottasie selle en kolomme te optimeer. Snelheidskonstantes vir die verskeie sub-prosesse is bepaal deur modelle te pas op konsentrasie profiele soos gemee op industriële aanlegte. Daar is getoon dat die gedrag van die skuim fase in die flottasie van sulfiede, goud en uraan beïnvloed word deur galvaniese interaksie tussen yster metaal en die onderskeie mineraal spesies. 'n Konseptuele model is voorgestel vir die flottasie gedrag van vrye goud in die teenwoordigheid van weerbarstige sulfiedes onder verskillende toestande van oksidasie en volgorde van reagens byvoeging.

'n Gedetailleerde verduideliking is gegee vir die aanwending van diagnostiese logging om die doeltreffendheid van mineraal prosesserings operasies te evalueer. Diagnostiese logging data is vir die eerste keer in verband gebring met mineraal vrystelling deur semi-empiriese vergelykings en neurale nette. Daar is verduidelik hoe die vrystellingspatrone van verskeie goud erts tipes onderskei kan word deur 'n topologiese afbeelding. Die werking van verskeie prosesse soos elektrokinetiese vloeistof/vastestof skeiding, vloei verdeling, geïnduseerde belugting en spuit reaktore is ook ondersoek.
Acknowledgements

My family has been most supportive of my research career, which has been very rewarding, but which has also involved considerable personal sacrifice. Nobody knows this better than my wife Tiny, who deserves the first place in a long list of acknowledgements. The love, support and patience that Tiny and my sons, George and Ben, have shown over the 19 years of this research work are greatly appreciated. Without their understanding and sacrifice my contribution to science and engineering would have been far less.

I wish to thank Leon Lorenzen for his technical and managerial contribution over many years, and for the fact that he has encouraged me to submit this dissertation. Successful research is possible only when the contributions of team members are integrated. Certain team members play a more pivotal role in contributing ideas and integrating knowledge. Without the original ideas, dedication and hard work by Markus Reuter, Chris Aldrich and Derick Moolman over many years this research would not have reached the same level of advancement. Their efforts to develop artificial intelligence techniques and computer vision systems are gratefully appreciated.

In addition, the contributions and hard work by following co-workers and research students have been substantial and are highly appreciated: Deon Annandale, Keith Anthony (deceased), Etienne Barnard, Morne Bezuidenhout, Gideon Botes, Dee Bradshaw, André Burger, Frikkie Cloete, Robert Dunne, Jacques Eksteen, Craig Goodall, Jim Green, Brent Loftus, Peter Marais, Gerhard Muller, Danie Nieuwoudt, Deon Oosthuizen, Kurt Petersen, Johan Rademan, Victor Ross, Marius Sinclair, Cathy McInnes, Greg Schmitz, Wayne Stange, Sam Swaminathan, Adam Teague, Wimpie van der Merwe, Tjaart van der Walt, Wynand van Dyk, Ross Veitch, Wayne Wilmans.
Most of the research work presented in this submission has been conducted in the Department of Chemical Engineering at the University of Stellenbosch. Since the end of 1995 this work has been continued in the Department of Chemical Engineering at the University of Melbourne. The infrastructural and financial support of both universities is gratefully acknowledged.

Funding from the following companies and institutions since 1981 is especially acknowledged: Anglo American Corporation, Anglovaal, Australian Research Council, De Beers, the former Foundation for Research Development, Gencor, Impala Platinum, Kenwalt, Mintek, Mount Isa Mines, Sasol and Stawell Gold Mines.
CONTENTS

Declaration i
Abstract ii
Samevatting iv
Acknowledgements vi
1. Scope of Submission 1
2. Personal Role in Research 4
3. List of Publications Included in this Submission 9
4. List of Publications Not Included in this Submission 18
5. General Statement of Impact 37
6. Summary of Submitted Publications 40
   6.1 Process Synthesis 40
   6.2 Knowledge Based Systems 42
   6.3 Neural Networks: Theoretical Concepts 44
   6.4 Neural Networks: Applications 47
   6.5 Computer Vision 50
   6.6 Froth Flotation and Interfacial Phenomena 53
   6.7 Fluid Mechanics 56
   6.8 Diagnostic Leaching 57
7. Publications on Process Synthesis
8. Publications on Knowledge Based Systems
9. Publications on Neural Networks: Theoretical Concepts
10. Publications on Neural Networks: Applications
11. Publications on Computer Vision
12. Publications on Froth Flotation and Interfacial Phenomena
13. Publications on Fluid Mechanics
14. Publications on Diagnostic Leaching
VOLUME III
Section 12  Publications on

Froth Flotation and
Interfacial Phenomena
The interactive effects of the sulphite ion, pH, and dissolved oxygen on the flotation of chalcopyrite and galena from Black Mountain ore

by V.E. ROSS* and J.S.J. VAN DEVENTER†

SYNOPSIS

These effects were investigated in batch flotation studies, and by the measurement of rest and pulp potentials. At low additions of sulphurous acid as the pH regulator, flotation rate increased with increasing concentrations of dissolved oxygen. The recovery of chalcopyrite dropped significantly below a pH value of about 6.5 at 25 p.p.m. of dissolved oxygen, and below a pH value of about 6 at a dissolved-oxygen concentration of 8.2 p.p.m.

The rest and pulp potentials measured indicated that dixanthogen is the dominant species formed on chalcopyrite surfaces during flotation with sodium ethyl xanthate. The results suggested that the same species might have formed on galena surfaces in the pulp after the ore had been milled in a ceramic mill under nitrogen. Increased additions of sulphurous, sulphuric, and hydrochloric acids increased the rest potentials, while the addition of sodium sulphite decreased these potentials.

SAMEVATTING

Hierdie effekte is ondersoek in losflotesetoeote en dour rus- en pulpopotensiaalmetings. Met klein byvoegings van swaweligsuur as pH-regulaar, het die flotaatieweekreekstempel vermom met toenemende opgelostesuurstof-konsentrasies. Die herwinning van chalkopiriet het aanmerklik afgeneem by 'n pH-waarde laer as ongeveer 6,5 en 'n opgelostesuurstof-vlak van 25,0 d.p.m., en by 'n pH-waarde laer as 6,0 en 'n opgelostesuurstof-vlak van 8,2 d.p.m.

Die gemete rus- en pulpopotensiale toon dat dixanthogen die belangrikste spesie is wat op chalkopirietoppervlakke gevorm word tydens flonasie met natriumsulfiet hierdie potensiale verlaag het. Groter byvoegings van swaweligsuur, swaweligsuur en soustuur het die ruspotensiale verhoog, terwyl die byvoeging van natriumsulfiet hierdie potensiale verlaag het.

Introduction

Although the flotation of sulphide has been practised for many years, the interaction between the flotation variables remains largely unclear. Many investigators have undertaken basic work on pure minerals, and to a much lesser extent on ores, in order to gain an understanding of the various mechanisms involved in the flotation of lead, zinc, and copper sulphides. Of special interest are investigations into the depressing influence of the sulphite ion in the flotation of galena, and the influence of the concentration of dissolved oxygen and the redox potential on the differential flotation of chalcopyrite and galena from Black Mountain ore. Pulp potentials and the subsequent flotation of galena were studied by investigators who correlated these results at Mount Isa, in Australia. Information on the reactions occurring at the surface of various sulphide minerals in xanthate solutions was obtained by the measurement of rest potentials, and the same technique was used to show that isopropyl ethylthionocarbamate (Z-200) reacts with chalcopyrite but not with galena, although the mechanism remains unclear.

In the flotation concentrator at Black Mountain, chalcopyrite, galena, and sphalerite are floated sequentially.

Both Z-200 and sodium ethyl xanthate are used as collectors in the copper-flotation circuit. Sulphurous acid is employed as a combined pH regulator and source of sulphite ions for the selective depression of galena. An increase in the pH of the flotation feed due to the back-filling of excavated mining areas posed metallurgical difficulties in flotation, since the copper rougher float is extremely sensitive to the rate and amount of sulphurous acid added.

The purpose of the study described here was twofold: (1) to investigate the effect of the sulphite ion on the floatability of chalcopyrite and galena at different concentrations of dissolved oxygen, and (2) to provide a better understanding of the way and extent to which the different variables influence one another under regulated conditions.

Experimental

Batch flotation tests were carried out in a 3-litre Wemco flotation cell with induced aeration. The impeller speed was kept constant at 900 r/min. Black Mountain ore, containing about 0.35 per cent copper, 6.5 per cent lead, and 2.2 per cent zinc, was used in all the experiments.

Before being floated, the ore was ground to 65 per cent smaller than 200 mesh (75 μm) under an atmosphere of nitrogen in a ceramic mill. The mill load was as follows: 1000 g of ore, ceramic balls, and 500 ml of deoxygenated tap water. After being milled, the ore was transferred to a...
flotation cell, deoxygenated tap water being added to bring the pulp density to 33 per cent solids.

So that the concentration of the dissolved oxygen in the pulp could be controlled during flotation, the entire flotation cell was placed inside an airtight container. The operator handled the concentrates and took the measurements using rubber gloves fitted to the Perspex front-piece of the container.

Partial flushing of the container with oxygen allowed the desired oxygen level in the flotation atmosphere to be maintained. The concentration of dissolved oxygen in the pulp was measured with a Schott CG 867 dissolved-oxygen electrode, which was standardized in a saturated sodium sulphite solution. The pulp in the cell (with no chemicals added) was aerated inside the closed container until the oxygen concentration in the pulp was in equilibrium with the environment in the airtight container. An aeration period of about 3 minutes was required.

Aeration was then stopped, and the pulp was conditioned for 3 minutes with a pH regulator, sodium sulphite or sodium sulphate. Subsequently, the pulp was conditioned with a collector for another minute, which was followed by the addition of a frother and conditioning of the pulp for a further minute. The flotation reagents used in this study are summarized in Table I. After the total conditioning time of 5 minutes, the level of dissolved oxygen in the pulp was reduced by about 3 p.p.m. for the maximum addition of sodium sulphite. The previous equilibrium level of dissolved oxygen was reinstated by intermittent aeration of the pulp for about 1 minute. The flow of air was adjusted to prevent a froth overflow. The concentration of dissolved oxygen was monitored continuously.

After conditioning and pre-aeration to the desired level of dissolved oxygen, the pulp pH was measured with a Beckman PH0 pH meter. The ore was then floated for 3 minutes. Samples of the concentrate were collected at intervals of 1 minute by manual scraping. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0,2 in extreme cases (i.e. at pH 5,3). The concentration of dissolved oxygen was monitored and stayed constant throughout the batch flotation test.

The possible effect of the sulphite ion at decreasing pH and also at constant pH was studied by increasing additions of sulphurous acid and sodium sulphite respectively. The corresponding effect of the sulphite ion was studied by additions of sulphuric acid and sodium sulphate. Variation in mineral floatabilities with pH was investigated by the use of hydrochloric acid as a pH regulator.

Sulphurous acid was obtained from Black Mountain as a 1 per cent H₂SO₃ solution. All the other acids and modulators were chemically pure.

Measurements of rest potential and pulp potential were taken at different pH values. These potentials were measured by the use of mineral electrodes (chalcopyrite from Prieska and galena from Tsumeb) and of platinum respectively. In all cases a saturated calomel electrode (SCE) was used as reference. In the preparation of the chalcopyrite and galena electrodes, a piece of mineral was sealed in the end of a glass tube, and contact was established through a layer of mercury above the mineral.

Before the measurements of rest potential were made, the surface of the electrode was cleaned thoroughly with a piece of waterpaper to ensure an uncontaminated surface. The rest and pulp potentials respectively were measured after the electrodes had been immersed for 10 minutes in a 25 mg/l sodium ethyl xanthate solution and in a pulp containing 33 per cent solids. The collector added to the pulp was a solution consisting of 20 mg/l xanthate to 1 litre of water, which is equivalent to 40 mg of xanthate per kilogram of ore. Different amounts of sodium sulphite, sodium sulphate, sulphurous acid, sulphuric acid, and hydrochloric acid were added to the pulp and solutions. The rest and pulp potentials were converted to the standard hydrogen electrode (SHE) scale.

All the measurements of rest and pulp potentials were conducted in solutions or pulps in which the concentration of dissolved oxygen was kept constant at 8,2 p.p.m. Even with the most concentrated sodium sulphite solutions used (i.e. 300 mg/l) with no aeration to maintain a constant level of dissolved oxygen, the rest potentials were found to be only 6 mV lower than when the dissolved oxygen was kept constant at 8,2 p.p.m.

The concentrations of residual sodium ethyl xanthate after 10 minutes of pulp conditioning were used in the calculation of Xₓ/Xⁿ reduction potentials at different pH values. At similar pH values, a slightly higher xanthate uptake was measured with hydrochloric acid than with sulphuric acid. In the calculation of the maximum Xₓ/Xⁿ reduction potentials, the former was used as a pH regulator but the pulp conditions were identical to those used in the measurement of rest potentials. After a conditioning time

---

**TABLE I**

<table>
<thead>
<tr>
<th>REAGENTS USED IN BATCH FLOTATION TESTS</th>
<th>pH regulators: H₂SO₄</th>
<th>H₂SO₃</th>
<th>HCl</th>
<th>Na₂SO₃</th>
<th>Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage</td>
<td>Varying</td>
<td>Varying</td>
<td>Varying</td>
<td>Varying</td>
<td>Varying</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH regulators: H₂SO₄</th>
<th>H₂SO₃</th>
<th>HCl</th>
<th>Na₂SO₃</th>
<th>Na₂SO₄</th>
<th>Dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH regulators: H₂SO₄</td>
<td>H₂SO₃</td>
<td>HCl</td>
<td>Na₂SO₃</td>
<td>Na₂SO₄</td>
<td>Dosage</td>
</tr>
<tr>
<td>pH regulators: H₂SO₄</td>
<td>H₂SO₃</td>
<td>HCl</td>
<td>Na₂SO₃</td>
<td>Na₂SO₄</td>
<td>Dosage</td>
</tr>
<tr>
<td>pH regulators: H₂SO₄</td>
<td>H₂SO₃</td>
<td>HCl</td>
<td>Na₂SO₃</td>
<td>Na₂SO₄</td>
<td>Dosage</td>
</tr>
</tbody>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th>CALCULATED DIXANTHENGXAXANTHATE REDUCTION POTENTIALS AT DIFFERENT pH VALUES IN PULP AFTER 10 MINUTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions:</td>
</tr>
<tr>
<td>Concentration of dissolved O₂: 8,2 p.p.m.</td>
</tr>
<tr>
<td>Temperature: 25°C</td>
</tr>
<tr>
<td>Initial Na₂Eix concn in solution:</td>
</tr>
<tr>
<td>20 mg/l = 1,39 x 10⁻⁴ M</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>8,2</td>
</tr>
<tr>
<td>7,5</td>
</tr>
<tr>
<td>7,0</td>
</tr>
<tr>
<td>5,5</td>
</tr>
<tr>
<td>5,0</td>
</tr>
</tbody>
</table>

---

14 JANUARY 1985

JOURNAL OF THE SOUTH AFRICAN INSTITUTE OF MINING AND METALLURGY

Stellenbosch University  https://scholar.sun.ac.za
of 10 minutes, a representative sample of pulp was taken and immediately vacuum filtered. The clear filtrate was then analysed spectrophotometrically for ethyl xanthate at a wavelength of 301 nm. The results are shown in Table II. The pulp temperature was maintained at 25°C during the measurement of rest potential.

Discussion

The Effect of the Milling Environment

The sensitivity of chalcopyrite and galena flotation to the addition of sulphurous acid is illustrated in Fig. 1, and the corresponding copper grade is plotted versus recovery in Fig. 2. In this case, contrary to all the other flotation experiments described in this paper, the ore was milled in a rubber-lined steel mill with mild-steel rods to a particle-size fraction 70 per cent smaller than 75 μm. After milling, the pulp was aerated for 15 minutes to increase the concentration of dissolved oxygen to 7.5 p.p.m. before the commencement of flotation. The total flotation time was 7.5 minutes in this case. The concentration of dissolved oxygen was monitored and stayed constant throughout the flotation test. Sodium ethyl xanthate was implemented as a collector at a dosage of 20 g/t.

These diagrams show that the maximum copper grade, as well as the maximum copper recovery and copper-lead selectivity, occurs at a pH value of about 6.0. Whereas galena is steadily depressed by increasing amounts of sulphurous acid, the recovery and grade of chalcopyrite increase as the pH is decreased. Below pH 6, the decrease in both the grade and the recovery of chalcopyrite may be caused by the reaction of the collector with soluble salts, thereby reducing the effective concentration of collector in the pulp.

A comparison of these results with the results obtained when the ore was milled under an atmosphere of nitrogen in a ceramic mill shows that milling in a steel mill followed by pre-aeration to a dissolved-oxygen concentration of 7.5 p.p.m. results in much higher copper grades.
Initially, the froth was very loose and runny, but it changed later to a foamy, solid texture. Whereas the concentrates recovered after 1 minute were very dark-coloured, those during the later stages of flotation became greyish. The copper grade increased slightly with flotation time. Although an attempt was made to facilitate the drainage of gangue particles to the pulp by flotation at a froth height of 7 cm, the copper grade was still very low. In many instances, the copper content of the first concentrate was lower than the copper content of the ore (0.35 per cent), which gives an indication of the extent to which the gangue was entrained. After 3 minutes of flotation, the copper grade increased to only about 0.9 per cent.

These froth effects vanished when the ore was milled in an iron mill, and a good copper grade and recovery were obtained easily. No explanations for this difference can be proposed at this stage.

The possible effect of the sulphite ion on the flotation of chalcopyrite and galena at different pH values is illustrated by the recoveries obtained when sulphurous acid and hydrochloric acid were used as pH regulators respectively (Figs. 3 and 4). At both concentrations of dissolved oxygen, there is a marked increase in the recovery of chalcopyrite when sulphurous acid is used as a pH regulator instead of hydrochloric acid. At pH values below 7, the recovery of galena is also increased if sulphurous acid is used as a pH regulator instead of hydrochloric acid.

When sulphuric acid is used as a pH regulator instead of hydrochloric acid, the recovery of chalcopyrite is increased at a dissolved-oxygen concentration of 8.2 p.p.m. but decreased at a dissolved-oxygen concentration of 25 p.p.m. In the recovery curves for chalcopyrite in Fig. 3, with sulphuric acid as the pH regulator, the effect of dissolved oxygen diminishes as the pH is decreased. Fig. 4 shows that, at both levels of dissolved oxygen, sulphuric acid, in comparison with hydrochloric acid, increases the recoveries of galena at pH values below 7. For both chalcopyrite and galena at both levels of dissolved oxygen, sulphurous acid gives higher recoveries than either hydrochloric or sulphuric acid. No explanation can be given for these phenomena.

Fig. 3 shows that, at pH values higher than about 5.8, the recovery of chalcopyrite increases when the concentration of dissolved oxygen is increased, while the opposite situation occurs at pH values lower than about 5.8 when sulphurous acid is used as the pH regulator. At a dissolved-oxygen level of 8.2 p.p.m., the maximum recovery of chalcopyrite occurs at a pH of about 6.1, while this maximum occurs at a pH of about 6.8 when the level of dissolved oxygen is 25 p.p.m. The occurrence of a maximum chalcopyrite recovery can be explained by the possible cleaning effect of the sulphite ion to render the chalcopyrite more hydrophobic, which is opposed by the possible formation of surface oxidation products as the pH is decreased. The higher dissolved oxygen level (25 p.p.m. as compared with 8.2 p.p.m.) shifts the occurrence of a maximum chalcopyrite recovery to a higher pH value when sulphurous acid is used as the pH regulator.

Fig. 4—Comparison of pH regulators in the recovery of galena. NaEtX addition: 20 g/t. 1 and 2 indicate the variation in recovery obtained from two independent experiments carried out under identical conditions.

Comparison of the pH Regulators Used

Figs. 3 and 4 illustrate the variation in the recoveries of chalcopyrite and galena when different pH regulators were used for a flotation time of 3 minutes. As indicated, the reproducibility of these results is satisfactory.

There was little variation in the recovery of both chalcopyrite and galena when hydrochloric acid was used as a pH regulator at a constant level of dissolved oxygen. The recovery of both minerals increased when the concentration of dissolved oxygen increased. Also, during the collectorless flotation of ore milled in a steel mill, it was observed that pre-aeration of the pulp before the addition of frother resulted in an increase in the recovery of chalcopyrite over that when there was no pre-aeration. Although it cannot be proved, a possible explanation for the increase in recovery of the minerals may be that increased adsorption of molecular oxygen promotes dehydration of the sulphide minerals, which renders them more hydrophobic.

Very low copper grades (about 0.5 per cent) were obtained when the ore was milled under an atmosphere of nitrogen in a ceramic mill and subsequently aerated before being floated. With increasing additions of sulphurous acid at a dissolved-oxygen concentration of 8.2 p.p.m., the recovery of water increased until a pH value of 6.1 was used, after which the recovery of water decreased slightly. Under these conditions, the froth poured over the lip of the cell during the initial stages of flotation (the first 2 minutes).
Fig. 4 shows that, with sulphurous acid, a maximum recovery of galena occurs at a slightly higher pH at a dissolved-oxygen concentration of 25 ppm than at 8.2 ppm. For pH values higher than about 6.4, an increase in the level of dissolved oxygen increases the recovery of galena, while the opposite happens at pH values lower than about 6.4. An increase in the level of dissolved oxygen decreases the maximum recovery of galena, as opposed to the effect of oxygen on the recovery of chalcopyrite. Optimum copper-lead selectivity can be attained from flotation at a dissolved-oxygen level of 25 ppm in the pH range between about 5.8 and 6.4. It is expected that a higher level of dissolved oxygen will slightly increase this optimum pH value.

Flotation studies with isopropyl ethylthionocarbamate (Dow Z-200) have indicated that this collector can be combined effectively with xanthate in the separation of chalcopyrite and galena. Essentially the same recovery-pH trends were observed with Z-200 as with sodium ethyl xanthate, but the selectivity is better with the former at higher concentrations of dissolved oxygen (Figs. 5 and 6). As with xanthate, maximum recoveries of both chalcopyrite and galena were observed at higher pH values when the level of dissolved oxygen was 25 ppm instead of 8.2 ppm. Bench-scale flotation tests in the flotation concentrator at Black Mountain indicated that a combined collector concentration of about 20 g/t (xanthate 7 g/t and Z-200 13 g/t) not only yields a higher copper recovery than when only xanthate is used, but the copper-lead selectivity is also greatly improved.
The Effect of Sulfite and Sulfate at Constant pH

Batch flotation with sodium sulfite and sodium sulfate was conducted at a constant pH of 8.2, so that the isolated effects of the sulfite and sulfate anions respectively could be investigated on the recovery of chalcopyrite and galena (Figs. 7 and 8).

At increasing sodium sulfite additions of up to 25 g/t, the recovery of chalcopyrite decreased, while galena was slightly depressed at low concentrations of dissolved oxygen. At higher sodium sulfite concentrations, however, the recovery of both minerals increased, together with a significant increase in the recovery of water. This complements the flotation results obtained with sulfurous acid as the pH regulator. These results show that increased additions of sulfite ion increase entrainment in the froth, although the effect on chalcopyrite is more pronounced than that on galena.

Increasing additions of sodium sulfate up to 25 g/t reduced the recovery of chalcopyrite, but higher additions increased its recovery only at lower levels of dissolved oxygen. The same effect was observed when sulfuric acid was used as the pH regulator. This may indicate that most of the variations in recovery obtained with sulfuric acid can be attributed to the effect of the sulfate ion, which does not influence the recovery of galena significantly.

Figs. 7 and 8 show that higher concentrations of dissolved oxygen promote copper-galena selectivity.

Measurement of Rest Potentials

The rest potentials of chalcopyrite and galena were studied in an effort to elucidate the reactions occurring on the respective mineral surfaces during flotation. Measurements of rest potentials in a $1.92 \times 10^{-4}$ M sodium ethyl xanthate solution, as well as in an aerated pulp (with an initial xanthate concentration of $1.39 \times 10^{-4}$ M), are presented in Figs. 9 to 12. Oxidation of the collector to its dimer occurs only on those minerals that display a rest potential above the corresponding reversible potential for dimer formation. Metal-collector compounds are formed instead for those sulfides that give a rest potential below this value.

The reduction potentials for the dixanthogen/xanthate couple

$$X_2 + 2e^- \rightarrow 2X^-$$

under the above-mentioned conditions were calculated according to the Nernst equation:

$$E_{\text{cell}} = E^{\circ} + \frac{0.0128 \ln (a_{X^-})}{2}$$

at a temperature of 25°C. The standard potential $E^{\circ}$ of $-0.06$ V was assumed to stay constant over the pH range studied. The minimum reduction potential for the conditions in the $1.92 \times 10^{-4}$ M NaEtX solution was calculated as +150 mV, indicated by dotted lines in Figs. 9 to 12. In other words, if allowance is made for a possible decrease in the concentration of the collector, the $X_2/X^-$ reduction potential would increase.

 Likewise, if allowance is made for the decrease in the concentration of xanthate in the pulp due to possible adsorption or reaction with the other species present, the dixanthogen/xanthate reduction potential increases. The maximum reduction potential at each pH value was calculated by use of the concentrations of residual xanthate in the pulp after 10 minutes and the Nernst equation. These potentials are presented in Table II as a function of pH and percentage of initial xanthate taken up. The initial concentration of xanthate was 40 mg per kilogram of ore, or $1.39 \times 10^{-4}$ M in the solution in the pulp. These potentials are indicated as broken lines in Figs. 9 to 12.

Figs. 9 and 10 show that the rest potentials of chalcopyrite and galena in the aerated pulp after 10 minutes are higher than the maximum $X_2/X^-$ reduction potentials at all pH values. This indicates that dixanthogen is probably formed on both minerals in the pulp. It is possible, however, that rest potentials may differ depending on the origin of the mineral. For this reason, although measurements of rest potentials may yield valuable information regarding the processes possible on the mineral surface, no absolute conclusions can be drawn from these data.

Measurements of rest potentials obtained in the $1.92 \times 10^{-4}$ sodium ethyl xanthate solution suggest that dixanthogen is probably the dominant surface species formed on chalcopyrite surfaces at pH values less than 7.0. However, lead xanthate is probably formed on galena because the rest potentials are lower than the calculated minimum reduction potential.

The formation of dixanthogen on chalcopyrite surfaces is in agreement with observations made by Allison et al.4.
Richardson and Maust have discussed contrasting results published on the formation of galena surface species. For example, Allison et al. found that lead xanthate, PbX₂, was the major product formed when galena was treated with xanthate solutions under conditions corresponding to an essentially unlimited oxygen supply. This is in agreement with the results shown in Fig. 10 for pure solutions with pH values higher than about 4. The results of Allison et al. are in contrast to the results of Fig. 10 for an aerated pulp, but those investigators did not determine rest potentials in pulps, but merely in pure solutions.

Figs. 9 and 10 reveal a linear relationship between rest potential and pH for chalcopyrite in pulps and xanthate solutions, and for galena in the pulp when hydrochloric acid is used as pH regulator. This supports an electrochemical oxidation of xanthate and the formation of dixanthogen on chalcopyrite in pulps and solutions at pH values below 7, as well as on galena in pulps. No such linear relationship between rest potential and pH exists for galena in solution, which may support the formation of lead xanthate under these conditions.

When sulphurous or sulphuric acid is used instead of hydrochloric acid, the reduced rest potentials observed are probably due to an interaction between the sulphite or sulphate ions in solution and the electrode surface.

The increase in the rest potentials of both chalcopyrite and galena at pH values less than 3 in the solutions concerned is presumably caused by hydrolysis of the sulphite and sulphate ions respectively. This may be the reason for the uncontrolled activation of galena at low pH values observed in the flotation circuit at Black Mountain.

Studies of contact angles have shown that, when dixanthogen is the dominant species formed on a mineral surface, a strongly hydrophobic surface results. Although electrochemical measurements have indicated that the initial chemisorbed xanthate layer on galena is hydrophobic and that flotation commences at potentials where this species is formed with only small amounts of dixanthogen present, this does not exclude the possibility that dixanthogen also plays an important supporting role. The formation of dixanthogen on galena surfaces in copper–lead separation would be seriously detrimental to the depression of galena because of the irreversibility of the xanthate adsorption reaction when the dimer is formed.

Figs. 11 and 12 show that, in solutions and pulps at a pH of 8.2, increasing additions of sodium sulphite result in a decrease in the rest potentials of both chalcopyrite and galena. The results indicate that dixanthogen is possibly formed on galena in the pulp at concentrations of up to 50 g of sodium sulphite per ton of ore, which was the concentration range used in the experiments illustrated in Fig. 8. Lead xanthate may be formed on galena surfaces in the solution. Fig. 11 shows that dixanthogen is probably formed on chalcopyrite surfaces in the pulp at sodium sulphite additions of up to about 138 g/t, which was higher than the concentrations used for the results shown in Fig. 7. Dixanthogen is probably not formed on chalcopyrite in the xanthate solution at a pH value of 9.6, as indicated in Fig. 11. Increasing additions of sodium sulphate have
virtually no effect on the rest potentials of either chalcopyrite or galena in both the pulp and the solutions.

The milling environment and the concentration of dissolved oxygen greatly affect the rest potentials of both chalcopyrite and galena in the pulp. Milling under a reducing atmosphere (dissolved-oxygen concentration 0.1 p.p.m.) results in low rest potentials for both minerals, as shown in Table III. Although no dixanthogen is formed on chalcopyrite under these circumstances, the dominant species formed on galena surfaces is probably chemisorbed xanthate. Subsequent aeration of the pulp (dissolved-oxygen concentration 8.2 p.p.m.) greatly increases the rest potentials of both chalcopyrite and galena. While dixanthogen is probably formed on chalcopyrite, imposing hydrophobicity on that mineral, the possible formation of multilayers of lead xanthate on galena would render the mineral hydrophilic and less floatable. These results are in accordance with the flotation results presented in Fig. 1.

<table>
<thead>
<tr>
<th>Table III</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INFLUENCE OF DISSOLVED OXYGEN ON REST POTENTIALS</strong></td>
</tr>
<tr>
<td>Dissolved Ozone</td>
</tr>
<tr>
<td>p.p.m.</td>
</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>8.2</td>
</tr>
</tbody>
</table>

![Fig. 11—Influence of sulphite and sulphate concentrations on the rest potential of chalcopyrite. X/μ reduction potentials: solution - - - , pulp ---.](image1)

![Fig. 12—Influence of sulphite and sulphate concentrations on the rest potential of galena. X/μ reduction potentials: solution - - - , pulp ---.](image2)

*Pulp Potential*

The pulp potential (Eh) is an important electrochemical parameter that has been correlated with flotation results. It is measured as the potential of a platinum wire relative to a saturated calomel electrode (SCE), both of which are inserted into a stirred pulp. The potential is then converted to the standard hydrogen electrode (SHE) scale. Information regarding these potentials can be very useful in the prediction of regions of optimal flotation, although the 'meaning' of the pulp potential in a complex pulp remains obscure. The Eh monitors the relevant electrochemical parameter that may determine the condition of the sulphide surface.

Eh measurements are presented in Figs. 13 and 14. Notable is the increased Eh when the addition of sulphurous acid is increased (as was observed with rest potentials). Increased additions of sodium sulphite result in a decrease in pulp potential, as indicated in Fig. 14. At no stage, however, was a potential in the region of +150mV approached, which was observed to cause the effective depression of galena at Mount Isa in Australia.

Laboratory batch flotation tests have shown that the initial Eh has a major influence on the flotation of chalcopyrite, as well as of galena. With the sulphite, the addition of the galena was suppressed for only a small decrease in Eh. This depression was due to the sulphite ion and not because of the slight variation in Eh. The results obtained...
Conclusions

The recoveries of chalcopyrite and galena are sensitive to the amount of sulphurous acid or sodium sulphite added. When either sodium ethyl xanthate or isopropyl ethylthionocarbamate is used as the collector, both minerals reveal a pH value at which maximum recovery is obtained when sulphurous acid is added as the pH regulator. This pH value increases slightly as the level of dissolved oxygen is increased.

Sulphite additions of more than 25 g/t result in an increased recovery of both chalcopyrite and galena, which is accompanied by a higher recovery of water.

Under the aeration conditions studied, poor copper grades are obtained when the ore is milled in a ceramic mill. Milling in a steel mill, followed by pre-aeration, greatly improves the copper grades and copper–lead selectivity when sulphurous acid is used as the pH regulator. In this case, an optimum pH also exists at which the recovery of chalcopyrite is at a maximum.

Although it cannot be proved, the sulphite ion appears to have a cleaning effect on chalcopyrite to increase recovery of the mineral.

The measurements of rest and pulp potentials showed that, at pH values of less than 8, increased additions of sulphurous acid increased these potentials. Dixanthogen was formed on chalcopyrite surfaces in the pulp and in the xanthate solution at pH values lower than about 7 when sulphurous acid was used as the pH regulator. Dixanthogen appeared to be formed on galena surfaces in the pulp, but lead xanthate was presumably formed on galena in solutions at pH values higher than about 4.

The effect of an increased concentration of dissolved oxygen on the recovery of chalcopyrite may suggest that, in practice, longer pre-aeration periods will slightly increase the pH values at which maximum copper recoveries will be obtained.

Acknowledgements

The authors gratefully acknowledge the financial and technical support of the Council for Mineral Technology (Mintek), as well as the supply of ore samples by the Black Mountain Mineral Development Company.

References

Shock-wave and high-strain-rate phenomena

EXPLOMET '85, an International Conference on Metallurgical Applications of Shock Wave and High-strain-rate Phenomena, is to be held in Portland, Oregon, from 28th July to 1st August, 1985.

EXPLOMET '85 will provide a forum for the exchange of information on the metallurgical and other materials effects and applications of shock wave and high-strain-rate phenomena. The excellent response obtained from survey cards sent with the initial announcement indicates that the conference will be as successful as the original EXPLOMET '81 held in Albuquerque, New Mexico. EXPLOMET '85 will consist of invited/plenary talks addressing broader areas and summarizing aspects of generic areas, and contributed talks reporting research efforts. The following keynote talks are currently confirmed:

- V.D. LINSE (Batelle — Columbus): The Particulate Nature of Dynamic Compaction.
- M. STELLY, and R. DORMEVAL (C.E.A., France): Adiabatic Shearing.

Contributed papers describing the results of research and/or developments and applications, especially novel applications of shock wave and high-strain-rate technologies in any of the following areas are solicited:

- High-strain-rate Deformation and Forming
- Explosive Metal Working
- Dynamic Fracture (Including Spallation)
- Hypervelocity Impact
- Adiabatic Shearing and Shear-band Phenomena
- Dynamic Consolidation (Metals/Ceramics/Composites)
- Novel Applications of Explosive and High-strain-rate Technologies
- Modification of Materials and Properties by Shock Waves
- Laser Shock Effects in Materials
- Applications in the Megahertz Regime

There will be no concurrent or parallel sessions, and each session will be structured to allow for considerable discussion and exchange of ideas; special workshop sessions will be developed. The papers presented will be edited and published in a book by a major international publishing house similar to those of EXPLOMET '81, which was published as "Shock Waves and High-strain-rate Phenomena in Metals: Concepts and Applications" (edited by M.A. Meyers and L.E. Murr) by Plenum Publishing Corp. in 1981.

EXPLOMET '85 will have as one of its objectives the acceleration of progress in the field of high-strain-rate deformation and fabrication. It will emphasize applications of shock physics and other fundamental high-strain-rate phenomena. It is intended to provide a forum for the exchange of state-of-the-art information on the metallurgical effects of high-strain-rate deformation and fabrication, and other shock-wave and explosive-technology applications in the materials sciences and engineering.

An abstract of 250 words or less detailing the work to be presented for consideration by the Conference organizers should be sent to the address below. The deadline for abstracts will be 1st March, 1985. Manuscripts of acceptable papers to be presented will be required for the Conference proceedings in a format to be sent with the notice of acceptance. Deadline for the (camera-ready) paper submission will be 15th June, 1985. Invited papers will be allowed 30 text pages while contributed papers will be allowed 15 pages.

Conference Chairman: L.E. Murr, Oregon Graduate Center, 19600 N.W. Walker Road, Beaverton, Oregon 97006 U.S.A. Telephone: (503) 645-1121
Electrokinetic solid–liquid separation of an ultrafine kimberlite suspension*

by W. WILMANS† and J.S.J. VAN DEVENTER‡

SYNOPSIS

Electrokinetic dewatering of kimberlite slime under constant direct currents of 0.5 to 2 A and dewatering under constant applied potentials of 16.5 to 46.5 V are considered. The combined effects of electrophoresis and the addition of 8.3 × 10⁻³ M Mg²⁺ ions on the one hand, and 1 to 10 p.p.m. of the anionic polyacrylamide flocculant Praestol 2935 on the other, were investigated in a 3-litre Perspex electrophoretic cell. The electro-osmotic dewatering experiments were conducted in a 3-litre Perspex electro-osmotic cell at various electrode spacings, as well as with a moving anode (top electrode).

During electrophoretic dewatering, the zeta potential of the kimberlite particles did not change significantly, whereas the pH and temperature showed marked increases with time. The addition of Praestol 2935 enhanced the settling of the sludge bed owing to the additional effect of flocculation. The addition of electrolyte Mg(CIO₄)₂ retarded the separation process, partly as a result of gel formation in the slurry. During the electro-osmotic experiments, the rate of dewatering was found to be approximately proportional to the applied constant direct current, and to be independent of the electrode spacing. In general, electro-osmotic dewatering seemed to be more energy-efficient than electrophoretic dewatering.

SAMEVATTING

Elektrokinetiese ontwatering van kimberlietslyk by konstante gelyksstromes tussen 0.5 en 2 A asook ontwatering by konstante spannings tussen 16.5 en 46.5 V word bespreek. ’n Perspex elektroforetiese sel met ’n volume van 3 liters is gebruik om die gekombineerde effek van elektroforetiese tesame met die byvoeging van 8.3 × 10⁻³ M Mg²⁺-ione te ondersoek, en die byvoeging van tussen 1 en 10 p.p.m. anioniene polakriekamid flokkulant Praestol 2935 andersys, te ondersoek. Elektro-osmose ekspersimente met verskillende elektrodespasierings asook met ’n bewegende anode (boonste elektrode) is uitgevoer in ’n Perspex elektro-osmose sel met ’n volume van 3 liters.

Gedurende elektroforetiese ontwatering het die zeta-potentiaal van die kimberlites deeltjies nie signifikant verander, maar die pH en temperatuur toegeneem met tyd. Die byvoeging van Praestol 2935 bevoordeel die uitsakking van die flodderbed a.g.v. die addisionele effek van flokkulasie. Die byvoeging van ’n elektroliet Mg(CIO₄)₂ benadeel gedeeltelik die skeidingsproses a.g.v. “gel”-vorming in die flodder. Gedurende elektro-osmose ekspersimente is gevind dat die tempo van ontwatering benaderd ewe redig is aan die konstante gelykstromige en onafhanklik is van elektroodespasiering. In die algemeen is gevind dat elektro-osmose ontwatering ’n beter energiebenutting lever as elektroforetiese ontwatering.

Introduction

It is well known that South Africa is experiencing a chronic shortage of water. Although the country is fortunate in having rapidly expanding mining and metallurgical industries, those industries are major consumers of water and depend heavily on its availability. This is the factor that makes the recycling of water in these industries of such vital importance. Other countries, including Australia, Botswana, and the U.S.A., depend largely on recycled water to meet their requirements.

Several methods are used internationally to recycle and re-use water in the mining and metallurgical industries. The use of thickeners to decrease the concentration of solids in water is a well-known and established practice, and flocculants are frequently used to enhance the consolidation of solids in suspension. Filtration is being used at a number of mines, and is a technique of solid–liquid separation that has been researched thoroughly.

However, filtration and thickening fail to produce clarified water from slimes containing a substantial amount of small (sub-micrometre) clayey particles. Kimberlite slimes produced in the diamond-mining industry in Southern Africa contain such fine particles, which hardly settle to a compact sediment. The recovery of water for recycling to the treatment plant is therefore impeded, while land suitable for the construction of further slimes dams is no longer readily available.

These clayey kimberlite particles possess a built-in negative surface charge, which can be exploited in an external electrical field to accomplish solid–liquid separation.

This paper describes the use of electrokinetic methods to dewater kimberlite slimes on a laboratory scale.

Industrial Applications

Although very little laboratory testwork has been done on the use of electrokinetic methods for solid–liquid separation, there are some industrial applications of this principle.

Sprute and Kelsh described such an application at the Henderson Mine in Colorado. Underground slimes are dewatered and consolidated in two large collection pits.
by the application of a direct current of about 400 A. In this application, electro-osmosis is used as a mechanism for separation. The slimes are treated electrically, and water is drained at the bottom of the pits to a collection sump. The authors claim that the process is economical and practical.

Similar work was done in tests on mines in Idaho and Mexico. The three-electrode system used in the tests divided the material into two layers, the upper layer containing slimes that resisted dewatering, and the bottom layer containing coarse, easily drained material. A direct current of 55 A was applied alternately to the two layers, yielding a sufficiently dry and firmly consolidated slime after about 2.5 hours.

Lockhart and Strickland investigated the use of electro-osmosis to dewater tailings ponds at a coal washery. Low voltages were used over long periods of time to produce a 'spadeable' solid (of 60 to 70 per cent solids content). The energy consumption during these field tests varied between 14 and 30 kWh per ton of dry solids. Thus, the large-scale electro-osmotic dewatering of tailings ponds seems to be a feasible proposition in the case of coal tailings.

Theory of Electrokinetic Dewatering

Slurries containing fine clayey particles can be dewatered and consolidated by the application of a direct electric current if the partially immobile clay particles carry an electrostatic charge relative to the liquid in the slurry. Siliceous clay particles, such as kimberlite, are normally charged negatively with respect to the surrounding water owing to the greater solubility of positive ions associated with these particles, and ion deficiencies in the interior of the clay particle.

The surface of the particle, once charged, attracts ions of the opposite sign towards it, but they are retained in the medium by virtue of their thermal or kinetic energy. An electrostatic double-layer is thereby created in the vicinity of each particle. At some distance within the electrostatic double-layer, a shear plane develops between the particle and the atmosphere of counter ions. The electrical potential at this shear plane is known as the zeta potential.

Electrophoretic dewatering depends on two fundamental mechanisms: electro-osmosis and electrophoresis. Under an applied direct electric current, the clayey particles could migrate through the surrounding stationary liquid phase to the positive electrode (anode). This would then represent a dominant electrophoretic mechanism. On the other hand, the applied direct electric current could cause positive ions in the surrounding liquid and in the outer diffused part of the electric double-layer to migrate towards the negative electrode (cathode). These cations mechanically draw with them the residual mass of free water, which results in a movement of liquid in the pore meshwork of fine particles. This is the classical principle of electro-osmosis.

Kimberlite slurries are very stable and do not show any tendency to settle by gravity alone. Mackenzie and Lovell investigated the effect of different electrolytes on the stability of kimberlite slurries, and concluded that it is possible to coagulate particles in a slime through the addition of Mg²⁺ ions. However, these tests were conducted on very dilute kimberlite slurries, which had a solids content of less than 1 per cent. The addition of polyvalent counter ions such as Mg²⁺ and Ca²⁺ tends to reduce the effective charge density in the diffuse double-layer and leads to a reduction in magnitude of the zeta potential and the stability of the colloidal system.

A distinct property of the kimberlite slurry is its ability to 'set' to a weak gel at high concentrations of solids. When 'gelling' conditions prevail, the platy particles are immobilized. In a stirred suspension, the particles are then no longer free to orientate themselves in the shear gradient, and the silky 'streakiness' disappears, as observed by O'Gorman and Kitchener.

Experimental

Samples of kimberlite slimes were obtained from the slimes dam of Premier Diamond Mine near Pretoria. The mineralogy and characteristics of the kimberlite slimes are listed in Tables I and II. Analytically pure magnesium perchlorate (Mg(ClO₄)₂), which is used as an electrolyte in electrokinetic experiments, was obtained from Merck. Two anionic polyacrylamide flocculants (Praestol 2830 and Praestol 2935), were supplied by the Diamond Research Laboratory of De Beers Mines Division in Johannesburg.

Electrophoretic Experiments

For the purpose of this paper, electrokinetic dewatering taking place with the positive electrode (anode) at the bottom of the experimental vessel is referred to as electrophoretic dewatering.

Fig. 1 is a schematic diagram of the electrophoretic cell, which is made of Perspex. The cubic container, A, with dimensions (13.5 by 13.5 by 13.5 cm³) is fitted with a tight-fitting lid, B. The two stainless-steel electrodes, C, are connected to two insulated copper rods that protrude through the container lid, B. The upper electrode (cathode) is held in position by an insulated stand, D. The two electrodes were connected to a 20 A/360 V power supply via insulated copper wires. The electrodes were of identical construction and the dimensions are given in Fig. 2.

TABLE I

<table>
<thead>
<tr>
<th>CONSTITUENTS OF KIMBERLITE SLIMES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂SO₄</td>
<td>9.03%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>48.12%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.61%</td>
</tr>
<tr>
<td>MgO</td>
<td>25.30%</td>
</tr>
<tr>
<td>Other</td>
<td>10.94%</td>
</tr>
</tbody>
</table>

TABLE II

<table>
<thead>
<tr>
<th>CHARACTERISTICS OF KIMBERLITE SLIMES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content (by mass)</td>
<td>8.1%</td>
</tr>
<tr>
<td>Cation-exchange capacity (meq/100 g)</td>
<td>27</td>
</tr>
<tr>
<td>Density of kimberlite (kg/m³)</td>
<td>2800</td>
</tr>
<tr>
<td>Density of slurry (kg/m³)</td>
<td>1050</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>80% &lt; 1 μm</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>-45</td>
</tr>
<tr>
<td>pH</td>
<td>9.0</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Stellenbosch University https://scholar.sun.ac.za
Exactly 2 litres of kimberlite slime was placed in the cell, giving a depth of about 10.5 cm. A direct current of constant magnitude was passed through the slurry for a certain time interval, after which the current was switched off and samples were taken.

By use of a pipette, four samples (50 ml each) were drawn through holes in the container lid at different levels in the slurry. Care was taken not to disturb the slurry; therefore, samples were drawn starting at the upper level and moving downward. These four samples were then combined into one sample to represent the slurry in the container.

After the pH had been measured, the sample was prepared for zeta-potential measurements. About 50 ml of sample was centrifuged at 4000 r/min for 2 hours. One drop (about 0.06 ml) of the remaining sample was placed in 25 ml of clear supernatant liquid, and the zeta potential was measured by the use of a Riddick zeta-meter.

The slurry in the container was then discarded, and the container was filled with 2 litres of ‘fresh’ kimberlite slime for the next experiment. Several parameters, such as pH, temperature, height of sludge bed, and potential, were monitored throughout the experiments. The electrophoretic experiments were conducted on kimberlite slurries with varying solids contents at different magnitudes of direct current and applied voltages. The addition of Mg²⁺ ions and the flocculant prior to the electrophoretic experiments was investigated.

**Electro-osmotic Experiments**

For the purposes of this paper, dewatering taking place with a negative electrode (cathode) at the bottom of the experimental vessel is referred to as electro-osmotic de-watering.

Fig. 3 is a schematic diagram of the Perspex electro-osmotic cell, which has the same shape and dimensions as the electrophoretic cell (Fig. 1). The bottom electrode (cathode), A, along with a cloth as filter material, is fixed to the bottom of the cell above the hollow conycylindrical base, B, which serves as a water outlet. The anode is held in position by a clamp, C. These two electrodes are identical, and were constructed from stainless-steel wire mesh having apertures of 2 mm and wire gauge of 1 mm.
The power supply used for the electro-osmotic experiments was the same as that used for the electrophoretic experiments. The electro-osmotic cell was filled with 2 litres of kimberlite slime for each experiment. A slight positive pressure was maintained in the conical base below the filter cloth to prevent any premature dewatering of slurry before the power was switched on. A direct current was then applied to the slurry to draw water to the cathode by electro-osmosis. Immediately after the water started to flow in part B, the total volume of water recovered by electro-osmosis was collected in a measuring cylinder.

The required voltage necessary to maintain the constant direct current was measured throughout the experiment. When the flow of water had decreased to such an extent that no significant dewatering occurred, the current was switched off. Electro-osmotic experiments were conducted at different fixed electrode spacings, as well as with the anode always in contact with the upper surface of the sludge bed. The effect of different current densities on electro-osmotic dewatering was also investigated.

Results and Discussions

Electrophoresis with No Additives

Fig. 4 shows settling results for a slurry with a solids content of 8.1 per cent treated by direct currents of 0.5, 1.0, 1.5, and 2.0 A. These graphs show clearly that an increase in the magnitude of direct current enhances electrophoretic dewatering.

![Graph showing change in height of the sludge bed during electrophoresis at different constant currents for a slurry with a solids content of 8.1 per cent.](image)

A definite increase in temperature accompanied the settling of the sludge bed during these experiments, and is illustrated in Fig. 5. This rise in temperature was mainly the result of hydrolysis that took place at the electrodes. The increased temperature of the slurry caused its resistivity to decrease, and the required electrical potential necessary to maintain a constant direct current of specific magnitude was reduced. (Fig. 6).

The increase in pH that took place during electrophoretic dewatering at constant direct currents is illustrated in Fig. 7. The change in pH from 9 to 12 can also be attributed to the hydrolysis that took place at the cathode and the anode. Evolution of hydrogen was visible at the cathode and corresponds to the following equation:

\[ 2 \text{H}_2\text{O} + 2 \text{e}^- = \text{H}_2 + 2 \text{OH}^- \]
However, very little evolution of gas was observed at the anode, which indicates that the principal reaction occurring was probably the oxidation of the anode. This insufficient evolution of oxygen, together with the free evolution of hydrogen, caused the pH value to rise. Such changes in temperature, potential, and pH were also observed by Sprute and Kelsh.

When a slurry with a solids content of 8.1 per cent was treated by the use of constant electrical potentials of 46.5, 36.5, 26.5, and 16.5 V, the results illustrated in Fig. 8 were obtained. From Fig. 8, the relation between the electrophoretic settling velocity, $U_E$, and the applied constant potential gradient, $E_{AV}$, was obtained at 30, 40, 50, and 60 minutes. These results are illustrated in Fig. 9, and show that $U_E$ varied linearly with $E_{AV}$ above 2.5 V/cm. Yukawa et al. observed this linear relationship at all values of $E_{AV}$ during the dewatering of a slurry of calcium carbonate.

Fig. 10 illustrates the results when slurries with solids contents of 8.1, 6.7, 4.65, and 3.09 per cent by mass were subjected to electrophoretic settling at a direct current of 2A. Dilution of the original slurry with a solids content of 8.1 per cent was achieved by the addition of clear supernatant liquor from kimberlite slurry prepared by centrifugal methods. The required electrical potential necessary to maintain a constant direct current of 2A was almost identical for all these experiments (Fig. 11). Figs. 10 and 11 show clearly that the concentration of kimberlite particles in the slurry does not significantly affect electrophoretic dewatering.

The zeta-potential response of the particles with time when a slurry with a solids content of 8.1 per cent was treated by direct currents of 1 and 2A is shown in Fig. 12. Since the zeta potential showed no significant change as time progressed, the settling of particles during electrophoretic dewatering is not the result of any change in zeta potential.

Figs. 8, 9, and 10 seem to indicate that the applied direct current and potential act as the main driving force for electrophoretic dewatering.

**Electrophoresis and Mg$^{2+}$ Addition**

In the discussion on zeta potential and its effect on the coagulation of particles in a slurry, it was mentioned that a decrease in the magnitude of the zeta potential is a necessary condition under normal circumstances for coagulation. With this in mind, an attempt was made to decrease the magnitude of the zeta potential in order to enhance coagulation, and simultaneously to treat the
slurry electrically to see whether any improvement in the rate of electrophoretic settling could be achieved.

For these experiments, Mg(ClO₄)₂ was used as the electrolyte. Mackenzie and Lovell found the ClO₄⁻ ion to be indifferent to the kimberlite lattice, and its effect on the zeta potential to be negligible. The addition of Mg(ClO₄)₂ to the slurry would therefore mean that only the Mg²⁺ would play a role in affecting the zeta potential. The effect of the concentration of Mg(ClO₄)₂ on the zeta potential of the particles is illustrated in Fig. 13. It is evident from this graph that the zeta potential becomes less negative with increasing concentration of Mg(ClO₄)₂.

Fig. 14 shows the results for an electrophoretic experiment in which a slurry containing 8.1 per cent solids and 8.3 x 10⁻³ M Mg(ClO₄)₂ was treated by direct currents of 1 and 2A. Only a slight degree of electrophoretic settling occurred, and the results were not as favourable as when electrophoresis occurred without the addition of electrolyte. (Compare with Fig. 4.) This unusual behaviour may be a direct result of kimberlite moving to a 'gel' state. Normally, when gel formation is not involved, a decrease in the negative zeta potential would enhance the coagulation of particles.

The electrical double-layer repulsion decreases with the addition of electrolyte, and the weaker London–Van der Waals forces of attraction begin to have an effect as the particles come into contact. An open 'house-of-cards' structure is established, and the slurry sets into a weak gel. Gel-forming slurries such as that of kimberlite show very little syneresis, and therefore retard the settling.
of the sludge bed during electrophoresis.

**Electrophoresis and Flocculant Addition**

It is commonly assumed that neutralization of the zeta potential is a logical basis for the selection of a flocculant. Accordingly, since kimberlite particles have a negative zeta potential, a cationic flocculant would be the most appropriate to use. Work done by O'Gorman and Kitchener exposed the fallacy of this assumption. The use of cationic flocculants is bound to be wasteful because the polyelectrolyte chains are strongly attracted to the surfaces of the particles and are therefore no longer available for bridging.

Both anionic polyacrylamide flocculants, viz Praestol 2830 and Praestol 2935, were compared regarding their ability to settle kimberlite particles without the use of electrophoretic treatment. Their respective influences on the rate of electrophoretic dewatering of slurry were also compared.

During batch settling tests with no flow of current, Praestol 2830 did not produce a clear mudline between the murky supernatant liquid and the consolidated solids. Praestol 2935 showed a clearer mudline, which settled slightly more slowly than the murky interface of Praestol 2830. However, the concentration of solids in the resulting supernatant liquids showed Praestol 2935 to be more favourable. From a slurry with an initial solids content of 8,1 per cent, 10 p.p.m. of Praestol 2935 produced a supernatant liquid with a solids content of 4,45 per cent, as against the solids content of 5,7 per cent in the supernatant liquid produced by 10 p.p.m. of Praestol 2830 after 60 minutes of consolidation.

At similar dosages, these two flocculants revealed no significant difference in the rate of dewatering after electrophoretic treatment of 60 minutes. Based on this fact, and the observation that Praestol 2935 produced a clearer supernatant liquid during batch settling tests, it was decided that Praestol 2935 should be used as the flocculant in further experiments.

The negative charge on a kimberlite particle may not be too high to prevent adsorption of Praestol 2935 onto the particle. The slight increase in negative zeta potential shown in Fig. 15 suggests some such adsorption. Fig. 16 shows electrophoretic results at a direct current of 1,5 A for a slurry with a solids content of 8,1 per cent containing 0, 1, 3, and 10 p.p.m. of Praestol 2935. As shown, the increased addition of Praestol 2935 enhanced the settling of the sludge bed. Fig. 17 reveals that no significant change in the pattern of potential decrease occurred with increased addition of flocculant while a direct current of 1,5 A was maintained. Therefore, the improved electrophoretic dewatering cannot be ascribed to any electrical effect but should be attributed to the additional effect of flocculation.

**Electro-osmotic Experiments**

Suspensions of fine clayey particles such as kimberlite settle slowly to form a highly viscous sediment that is difficult to dewater because of the fineness of the pores between particles. Since electro-osmotic flow is relatively insensitive to pore size, it is an attractive method for the dewatering of suspensions of fine particles.

During electro-osmotic dewatering, the positive upper electrode can either be kept at a constant distance from the negative electrode at the bottom of the vessel or can follow the descent of the mudline as dewatering progresses. Fig. 18 shows results for the electro-osmotic flow of water when a slurry with a solids content of 8,1 per cent was treated by direct currents of 0,5 to 2,5 A at a constant electrode spacing of 30 mm. From this graph, it is evident that electro-osmotic dewatering is approximately proportional to the applied direct current.

Patterns of changes in pH, temperature, and applied potential similar to those observed during electrophoretic dewatering (Figs. 5, 6, and 7) were also obtained during electro-osmotic dewatering. The same arguments as were used to explain these changes also apply in the case of electro-osmosis.
Electro-osmotic experiments were also conducted at different constant electrode spacings. Fig. 19 illustrates electro-osmotic dewatering at constant electrode spacings of 30, 40, and 55 mm and a constant direct current of 1.5 A. Fig. 19 also shows the result when the anode (top electrode) follows the descent of the mudline during electro-osmotic dewatering. No significant change in dewatering occurred at different electrode spacings.

Fig. 20 shows that the applied potential necessary to maintain a constant direct current of 1.5 A decreased with decreasing electrode spacing. These results were recalculated to yield Fig. 21. No significant change of gradient in the applied potential was evident during the first 30 minutes of electro-osmotic dewatering with fixed electrodes. The more obvious change in applied potential gradient after 30 minutes cannot be ascribed to different patterns of increase in temperature, since almost identical patterns were measured for different spacings of the fixed electrodes. However, the steadily increasing concentration of solids between the two electrodes with decreasing electrode spacing increases the resistance of the slurry, and this may be responsible for the increased gradient in applied potential.

When fixed electrodes were used, slurry had to be...
drawn through the porous cake that formed at the bottom of the anode. This increased the effective resistance of the material between the two electrodes. In the case of a moving anode, all the slurry to be dewatered was below this porous cake, which resulted in less resistance to the flow of current. Therefore, lower potential gradients were required when a moving anode was used, as shown in Fig. 21.

**Efficiencies of Electrophoresis and Electro-osmosis**

The volume of water recovered after a certain time interval and the accompanying energy consumption are two useful criteria in a comparison of electrophoretic and electro-osmotic dewatering. The consumption of electrical energy for the various electrokinetic experiments is illustrated in Figs. 22 to 24.

Tables III to VII reflect the experimental conditions, as well as the volume of water recovered and the power consumption after 60 minutes of electrokinetic treatment. In general, electro-osmotic dewatering seems to be more energy-efficient than electrophoretic dewatering (compare Tables III and VI). The addition of flocculants produced an increase in the volume of recovered water and led to a more efficient process (Table V). However, the best
result when flocculant was added was still not as good as the worst result during electro-osmotic dewatering at constant direct currents (compare Tables V and VI).

From Tables III to VII it seems as if electro-osmotic dewatering of kimberlite slimes takes place at a higher rate than electrophoretic dewatering. This was also observed visually during the experiments since electro-osmotic dewatering began immediately after the power was switched on, while electrophoretic dewatering took some time before the mudline started to descend.

**Conclusions**

(1) The electrophoretic settling velocity, \( U_p \), varies linearly with the average applied potential gradient, \( E_{AV} \), above 2.5 V/cm and is not very dependent on the concentration of particles in the kimberlite slurry.

(2) Electrophoretic treatment does not change the zeta potential of the kimberlite particles significantly. Therefore, electrophoretic settling cannot be ascribed to a change in zeta potential.

(3) Although some adsorption of the flocculant Praestol 2935 occurred onto the kimberlite particles, this adsorption did not influence the electrical behaviour of the slurry. The improved electrophoretic dewatering with increasing additions of Praestol 2935 could therefore be attributed to the additional effect of flocculation.

(4) Although the addition of \( \text{Mg}^2+ \) ions lowered the magnitude of the zeta potential of the kimberlite particles, this did not lead to coagulation in the slurry. A weak ‘gel’ developed and contributed to the poor electrophoretic dewatering that occurred with the addition of \( \text{Mg(ClO)}_2 \).

(5) Electro-osmotic dewatering was found to be approximately proportional to the applied constant direct current. No relationship was found between the rate of electro-osmotic dewatering and the distance between the two electrodes.

---

**TABLE III**

<table>
<thead>
<tr>
<th>Electrolysis at Different Constant Direct Currents*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current, A</td>
</tr>
<tr>
<td>Units of electricity, W min</td>
</tr>
<tr>
<td>Vol. of H2O recovered, ml</td>
</tr>
<tr>
<td>Power consumption, kWh/kl</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>2.0</td>
</tr>
</tbody>
</table>

* From Figs. 4 and 22

---

**TABLE IV**

<table>
<thead>
<tr>
<th>Electrolysis at Different Particle Concentrations*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current, A</td>
</tr>
<tr>
<td>Solids, %</td>
</tr>
<tr>
<td>Relative density</td>
</tr>
<tr>
<td>Units of electricity, W min</td>
</tr>
<tr>
<td>Vol. of H2O recovered, ml</td>
</tr>
<tr>
<td>Power consumption, kWh/kl</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

* From Figs. 10 and 22

---

**TABLE V**

<table>
<thead>
<tr>
<th>Flocculation at Different Additions of Flocculant*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage of Praestol 2935, p.p.m.</td>
</tr>
<tr>
<td>Current, A</td>
</tr>
<tr>
<td>Units of electricity, W min</td>
</tr>
<tr>
<td>Vol. of H2O recovered, ml</td>
</tr>
<tr>
<td>Power consumption, kWh/kl</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

* From Figs. 16 and 22

---

**Fig. 24**—Consumption of electricity during electro-osmosis at different electrode spacings.
(6) In general, electro-osmotic dewatering seemed to be more energy-efficient than electrophoretic dewatering.

Acknowledgements
The financial and technical assistance of De Beers Diamond Research Laboratories is gratefully acknowledged.

References

Development of PROTEC

PROTEC (Programme for Technological Careers) continues to develop despite the deteriorating condition of formal schooling in the Black communities. PROTEC now has nearly 2000 high-school students involved in its seven active branches—in Soweto, Alexandra, the East Rand, Johannesburg Western Areas, Sasolburg, Mmabatho, and Richards Bay.

Several hundred additional students from among the 1984 and 1985 school leavers are still involved with PROTEC, and are showing promising career progress. A large proportion of them are at university, technikon, or technical college, or receiving in-service training. Some are doing very well at university and at colleges.

The active involvement of students and parents in the programme, and the positive response of the communities, are healthy indicators for the future.

As a non-formal education programme, PROTEC is grappling with pressures to become more involved in formal schooling because of the general breakdown in this area in several of the branches. While alternative solutions are being devised in certain cases, PROTEC can never be a substitute for ongoing formal schooling. It is significant, however, that PROTEC retains credibility and communication with the communities, including the students, in finding short- and medium-term alternatives.

In these troubled times, PROTEC is serving an extremely important function in communicating and bridging a widening gap between employers and the communities concerned. PROTEC’s emphasis has shifted from serving the needs of employers in terms of narrow vocational development alone, to also meeting the human and long-term life needs of the communities and of donors, who are often subject to local and international pressure.

In response to this, it has become necessary for PROTEC to consider restructuring its Council to reflect more community and branch representation, and less control by the engineering societies. This should in no way be interpreted as a reduction in recognition of the valuable role being played by the engineering profession, which started PROTEC. Indeed, there is a growing need for this type of involvement but, with the expansion and decentralization of PROTEC, the emphasis will be increasingly on contributions through the Branch Boards.

Should you wish to have more information about PROTEC, please contact

Celia Stephens
Public Relations Co-ordinator
P.O. Box 52657
Saxonwold
Johannesburg 2132.

Telephone: (011) 788-8652/7209.
Intensification of flotation with an air-sparged hydrocyclone

by J.S.J. VAN DEVENTER*, A.J. BURGER†, and F.L.D. CLOETE‡

SYNOPSIS

Tests indicated that effective recovery of pyrite from a coarse Witwatersrand quartzitic ore can be accomplished by intensified flotation in an air-sparged hydrocyclone. Air is fed through the porous cylindrical wall of the hydrocyclone into a swirling layer of slurry. Hydrophobic particles are attached selectively to small air bubbles, which form a froth and are recovered through the overflow. Hydrophilic particles pass out in the underflow. A spigot in which flow is restricted by an orifice was found to be more successful in preventing blockage by wood chips than an annular opening between a pedestal and the cylinder wall.

Pyrite recoveries of 85% to 40% per cent sulphur were obtained in the air-sparged hydrocyclone with residence times of about 1 second. Comparative tests in a batch flotation cell at 320 seconds yielded average recoveries of up to 96 per cent, but with a mean grade of 32.5 per cent sulphur. A high collector dosage of 120 g/t was required in the cyclone, compared with the 40 g/t used in conventional operations. An air feed rate of about 150 l/min was adequate at a slurry feed rate of 35 l/min. Particle sizes between 38 and 106 μm yielded the best flotation results.

SAMEVATTING

Toetse het getoon dat doeltreffende herwinning van pieniet uit 'n groewe kwartsfase Witwatersranderts bewerkstellig kan word deur verskerpte flottasie in 'n luggeblaasde hidrosikloon. Lug word deur die poreuse laag flooder ingevoer. Hidrofobiese partikels word selektief aan klein lugborrels geheg wat 'n skuim vorm en deur die oorloop herwin word. Hidrofiliese partikels gaan in die onderloop uit. Daar is gevind dat 'n aftakpelkaart waarin vloeiend deur 'n opening beperk word, meer geslaagd as 'n ringvormige opening tussen 'n voetstuk en die cilinderraam is om verstopping deur houtspaaners te voorkom.

Pyrietverwinnings van 85 tot 40 persent met grade van 35 tot 40 persent swael is in die luggeblaasde hidrosikloon verkry met 'n verblyf van ongeveer 1 sekonde. Vergelykende toetse in 'n flottasiesel het na 320 seconde gemiddelde herwinning van tot 95 persent gelever, maar met 'n gemiddelde graad van 32.5 persent swael. 'n Hoë verbeteraardos van 120 g/t was in die sikloon nodig vergeëgie met die 40 g/t wat in konvensionele bewerkings gebruik word. 'n Lugvloeteempo van ongeveer 150 l/min was voldoende met 'n flooderstoetetoempo van 35 l/min. Partikelgroot- tes tussen 38 en 106 μm het die beste flottasieresultate gelever.

Introduction

The beneficiation of minerals by froth flotation is based upon controlled hydrophobicity. However, fine particles are recovered inefficiently, and this results in a loss to the tailings of large quantities of valuable minerals worldwide1. It has been found that every mineral has a limiting particle size below which its floatability decreases significantly, and that the probability of collision and attachment in conventional flotation cells is low owing to the relatively low intensity of the turbulence.

Consideration of these constraints led to the development of an air-sparged hydrocyclone (ASH) in the late 1970s at the University of Utah2. This device was designed to utilize the powerful centrifugal force developed in a cyclone, together with a high concentration of small bubbles, to achieve effective flotation of fine particles at an increased rate. Air is fed to the cyclone through its porous walls. Pressure relief of air-saturated slurries in a hydrocyclone has been proposed for enhancing the rate of flotation1,4.

The rate of flotation in an ASH is limited by bubble-attachment phenomena, rather than by the rates of collision or air flow2. In this highly intensified flotation device, separations can be achieved for residence times of about 1 second, rather than minutes as in conventional cells. Miller and his co-workers demonstrated their concept successfully in the flotation of the ASH in oil shale3, fine coal,1 copper sulphide ore4, fine gold,4 resin from coal5, and oil from water6. Fundamental work has also been performed on the swirl flow2 and swirl-layer thickness5, bubble formation11, velocity profiles2, Prandtl's mixing length12, phase split11, hold-up volume13, and mean residence times11.

The ASH has not been tested in the South African mining industry, although tens of millions of tons of gold-bearing pyritic ore pass annually through its flotation plants. The work by Burger14 reported here was undertaken to study the applicability of Miller's ASH to the flotation of pyrite from a coarse Witwatersrand quartzitic gold ore. This paper reports the effects of operating variables on the efficiency of flotation in the ASH.

Experimental

Air-sparged Hydrocyclone and Ancillary Equipment

Fig. 1 shows a schematic diagram of the ASH used by...
The porous cylinder has pores with a median size of 1.0 μm and is arranged vertically, with tangential slurry feed at the top, froth overflow through the central vortex finder, and an annular opening between the wall and the pedestal for the downward flow of tailings. Air bubbles sparged radially through the ceramic porous wall are dispersed to the rising froth phase. Miller and Van Camp\textsuperscript{15} recommended that a vertical cyclone with tangential feed at the top would be the preferred design.

The porous cylinder has a magnetic flowmeter was used to monitor the feed slurry pumped by a centrifugal slurry pump.

**Characteristics of the Ore**

The ore used was an easily floatable coarse pyritic ore from the reclaimed dumps of Ergo Ltd on the eastern Witwatersrand. The average sulphur content was 1.74 per cent by mass (which corresponds to 3.26 per cent FeS\textsubscript{2}), and the absolute density was 2.747 kg/m\textsuperscript{3}. Table I gives the particle-size distribution, as well as the distribution of sulphur with size fraction. It is clear that 68 per cent of the sulphur in the ore was present in the fraction between 53 and 150 μm. All the particles passed through a 300 μm sieve.

**Operating Procedures**

The slurry was prepared from tap water and fresh ore taken from sealed drums. Commercial-grade potassium amyl xanthate (a collector) and a proprietary frother (Dowfroth 250: polypropylene glycol methyl ether) were added to the slurry at a pH value of 4.0 to 4.5 before conditioning for 10 minutes. Most of the runs used feed slurry of 10 per cent solids by mass containing 160 g/t of collector and 30 to 50 p.p.m. of frother, although some tests were done under different conditions.

Samples of overflow and underflow products from the ASH were taken simultaneously and weighed. Discrepancies in the mass balances for sulphur, total solids, and water were below 5 per cent. The solids were filtered, dried, and assayed for sulphur, and the particle-size fractions were determined by dry sieving down to 38 μm and wet sieving below that size.

**Batch Flotation Tests**

A set of experiments was also performed on the same ore and reagents in a 3-litre modified Leeds batch laboratory flotation cell. The conditions used were 30 per cent solids by mass, an air flowrate of 6.5 l/min, a pH value of 4.5, a froth height of 2.4 cm, a frother addition of 50 p.p.m., a collector addition of 40 g/t, a water feed rate for froth drainage of 0.03 l/min, and a stirring speed of 1500 r/min.

---

**Table I**

<table>
<thead>
<tr>
<th>Size fraction μm</th>
<th>Mass %</th>
<th>% in size range</th>
<th>Mass % of total S in ore in size range</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 212</td>
<td>11.5</td>
<td>0.322</td>
<td>2.13</td>
</tr>
<tr>
<td>+ 150</td>
<td>30.0</td>
<td>0.748</td>
<td>13.0</td>
</tr>
<tr>
<td>+ 106</td>
<td>22.4</td>
<td>2.08</td>
<td>26.9</td>
</tr>
<tr>
<td>+ 75</td>
<td>15.5</td>
<td>2.70</td>
<td>24.2</td>
</tr>
<tr>
<td>+ 53</td>
<td>9.3</td>
<td>3.14</td>
<td>16.8</td>
</tr>
<tr>
<td>+ 38</td>
<td>2.8</td>
<td>3.61</td>
<td>5.82</td>
</tr>
<tr>
<td>- 38</td>
<td>8.5</td>
<td>2.29</td>
<td>11.2</td>
</tr>
<tr>
<td>All fractions</td>
<td>100.0</td>
<td>1.74</td>
<td></td>
</tr>
</tbody>
</table>
Results and Discussion

Recovery of Water with No Solids Present

In some experiments, clear water containing no reagents was fed to the ASH in order to characterize its flow behaviour by use of the simplest possible system. Figs. 2 and 3 depict the results for the two types of spigots used.

![Fig. 2-Recovery of water in the overflow with no solids present, using the brass pedestal of 48.0 mm diameter](image1)

![Fig. 3-Recovery of water in the overflow with no solids present, using the polyethylene spigot with an orifice diameter of 15.0 mm](image2)

Miller et al.\textsuperscript{1,17} observed that the thickness of the swirl layer in an unrestrict ed vertical cylinder increased slightly with axial distance from the header. Baker et al.\textsuperscript{13} observed that the thickness of the swirl layer in a restricted cylinder was 5 to 7 per cent of the diameter of the cylinder, and increased with both air flowrate and water flowrate.

It can be expected that the flow of air reduces the effective centrifugal force experienced by a fluid element. For water feed rates of less than about 15 l/min, the centrifugal forces were so weak that water was easily entrained. Figs. 2 and 3 show that an increase in the water feed rate within this range resulted in an increased recovery of water in the overflow. As the feed rate of water increased further, its centrifugal force overcame the entraining effect of air to reduce the recovery to a minimum.

At higher feed rates of water, and therefore greater thickness of the swirl layer, the restricting effect of the annular opening or orifice area forced more water to the overflow. With an increase in the air flowrate, an increased feed rate of water was required to counteract the entraining effect of the air, so that the position of minimum recovery moved to the right in Figs. 2 and 3. The minimum recovery occurred at a feed rate of 40 l/min when frother was added.

Figs. 2 and 3, as well as further work by Burger\textsuperscript{14}, showed that both the negative and the positive slopes of the recovery curves for the orifice-limiting spigot were steeper than those for the conical brass pedestal. It is noteworthy that the flowrate of air did not appear to have any effect on the recovery of water in the range of higher water feed rates when an orifice-limiting spigot was used.

Recovery of Water and Solids Using Reagents

Figs. 4 to 9 illustrate the recovery of water, total solids, and sulphur under different operating conditions. The general trends of these curves is discussed below.

According to Figs. 4 to 6, the water recovery was similar to that observed in Figs. 2 and 3. It appears as though the recovery of water was higher when solids were present, probably owing to the increased thickness of the swirl layer\textsuperscript{22} and the stabilization of the froth phase by fine particles\textsuperscript{15}. In general, the recovery of solids decreased sharply as the feed rate of slurry to the ASH increased.

Burger\textsuperscript{14} showed that, when no reagents were used, only particles smaller than 38 \(\mu\)m were entrained significantly to the overflow at slurry feed rates higher than about 35 l/min. The recovery of sulphide particles larger than 38 \(\mu\)m was inhibited at higher feed rates of slurry, while the opposite held\textsuperscript{16,17} for particles smaller than 38 \(\mu\)m. High turbulence and strong centrifugal forces tend to rupture the hydrophobic particle–bubble aggregates, yet increase the collision efficiency of small particles\textsuperscript{16,17}.

According to Figs. 7 to 9, the grade of sulphur in the concentrate showed a general increase with an increase in centrifugal force at lower feed rates of slurry. A maximum grade was attained near the slurry feed rate that yielded the minimum recovery of water. It is noteworthy that the decreased recovery of total solids at lower feed rates of slurry was associated with an almost constant recovery of sulphur. This means that the increased centrifugal force had a cleaning action on the froth\textsuperscript{15,16} so that the increase in grade is understandable.

An unexpected change in the shape of the grade curves (Figs. 7 to 9) and in the recovery of total solids (Figs. 4 and 6) occurred at a slurry feed rate between 30 and 40 l/min. This behaviour was more pronounced for the coarse particles, and was reproducible\textsuperscript{14}. 

JOURNAL OF THE SOUTH AFRICAN INSTITUTE OF MINING AND METALLURGY

OCTOBER 1988 327

Stellenbosch University  https://scholar.sun.ac.za
Fig. 4—Recovery of water and solids at two diameters of the brass pedestal (solids in feed = 30 mass %, air flowrate = 205 l/min, collector = 80 g/t, frother = 50 p.p.m.)

Fig. 5—Recovery of water and solids at different flowrates of air using a polyethylene spigot (solids in feed = 10 mass %, collector = 160 g/t, frother = 35 p.p.m.)

Fig. 6—Recovery of water and solids at different densities of slurry using a polyethylene spigot (air flowrate = 200 l/min, collector = 160 g/t, frother = 35 p.p.m.)

Fig. 7—Grade and recovery of sulphur at two diameters of the brass pedestal (solids in feed = 30 mass %, air flowrate = 205 l/min, collector = 80 g/t, frother = 50 p.p.m.)
These tests showed that the ASH as used by Burger is capable of a pyrite recovery of over 85 per cent and a concentrate grade of 40 per cent sulphur (i.e. 75 per cent FeS₂) at slurry feed rates of between 30 and 40 l/min. Such results compare favourably with those normally obtained for rougher flotation in plants operating on the same ore.

**Effect of Underflow Opening**

Figs. 4 and 7 show results for conical brass pedestals of diameters 48,8 and 49,0 mm, which extended 30,4 and 34,0 mm respectively into the porous cylinder. A reduction of 16,5 per cent in the annular area (Fig. 4) increased the-recovery of water at all slurry feed rates, and caused a smaller increase in the recovery of total solids. The recovery and grade of sulphur were not affected significantly.

**Effect of Air Flowrate**

Fig. 5 illustrates an increase in water recovery with an increase in air flowrate at lower slurry feed rates, and a concomitant shift of minimum water recovery to higher slurry feed rates. This behaviour can be explained in the same way as that observed for Figs. 2 and 3. It is evident that the recovery of total solids was not influenced by the flowrate of air, and it is therefore surprising that the flowrate of air affected the recovery of water adversely at high slurry feed rates.

An increase in the air flowrate (Fig. 8) enhanced the recovery of pyrite, especially at high slurry feed rates. This effect was similar for all the size fractions, which could indicate that the dense pyrite particles were recovered preferentially in the froth.

**Effect of Slurry Density**

The significant increase in water recovery obtained with increased solids content of the slurry is illustrated in Fig. 6. The throttling effect of the spigot with an increase in the solids content from 30 to 45 per cent was the likely cause of the dramatic increase in the recovery of water, especially at high slurry feed rates.

An enhanced recovery of total solids and pyrite, together with a decrease in the sulphur grade with increased solids content of the feed, was measured as shown in Figs. 6 and 9. The shapes of the curves for the recovery of water do not appear to be influenced significantly by the solids content, apart from the curve for 45 per cent solids. This means that a relatively dilute slurry could be used in studies on an ASH.

**Effect of Collector Addition**

The particle–bubble aggregates could become more stable with increased additions of collector. This, in turn, would stabilize the froth and increase the recovery of water, as is evident from Fig. 10. It is significant that the addition of collector exerted an influence only at higher slurry feed rates, where high centrifugal forces come into effect.

When the addition of collector was increased, the point of minimum water recovery tended to occur at lower slurry feed rates. An increase in the recovery of pyrite at all feed rates of slurry is shown in Fig. 11. It is difficult to draw a general conclusion about the effect of
collector addition on the recovery of total solids or the grade of concentrate.

An addition of 120 g/t seems to be sufficient for this type of ore. The dosage of 40 g/t that is used in conventional plants would have been quite inadequate, owing to the high shearing forces on the particle–bubble aggregates in the ASH.

The influence of collector addition revealed the same trends for all size fractions, but the sulphur grade of the coarser particles appeared to be enhanced relatively more.

**Effect of Frother Addition**

Miller *et al.*\(^1\) showed that the recovery of water increased with increased addition of frother. This effect is confirmed by the results illustrated in Fig. 12, which show that the increased recovery of water at all feed rates of slurry was accompanied by an increase in the recovery of solids.

The corresponding decrease in sulphur grades shown in Fig. 13 was a result of this enhanced recovery of hydrophilic particles. At slurry feed rates below 40 l/min, the recovery of pyrite decreased with an increase in frother addition. This behaviour was the opposite to that observed for conventional flotation.

Fig. 14 shows the recovery and grade curves for all the particle-size fractions at a slurry feed rate of 35 l/min. The shapes of these curves are explained by Burger\(^4\), and are similar to those observed by Miller *et al.*\(^5\). At slurry feed rates higher than 40 l/min, a more stable froth resulting from increased additions of frother enhanced
the recovery of pyrite, as illustrated in Fig. 13. Baker et al.\textsuperscript{13} showed that frother additions above 40 p.p.m. did not have any significant influence on the hold-up volume in the ASH.

**Comparison with Batch Flotation**

The batch results shown in Fig. 15 demonstrate that all the size fractions yielded recoveries of over 90 per cent after 300 seconds. Burger\textsuperscript{24} obtained recoveries of pyrite of up to 96 per cent after 320 seconds, but with a relatively low average sulphur grade of 32.5 per cent.

These batch results could be used in a comparison of the performance of the ASH with that of a conventional rougher cell\textsuperscript{13}. The mean residence time for a similar ASH was measured as 0.5 to 1.0 second\textsuperscript{13}. The throughput per unit volume of the ASH is thus about 500 times that of a conventional cell.

Burger\textsuperscript{24} observed an optimal addition of collector of 50 g/t during batch flotation. For short residence times, an increased addition of collector significantly decreased the recovery of pyrite. This phenomenon is known as over-xanthating\textsuperscript{19}. In comparison with the results illustrated in Fig. 11, it is clear that significantly lower additions of collector were required in the batch cell.

**Conclusions**

Pyrite can be recovered effectively from a coarse Witwatersrand quartzitic ore by intensified flotation with an air-sparaged hydrocyclone (ASH). Recoveries of pyrite from 85 to 93 per cent at grades of 35 to 40 per cent sulphur were obtained in the ASH. Optimal recoveries and grades were obtained for particles between 38 and 106 μm.

The separation achieved after 0.5 to 1 second in the ASH was comparable with that attained in conventional batch flotation tests after 300 seconds. The ASH has a potential advantage over conventional cells in its very high throughput per unit volume, which was 300 to 1 for this ore.

A disadvantage of the ASH is that it requires three times as much collector as a conventional flotation cell.

The proposed new design of an orifice-limiting spigot instead of an annular-limiting spigot proved to be successful in preventing blockage by wood chips.

**Acknowledgements**

This paper is published with the permission of the Council for Mineral Technology (Mintek), whose finan-
cial assistance is greatly appreciated. Thanks are extended to Mr R.C. Dunne and Dr W.A.M. te Riele for valuable discussions during the course of this work.

References
8. Kinneberg, D.J., and Miller, J.D. Copper sulfide flotation in an air-sparged hydrocyclone. USBM final report for research done on Grant G1115429. Department of Metallurgy, University of Utah, Salt Lake City, May 1983.
THE INFLUENCE OF DESIGN VARIABLES ON THE FLOTATION OF PYRITE IN AN AIR-SPARGED HYDROCYCLONE

D.J. NIEUWOUDT†, J.S.J. VAN DEVENTER†, M.A. REUTER* and V.E. ROSS§

† Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7600, South Africa
* Present address: Institut für Metallhüttenwesen und Elektrometallurgie, Der Rhein.-Westf. Techn. Hochschule Aachen, Intzstraße 3, 5100, Aachen, FRG
§ Minerals Engineering, Mintek, Private Bag X3015, Randburg 2125, South Africa
(Received 11 July 1989; accepted 6 November 1989)

ABSTRACT

Two batches of ore, A and B, from the reclaimed dumps of ERGO Ltd on the East Witwatersrand were used to investigate the effect of design parameters on the flotation of pyrite in an air-sparged hydrocyclone (ASH). In the ASH, air is sparged radially through a porous cylinder and dispersed by the high velocity of slurry in swirl flow, countercurrent to the froth phase rising axially in the centre of the cylinder. The concentrate overflows through the vortex finder, while the tailings flow downward. A spigot where flow is restricted by a horizontal baffle, positioned 30mm above the orifice, proved to be more successful than a spigot consisting of an annular opening between a pedestal and the cylindrical wall, and a flow restricting orifice below.

Pyrite from both samples A and B was difficult to float efficiently. Sample A, which contained only 0.14%S, yielded typical sulphur recoveries of 40% and associated grades of 4%S in the ASH, while batch flotation yielded recoveries of 65% and grades of 11%S. The corresponding results for Sample B with a head grade of 1.42%S, were 40% and 7.5%S in the ASH, and 56% and 6%S in batch tests. From a variety of runs, it can be concluded that flotation in the ASH is influenced mainly by the tangential velocity and the hold-up of slurry. Hence, the effective design of an ASH is critically dependent on the dimensions of the cylinder, vortex finder and the spigot. For some ASH designs, flotation performance could be improved noticeably by sealing off the lower part of the porous cylinder.

Keywords
Flotation; hydrocyclone; pyrite; slurry; sulphides; air-sparged hydrocyclone

INTRODUCTION

The inefficient recovery of fine particles in conventional froth flotation results in large quantities of valuable minerals being lost to tailings [1]. Owing to the relatively low intensity of micro-turbulence, the probabilities of collision and attachment in conventional flotation cells are low. Consideration of these constraints led to the development of an air-sparged hydrocyclone (ASH) in the late seventies at the University of Utah [2]. The powerful centrifugal forces developed in a hydrocyclone, together with a high concentration of small bubbles are utilized to achieve effective flotation of fine particles at an increased rate. Bubble attachment phenomena, rather than the rate of collision or air flow, limit the rate of flotation in an ASH [3]. In an ASH, separations can be achieved for residence times of about one second rather than minutes as in conventional flotation cells.
The ASH consists of a vertical porous cylinder with slurry fed tangentially at the top. The concentrate overflows through the vortex finder, while the tailings flow downward through a spigot. The high velocity of slurry in swirl flow, countercurrent to the froth phase rising axially in the centre of the cylinder, disperses the air which is sparged radially through the porous cylinder wall.

Miller and co-workers have proved their concept in the flotation of oil shale [4], fine coal [5], copper sulphide ore [6] and fine gold [7]. They have also conducted fundamental work on the dynamic performance of the ASH [3,8,9]. Burger [10] and Van Deventer et al. [11] showed that the ASH could be used successfully for the flotation of a coarse pyritic ore containing 1.74%S, and investigated the effect of operating variables. Although Miller and co-workers have conducted a wide range of fundamental research on the ASH, it is believed that factors influencing the design of an ASH are still understood poorly.

This paper reports the influence of design variables on the flotation performance of an ASH using two quartzitic gold ores from the Witwatersrand. These ores were of a lower grade and less amenable to flotation than that used by Burger [10]. The effect of the operating parameters such as the head grade and the mass % of solids in the slurry will also be discussed. This paper will be a further advance towards an understanding of the ASH, but does not attempt to analyse the very complex flow patterns in the ASH.

EXPERIMENTAL

Air-Sparged Hydrocyclone (ASH)

Two different air-sparged hydrocyclones, ASH I and ASH II, were used to generate the results presented in this paper. Figure 1 shows a schematic diagram of the ASH, with basic features being similar to the ASH used by Miller and co-workers [2-9, 12] and Burger [10]. The porous cylinder is arranged vertically, with tangential slurry feed at the top, and froth overflowing through the central vortex finder. Air bubbles sparged radially through the porous cylinder are dispersed by the high velocity of slurry in swirl flow countercurrent to the rising froth phase.

ASH I consisted of a slurry inlet of 15.8 x 5.4 mm², vortex finder of diameter 13.7 mm and length 50 mm, porous ceramic cylinder of internal diameter 50 mm, length 410 mm and porosity 1 micron, and a 44.1 mm diameter pedestal above the spigot with an orifice of diameter 10 or 15 mm. This configuration was similar to that used by Burger [10]. He showed that a spigot in which flow is restricted by an orifice, instead of an annular opening between the pedestal and the cylinder wall [3], was more successful in preventing blockage by wood chips.

ASH II was fitted with porous sintered bronze cylinders of thickness 2.0 mm, and this design permitted a variety of hydrocyclone configurations as shown in Table 1. A simple horizontal baffle with length equal to the internal diameter of the cylinder, height of 8 m and thickness of 4 mm, was positioned in ASH II 30 mm above the orifice. More details about the mechanical design of ASH I and II are shown in Figure 1.

Characteristics of the Ores

Two different batches of ore, A and B, obtained from the reclaimed dumps of ERGO Ltd. on the East Witwatersrand, were used. Table 2 gives the distribution of total mass and sulphur in the particle size fractions. It is clear that ore A was much coarser than ore B. The bulk of the pyrite in ore B was in the -38 micron fraction.

Batch flotation tests were conducted in a 2.5 l Leeds open-top cell. The conditions used were an air flow rate of 6 l/min, a froth height of 12 mm, impeller speed of 1100 r.p.m. and the concentration of both collector (sodium isobutyl xanthate) and frother (Dowfroth 250E) was 50 p.p.m.
Fig. 1 Schematic diagram of the ASH showing different underflow configurations

Batch tests at 28.6 mass % solids on ore A yielded an optimal sulphur recovery of 65% and an associated grade of 11% S, while the corresponding values for ore B were 56% and 6% S respectively. At 50 mass % solids, ore B yielded a sulphur recovery of 66% and a grade of 5% S.

These results prove that neither of the ores floated easily. Although ore B had a high head grade of sulphur, it was the large percentage of fine pyrite bearing particles that could not be floated.
TABLE 1 Design dimensions used in ASH II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry inlet area (mm²)</td>
<td>15x6</td>
</tr>
<tr>
<td>Diameter of vortex finder (mm)</td>
<td>13.7</td>
</tr>
<tr>
<td>Length of vortex finder (mm)</td>
<td>50</td>
</tr>
<tr>
<td>Internal diameter of cylinder (mm)</td>
<td>46</td>
</tr>
<tr>
<td>Length of cylinder (mm)</td>
<td>300</td>
</tr>
<tr>
<td>Porosity of cylinder (micron)</td>
<td>2</td>
</tr>
<tr>
<td>Diameter of orifice (mm)</td>
<td>10.5</td>
</tr>
</tbody>
</table>

(Numbers in bold depict the standard dimensions for ASH II. These standard conditions were used, except where mentioned otherwise in the figures.)

TABLE 2 Distribution of particle size and sulphur in ores A and B

<table>
<thead>
<tr>
<th>Size fraction (micron)</th>
<th>Mass %</th>
<th>Mass % of total S in size fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ore A</td>
<td>Ore B</td>
</tr>
<tr>
<td>+300</td>
<td>15.9</td>
<td>3.2</td>
</tr>
<tr>
<td>-300 +212</td>
<td>17.3</td>
<td>3.7</td>
</tr>
<tr>
<td>-212 +150</td>
<td>23.5</td>
<td>7.7</td>
</tr>
<tr>
<td>-150 +106</td>
<td>23.6</td>
<td>21.4</td>
</tr>
<tr>
<td>-106 + 75</td>
<td>9.2</td>
<td>10.6</td>
</tr>
<tr>
<td>-75 + 53</td>
<td>6.9</td>
<td>9.0</td>
</tr>
<tr>
<td>-53 + 38</td>
<td>2.2</td>
<td>6.4</td>
</tr>
<tr>
<td>-38</td>
<td>1.4</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Average mass %S 0.14 1.42

Operating Procedures

A quartzitic slurry containing 10 mass% solids was prepared in a 470 l conditioning tank using tap water. The slurry was mixed for 15 minutes before 160 p.p.m. of sodium isobutyl xanthate was added. Another 5 minutes followed before 40 g/t of Dowfroth 250E was added. Ten minutes after frother addition, the slurry was pumped to the ASH. Samples of the overflow and underflow were taken simultaneously and weighed. The solids were filtered, dried and assayed for sulphur. Mass and sulphur balances were accurate within 5%. For ASH I the air flowrate was 200 l/min. The air flowrate for ASH II of length 500 mm and inner diameter 46 mm was 205 l/min, and for other configurations of ASH II the air flowrate was scaled-up on a volumetric basis as shown in Table 3.
TABLE 3 Flowrates of air in ASH II

<table>
<thead>
<tr>
<th>Cylinder Length (mm)</th>
<th>Cylinder Diameter (mm)</th>
<th>Air Flowrate (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>46</td>
<td>123</td>
</tr>
<tr>
<td>300</td>
<td>96</td>
<td>536</td>
</tr>
<tr>
<td>400</td>
<td>46</td>
<td>164</td>
</tr>
<tr>
<td>400</td>
<td>96</td>
<td>714</td>
</tr>
<tr>
<td>500</td>
<td>46</td>
<td>205</td>
</tr>
<tr>
<td>500</td>
<td>76</td>
<td>560</td>
</tr>
<tr>
<td>500</td>
<td>96</td>
<td>893</td>
</tr>
</tbody>
</table>

Experiments were conducted where porous sections along the length of the ASH were sealed off, as shown in Figure 1. The flow of air was maintained at a constant level for a specific ASH system, so that the flux of air increased through the remaining aerated area. For ASH I, 25% of the cylinder was sealed off at different positions, while only the bottom 30% was sealed off in the case of ASH II.

RESULTS AND DISCUSSION

Design of Underflow Outlet

ASH I was used here to improve the design proposed by Burger [10] and Van Deventer et al. [11].

The effect of a pedestal, as suggested by Miller and Kinneberg [3], was investigated by feeding slurry A to ASH I. The underflow outlet for ASH I was fitted with a pedestal, which was supported by three baffles spaced at angles of 120°, and followed by an orifice below. In this case the underflow was limited by the orifice below the pedestal, and not by the annular opening between the pedestal and the cylinder. Orifice diameters of 10 or 15mm were used.

When this pedestal was removed, the recoveries of solids and water changed very little, while the recovery of pyrite increased slightly, as illustrated in Figure 2. Hence, for this particular design and operating conditions, it could be concluded that a pedestal is not required in the ASH. The concentrate grade changed very little at an orifice diameter of 10mm, but increased significantly at 15mm according to Figure 3.

When the outlet, as mentioned above, was replaced by an orifice without any baffles, it was found that the water recovery increased at high feed rates of slurry, while the sulphur recovery and grade decreased correspondingly, as shown in Figures 2 and 3. This could be attributed to the absence of baffles which decelerated the swirl flow near the bottom of the ASH. A horizontal baffle placed slightly above the orifice is possibly the simplest method by which deceleration of the swirl flow can be achieved. Hence, the spigot for ASH I consisted of an orifice and a horizontal baffle, placed at a height of 30mm above the orifice. Figure 1 shows more details.

It was possible that this deceleration reduced turbulence in the froth phase, which inhibited the entrainment of water. The recovery of pyrite particles, however, would be enhanced in view of the lower shearing forces on particle-bubble aggregates.
Area of Slurry Inlet

Owing to the complex flow patterns in the ASH and the wide range of variables affecting its performance, it is difficult to draw general conclusions from one set of results. Nevertheless, Figures 4 and 5 indicate that the recovery of pyrite decreased generally with an increase in the feed rate of slurry, while the sulphur grade reached a maximum at intermediate feed rates.

The increased centrifugal force associated with an increase in the feed rate caused more particles to report to the underflow. As a result of the low density of the hydrophobic particle-bubble aggregates, relatively more hydrophilic particles than hydrophobic particles were affected in this way. It appeared that the recovery of total solids reached an asymptotic level at higher feed rates owing to the restriction of flow through the vortex finder. The decrease in the sulphur grade at higher feed rates can thus be explained by the decrease in recovery of pyrite relative to the recovery of total solids.
Figure 4 shows that the dimensions of the slurry inlet did not affect the recovery of sulphur substantially. However, the centrifugal velocity associated with the point of maximum sulphur grade in Figure 5 shifted to higher feed rates at larger inlet areas.

**Diameter of Vortex Finder**

According to Ye et al. [12] the concentration of hydrophobic particles decreases radially from a maximum in the centre of the froth phase to a minimum in the slurry layer. When the diameter of the vortex finder is increased, the froth core recovered will increase in diameter. This will result in an increased recovery of hydrophobic particles, but a decrease in concentrate grade [12]. Table 4 shows that an increase in the diameter of the vortex finder from 13.7 to 21.7 mm confirmed this hypothesis concerning the decrease in grade, but yielded almost no improvement in recovery.

When the diameter was increased to 27.7 mm, the recovery of pyrite in Table 4 decreased, while the recovery of total solids also decreased. Table 4 shows that the grade did not change noticeably at lower feed rates, but increased slightly at higher centrifugal velocities.
An explanation for this behaviour could be that the resulting drop in pressure over the length of the ASH had a more pronounced effect than the increase in the diameter of the froth core. Furthermore, the hydrophobic particle–bubble aggregates could have a lower sensitivity to this drop in pressure than have the hydrophilic particles. This would have resulted in a relatively lower recovery of gangue associated with the decrease in recovery of pyrite, and consequently an improvement in the grade.

**Length of Vortex Finder**

As the vortex finder penetrates deeper into the ASH, it could be expected that the effective length of the froth core will decrease. This will result in a reduced transition of particles into the froth, and hence lower recoveries of total solids and pyrite. Table 5 shows corresponding results for the lengths of 75 and 100 mm. When a length of 50 mm was used, the recovery decreased below that of the 75 mm length at low feed rates. A possible explanation for this could be the destabilization of the froth by the highly turbulent region near the slurry inlet. This reversed trend was also observed in the case of a vortex finder diameter of 27.7 mm and a porosity of 2 micron.

**TABLE 5 Recovery and grade of sulphur for ASH II with slurry A and vortex finders of different lengths**

<table>
<thead>
<tr>
<th>Vortex Finder Length, mm</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry Feed Rate, l/min</td>
<td>Rec %</td>
<td>Grade %S</td>
<td>Rec %</td>
</tr>
<tr>
<td>25</td>
<td>36</td>
<td>2.4</td>
<td>41</td>
</tr>
<tr>
<td>35</td>
<td>35</td>
<td>3.5</td>
<td>40</td>
</tr>
<tr>
<td>50</td>
<td>28</td>
<td>4.2</td>
<td>28</td>
</tr>
<tr>
<td>65</td>
<td>20</td>
<td>3.0</td>
<td>20</td>
</tr>
</tbody>
</table>

It could be assumed that the grade in the froth core increased from the bottom to the top of the ASH. Hence, an increase in the length of the vortex finder will result in lower grades, as illustrated in Table 5.
Diameter and Length of Porous Cylinder

It was clear that the effects of the diameter and length of the cylinder were interrelated, and should therefore be discussed simultaneously. As illustrated in Table 6, and Figures 6 and 7, a diameter of 46mm was most appropriate for an ASH length of 500mm, while a diameter of 96mm decreased the performance significantly. This decrease could be explained in terms of the low centrifugal velocity expected near the bottom of the 500mm x 96mm ASH, which would destabilize the froth. As shown in Table 6, the performance of this ASH could be expected to improve towards higher feed rates for ore A. However, this trend could not be observed for the much finer ore B.

**TABLE 6 Recovery and grade of sulphur for ASH II with slurry A and porous cylinders of different diameters**

<table>
<thead>
<tr>
<th>Cylinder Diameter, mm</th>
<th>46</th>
<th>76</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry Feed Rate, l/min</td>
<td>Rec %</td>
<td>Grade %S</td>
<td>Rec %</td>
</tr>
<tr>
<td>20</td>
<td>43</td>
<td>1.4</td>
<td>24</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>3.1</td>
<td>34</td>
</tr>
<tr>
<td>60</td>
<td>36</td>
<td>3.2</td>
<td>27</td>
</tr>
</tbody>
</table>

Figures 6 and 7 show that the 500mm ASH yielded better grades for a diameter of 96mm, but lower recoveries compared with a diameter of 46mm. Better recoveries were obtained when using a diameter of 96mm than 46mm for lengths of 400 and 300mm, although the grades did not change much. For the shorter cyclones with a diameter of 46mm, the hold-up of slurry could proportionally be higher than that for a diameter of 96mm. Hence, the slurry flow layer could be shearing too much on the outside of the froth phase and thus losing valuable particles to the tailings. In the case of the smaller cyclones, the
proportionally higher hold-up of slurry caused the ASH to act primarily as a flow splitter, so that the effect of flotation was inhibited.

Fig. 7 Sulphur grade of concentrate for ASH II with slurry B and cylinders of different inner diameters and lengths

Porosity of Cylinder

Ye et al. [12] argued that bubble-particle attachment in the ASH occurs by collision contact rather than by sliding contact. Hence, the efficiency of flotation will improve with an increase in the total external surface area associated with the production of smaller bubbles by a lower cylinder porosity. As shown in Figure 8, the recovery of pyrite increased in general with the production of smaller bubbles. Moreover, the higher water recovery associated with lower porosity enhanced entrainment of gangue, which caused a general reduction in the grade as illustrated in Figure 9.

Fig. 8 Recovery of sulphur for ASH II with slurry A and cylinders of different porosities
Diameter of Underflow Outlet

If the orifice diameter is increased moderately, it could be assumed that the hold-up of slurry decreased. This would have resulted in a larger contact area between the slurry flow and the froth core, and thus an improvement in the recovery of pyrite (Table 7). The larger the diameter of the orifice, the lower the recoveries of both water and solids. This was clearly accompanied by an increase in the concentrate grade, as illustrated in Table 7. When the orifice diameter was increased even further, the low hold-up, and hence a low pressure difference across the ASH, was not sufficient to maintain a stable froth core. Consequently, the recovery of pyrite dropped significantly at lower feed rates, as shown in Table 7. At higher feed rates, however, the hold-up and pressure increased sufficiently to counteract the effect of the larger spigot diameter, so that the recovery of pyrite increased gradually. The relatively high grades obtained at high slurry feed rates and larger diameters of the orifice show that the latter variable is extremely important in the control of the ASH.

### TABLE 7 Recovery and grade of sulphur for ASH II with slurry A and orifices of different diameters

<table>
<thead>
<tr>
<th>Orifice Diameter, mm</th>
<th>10.5</th>
<th>14.0</th>
<th>22.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry Feed Rate, l/min</td>
<td>Rec</td>
<td>Grade</td>
<td>Rec</td>
</tr>
<tr>
<td>30</td>
<td>34</td>
<td>1.1</td>
<td>39</td>
</tr>
<tr>
<td>40</td>
<td>29</td>
<td>1.1</td>
<td>40</td>
</tr>
<tr>
<td>50</td>
<td>23</td>
<td>1.1</td>
<td>40</td>
</tr>
<tr>
<td>70</td>
<td>19</td>
<td>1.3</td>
<td>32</td>
</tr>
</tbody>
</table>

Aeration Area of Cylinder

In this section results obtained when sealing off portions of the cylinder, will be presented. As illustrated by Figures 10 and 11, inert sections above the centre of ASH I yielded the highest recovery of sulphur, but did not enhance the grade significantly. Inert sections
below the centre of the cylinder yielded a more moderate increase in recovery, but enhanced the grade to levels comparable to that obtained in batch tests. According to Burger [10], an increase in the flow rate of air as such did not produce similar effects, which means that the efficiency of the ASH was sensitive to the distribution of air along the length of the ASH.

Fig. 10 Recovery of sulphur for ASH I with slurry A, an orifice diameter of 15 mm and different positions of the inert sections along the length of the ASH

Fig. 11 Sulphur grade of concentrate for ASH I with slurry A, an orifice diameter of 15 mm and different positions of the inert sections along the length of the ASH

According to Figures 12 to 15, a decrease of 30% in aeration area was detrimental to recovery and grade for all length-diameter combinations of ASH II, except for the ASH of 400 mm length and 46 mm diameter. This result is surprising, especially in view of the significant enhancement of recovery and grade obtained with two cyclones of about 400 mm x 50 mm. (The bottom 30% of ASH II was sealed off in these experiments.)

Figures 14 and 15 suggest that the 500 mm x 96 mm ASH could possibly yield a similar improvement at sufficiently high feed rates. These observations suggest that the fractional hold-up of slurry, the position of the slurry-froth interface, and the pressure drop across
the ASH should all be within certain ranges before such improvement could be observed. As stated before, the 300mm x 46mm ASH would be expected to have a relatively large hold-up, so that a change in the pattern of aeration did not have a great influence.

![Figure 12](image1.png)  
**Fig. 12** Recovery of sulphur for ASH II with slurry B, cylinders of different lengths and different areas of aeration

![Figure 13](image2.png)  
**Fig. 13** Sulphur grade of concentrate for ASH II with slurry B, cylinders of different lengths and different areas of aeration

**Effect of Head Grade**

Figures 16 to 19 illustrate results for slurries A and B when enriched artificially with pyrite. Recovery of solids increased to an upper limit, while the recovery of water decreased to a lower limit with an increase in head grade. Figures 16 and 17 illustrate that both the recovery of pyrite and the grade reached a maximum. For head grades exceeding about 1% S the recovery of pyrite decreased considerably.

Ye et al. [12] found that the diameter of the vortex finder controlled the diameter of the froth core entering the overflow. Also, the highest concentration of hydrophobic particles occurs at the mouth of the vortex finder. Hence, it is possible that this diameter could limit
the recovery of high concentrations of pyrite from the froth, as illustrated in Figure 16. The results shown in Figures 18 and 19 revealed that a larger vortex finder alleviated this restriction at higher flow rates.

![Figure 14](image.png)  
**Fig.14** Recovery of sulphur for ASH II with slurry B, a cylinder diameter of 96mm, cylinders of different lengths and different areas of aeration

![Figure 15](image.png)  
**Fig.15** Sulphur grade of concentrate for ASH II with slurry B, a cylinder diameter of 96mm, cylinders of different lengths and different areas of aeration

**Effect of Mass % Solids in Slurry**

For 50 mass % solids as opposed to 10 mass % solids in the slurry, the recovery of solids and water increased significantly. Table 8 illustrates an increase in the recovery of pyrite and a corresponding decrease in the sulphur grade. At higher feed rates, the grades tended to be more or less the same. It is therefore possible to beneficiate relatively concentrated slurries in the ASH without sacrificing efficiency.
Fig. 16 Recovery of sulphur for ASH II with slurry A at different head grades of sulphur (artificially enriched)

Fig. 17 Sulphur grade of concentrate for ASH II with slurry A at different head grades of sulphur (artificially enriched)

TABLE 8 Recovery and grade of sulphur for ASH II with slurry B at different mass % of solids

<table>
<thead>
<tr>
<th>Mass % Solids</th>
<th>10</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry Feed Rate, 1/min</td>
<td>Rec</td>
<td>Grade</td>
</tr>
<tr>
<td>30</td>
<td>43</td>
<td>7.9</td>
</tr>
<tr>
<td>40</td>
<td>43</td>
<td>8.3</td>
</tr>
<tr>
<td>60</td>
<td>32</td>
<td>5.0</td>
</tr>
</tbody>
</table>
CONCLUSIONS AND SIGNIFICANCE

The two batches of ore, A and B, from the reclaimed dumps of ERGO Ltd, were difficult to float efficiently. Sample A, which contained only 0.14% S, yielded typical sulphur recoveries of 40% and associated grades of 4% S in the ASH, while batch flotation yielded recoveries of 65% and grades of 11% S. The corresponding results for Sample B with a head grade of 1.42% S, were 40% and 7.5% S in the ASH, and 56% and 6% S in batch tests. Despite the poor floatability of the ores, the ASH proved to be a viable alternative to conventional flotation. Slurries containing 50 mass % solids could be used effectively in the ASH.

Contrary to Miller and Kinneberg’s [3] suggestion of an annular discharge and a froth pedestal, it was found here that a simple spigot consisting of a horizontal baffle positioned 30mm above an orifice yielded the best results. From a variety of runs, it can be concluded
that flotation in the ASH is influenced mainly by the tangential velocity and the hold-up of slurry. Hence, the effective design of an ASH is critically dependent on the dimensions of the porous cylinder, the vortex finder and the spigot. The diameter of the vortex finder should be increased if it is found to limit the recovery of pyrite from high concentrations in the froth.

The performance of the ASH could be improved significantly by sealing off the lower part of the porous cylinder when the fractional hold-up of slurry, the position of the slurry-froth interface, and the pressure drop across the ASH are all within certain ranges.

The ASH has potential as a rougher cell in closed circuit with a mill, to produce concentrate as feed to a column flotation cell, and where the higher capital costs of a conventional flotation plant could not be justified. In view of its compactness, the ASH could also be used in mobile plant and in underground processing.

ACKNOWLEDGEMENTS

This paper is published with the permission of Mintek, whose financial support and technical assistance throughout the project are greatly appreciated. Thanks are extended to Dr. W.A.M. te Riele for valuable discussions during the course of this work.

REFERENCES

A SEMI-EMPIRICAL MODEL FOR THE ELECTRO-OsmOTIC DEWATERING OF SLURRIES BETWEEN FIXED ELECTRODES

M.A. REUTER, J.S.J. VAN DEVENTER* and W. WILMANS

Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7600, South Africa
(* Author for correspondence)
(Received 12 September 1991; accepted 25 October 1991)

ABSTRACT

Force and material balance equations were developed for the electro-osmotic dewatering of slurries between two fixed electrodes. It was assumed that the resistance to flow caused by the dewatered bed could be described in terms of Darcy's law for laminar flow. Specific cake resistances were extremely low due to the formation of channels through the dewatered bed. Owing to the complex particle-fluid interactions in the system, both the cake resistance and the electro-osmotic coefficient had to be estimated from experimental dewatering data and could not be predicted accurately from fundamental equations.

Any change in the temperature of the system was accounted for by a change in the conductivities of the slurry and the dewatered bed. The temperature profiles were not predicted, but merely simulated by empirical equations. Independent measurements showed that the conductivity of the slurry increased linearly with temperature. The conductivity of the dewatered cake decreased linearly with temperature owing to the enhanced conversion of water to steam. Reasonable agreement was obtained between experimental data and model predictions of the rate of dewatering as well as the potential across the electrodes. Ultra-fine kimberlite and coal slurries were used at different electrode spacings and constant currents.

Keywords
Electro-osmosis; dewatering; slurries; kimberlite; coal

INTRODUCTION

Mining and metallurgical operations worldwide consume large quantities of water, so that much effort has been devoted to the reclamation of process water. Standard techniques such as sedimentation, flocculation and filtration work well for coarse particles, but fail when ultra-fine particles are to be separated from water.

It is well known that siliceous clayey particles possess a negative surface charge in water, due to the higher solubility of the cations associated with these particles [1]. Associated with each of these clayey particles is a cloud of cations which are attracted to it, but are retained in the water by virtue of their thermal energy. Hence, solid-liquid separation of these negatively charged clayey particles and cations may be achieved in an external electric field or due to the application of a constant current [2]. This technique called electrokinetic separation offers an opportunity for the separation of ultra-fine slurries.
Under the influence of an electric field the cations surrounding the clayey particles could migrate to the negative electrode and mechanically draw with them some water. This phenomenon called electro-osmosis was formulated by Adamson et al. [3].

Electro-osmotic dewatering of clayey slurries may be performed with a moving positive electrode on top of the bed of dewatered solids, or between fixed electrodes, with the dewatering slurry extending above the top electrode. In the latter case the slurry must flow through the upper electrode and dewatered solids. In both cases a dewatered consolidated bed accumulates below the upper electrode.

Yukawa et al. [4] reviewed the modelling of electrically enhanced solid-liquid separation. It was clear that models had been formulated for limited conditions only. Yukawa et al. [4-6] modelled the recovery of water and the voltage drop for a moving upper electrode under conditions of constant current and constant potential respectively. Their linear models fitted experimental data well for short periods, but started to deviate substantially as time increased owing to their assumption of constant conductivities. Furthermore, no attempt has been made to model the electro-osmotic recovery of water between fixed electrodes.

In this paper conductivity is considered to be a function of temperature. A semi-empirical model is presented here for the recovery of water by electro-osmosis and the voltage drop across electrodes of constant spacing. The resistance of the bed of consolidated solids to the flow of water is also accounted for. It is not the aim of this paper to model the heat transfer characteristics of the cell, so that the measured temperature-time relationships will be simulated merely by empirical equations. Under industrial conditions electro-osmotic dewatering occurs non-isothermally, so that the proposed semi-empirical model is more realistic than those published earlier.

FORMULATION OF MODEL

Description of Process

Figure 1 gives a schematic diagram of a cell for electro-osmotic dewatering, with the electrodes being a constant distance \( R \) apart. Three regions may be identified in the slurry during electro-osmotic dewatering at a constant current and with fixed electrodes:

Region I represents untreated slurry;

Region II represents a compressible bed of consolidated, dewatered solids which accumulate below the metal of the porous upper electrode;

Region III represents slurry that is in the process of being dewatered.

During dewatering a constant current is passed through the compressible bed of solids (II) and the dewatering slurry (III). The polarity of the electrodes is selected according to the sign of the zeta-potential of the particles, so that water in the slurry is removed towards the bottom electrode of the cell. As water is removed, a dewatered sludge bed (II) is created immediately below the top electrode. In order to replenish the water and to restore contact between the two electrodes, untreated slurry (I) must flow through the consolidated bed (II) to the dewatering slurry bed (III). This bed (II) is created essentially from accumulated solids from the flow of untreated slurry. The process of dewatering terminates once the untreated slurry is depleted.

The temperatures of both the dewatered sludge bed (II) and the dewatering slurry (III) rise during electro-osmosis. Gas that accumulates in the dewatered sludge bed (II) due to electrolysis decreases the conductivity of this bed markedly. This affects the dewatering process adversely.
Specific Assumptions

Specific assumptions used in the derivation of the theoretical model are given below:

(a) Although the porosities of the water fraction in the consolidated sludge bed and the dewatering slurry vary throughout the dewatering process, average values of $\varepsilon_2$ and $\varepsilon_3$ are used here.

(b) Regions I and III exhibit the same mean porosities, and the same conductivity-temperature relationships.

(c) It is assumed that the rate of accumulation of solids in region II equals the rate of removal of solids from region I.

(d) Owing to the lack of electro-osmotic models for concentrated suspensions of fine non-spherical particles, the electro-osmotic velocity cannot be calculated from fundamental equations such as those of Debye-Hückel or Helmholtz-Smoluchowski.

(e) The conductivities of both the dewatering slurry and the consolidated sludge change as a result of an increase in the temperature with time. It can be expected that $\mu_2$ will increase with temperature. The increase in temperature in region II results in more water being converted to steam and gas, so that $\mu_2$ could be expected to decrease with temperature.

(f) The dewatered sludge bed II creates a resistance to the flow of untreated slurry. When the current is increased, more gas is generated in this bed which restricts the flow of slurry even further. It is assumed that the total resistance is proportional to the current under the conditions investigated. The velocity of dewatering is low, so that laminar flow is assumed, and hence Darcy’s law will be applied to region II. The dewatered solids accumulate only below the solid part of the upper electrode, so that channels are formed in region II. These channels cause the specific cake resistances to be significantly lower than those usually measured for filter cakes.

(g) Gravitational forces can be neglected, as no sedimentation of solids from the slurry occurs.
MODELLING EQUATIONS

With the above assumptions in mind, a pressure balance for the water fraction of the dewatering slurry in region III yields:

$$\varepsilon_3 \sigma (R-Z_2) \left[ \frac{d(U_e-Q/A)}{dt} \right] = P_c$$  (1)

where $P_c$ is the pressure drop across region II.

The electro-osmotic coefficient $\alpha$ relates the electro-osmotic dewatering velocity $U_e$ to the electric field strength $E_3$:

$$U_e = \alpha E_3$$  (2)

The Helmholtz-Smoluchowski or Debye-Hückel equation can sometimes be used to calculate $\alpha$:

$$\alpha = \frac{D E}{(k \pi \Gamma)}$$  (3)

As explained by Street and Buchanan [7] and Sennet and Olivier [8], this expression is based on a number of assumptions which are not necessarily true for the slurries under consideration. O’Gorman and Kitchener [9] observed that kimberlite particles could form rigid “house-of-cards” structures in a gel at concentrations as low as 7 mass% solids. Equation [3] was formulated for dilute suspensions, and it is dubious whether it can be applied to concentrated suspensions of a gel nature. Coal particles are conductive, which is not taken into account in this expression. Also, the shape factors $k$ for the different particles are not known, and the viscosity of liquid in such suspensions is not determined easily. Hence, $\alpha$ in this model will not be calculated a priori, but estimated from experimental data.

Ohm’s law applied to the volume of the dewatering slurry between the two electrodes gives the strength of the electric field [5]:

$$E_3 = I_o/\mu_3$$  (4)

It has been stated that the dewatered solids did not form a homogeneous region, but contained channels according to the geometry of the upper electrode. This would cause the cake to exert low average resistances to flow through region II. Nevertheless, Darcy’s law can still be assumed due to the slow laminar flow:

$$Q = P_c A / [\Gamma \Phi(I_o) \sigma_s Z_2(1-\varepsilon_2)]$$  (5)


$$\frac{dQ}{dt} = \alpha I_o A \left[ \frac{d(1/\mu_3)}{dt} \right] - K[Z_2 Q/(R-Z_2)]$$  (6)

where

$$K = \Gamma \Phi(I_o) \sigma_s (1 - \varepsilon_2)/\varepsilon_3 \sigma$$  (7)

A material balance on the solids yields:

$$(1-\varepsilon_2)(dZ_2/dt) = -(1-\varepsilon_1)(dZ_1/dt)$$  (8)

A material balance on the liquid phase gives:

$$-A \varepsilon_1(dZ_1/dt) = Q$$  (9)
Equations [8] and [9] give:

$$\frac{dZ_2}{dt} = \frac{(1-\varepsilon_1)}{[(1-\varepsilon_2)A\varepsilon_1]}Q$$

(10)

The total volume of clear liquid recovered from the bottom electrode at any time $t$ may be calculated from:

$$V = \int_{t=0}^{t} Q\ dt$$

(11)

Equations [6], [10] and [11] can now be solved simultaneously by a numerical method such as Runge-Kutta to obtain the profile of $V$ with respect to time. The parameter $\alpha$ can be estimated from the initial slope of the $V - t$ profile, while $\Phi(I_0)$ should be estimated by fitting the total model. These two parameters can also be estimated simultaneously.

Sprute and Kelsh [1] and Lockhart [10] postulated that the volume of water recovered is proportional to the current density and the dewatering time. The model proposed here states that the volume of water recovered between fixed electrodes is a function not only of the current density and dewatering time, but also of temperature, which affects the conductivity $\mu_3$, and the height of the dewatered sludge bed $Z_2$. It is clear that Equation [6] reduces to the equation proposed by Yukawa et al. [5] under conditions of constant temperature (constant $\mu$) and if $K=0$, i.e. the effect of the dewatered sludge bed is disregarded.

The total voltage $V_t$ required to maintain a constant current density between the electrodes may be derived from Ohm’s law [5]:

$$V_t = I_o \left( \frac{Z_3}{\mu_3} + \frac{Z_2}{\mu_2} \right)$$

(12)

An expression that gives the temperature derivative of $(1/\mu_3)$ must also be defined. It should be obvious that the heat transfer process in a non-isothermal electro-osmotic cell with fixed electrodes is very complex. The heat transfer is a problem in its own right and will not be discussed here in detail. Consequently, the time dependence of $\mu_3$ was approximated here by empirical expressions which were fitted to experimental conductivity-temperature and temperature-time data.

**EXPERIMENTAL PROCEDURE**

Two samples of kimberlite slimes, A and B, were obtained from the Premier Diamond Mine, while the coal slurry was obtained from the Greensides Colliery in South Africa. Some properties of these slurries are summarised in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1 Characteristics of slurries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Mass % solids</td>
</tr>
<tr>
<td>Solids density [kg/m³]</td>
</tr>
<tr>
<td>Slurry density</td>
</tr>
<tr>
<td>Particle size [µm]</td>
</tr>
<tr>
<td>Zeta potential [mV]</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Surface area [m²/g]</td>
</tr>
</tbody>
</table>
The experimental procedure followed here is similar to that used by Wilmans & Van Deventer [11]. Two Perspex vessels, 1 and 2, differing in geometry and electrode area, were used to investigate the electro-osmotic dewatering of the above mentioned slurries. Vessel 1 was cylindrical with an internal diameter of 9.0 cm, having round electrodes with an area of 64 cm$^2$. Vessel 2 was cubic with dimensions (13.5 x 13.5 x 13.5 cm$^3$), having square electrodes with an area of 182 cm$^2$. For each cell the two electrodes were identical. All electrodes were constructed from a stainless steel wire mesh, having apertures of 2 mm and a wire gauge of 1 mm. The top electrode (anode) was positive due to the negative zeta potential of the slurry particles, while the cathode at the bottom supported a filter cloth.

A slight positive pressure was maintained below the filter cloth to prevent any premature dewatering of slurry before the direct current from a power supply of 20 A / 360 V was switched on. Thermometers were used to monitor the temperatures of the dewatering slurry and the consolidated sludge bed. No attempt was made to thermally insulate the vessels. The conductivities of the dilute slurry as well as the dewatered solids were measured at various temperatures in a separate conductivity cell [12]).

RESULTS AND DISCUSSION

Three sets of experiments (1 to 3) were conducted, each utilising a different slurry. Experimental conditions are given in Tables 2 to 4, and results are illustrated in Figures 2 to 15. The solid lines depict model predictions or fitted curves.

**TABLE 2** Parameters and conditions for experiment 1: Kimberlite slurry A in vessel 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$I=2.0$ A</th>
<th>$I=1.0$ A</th>
<th>$I=0.5$ A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$a$</td>
<td>$3.2 \times 10^{-1}$</td>
<td>$3.2 \times 10^{-1}$</td>
<td>$3.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$c$</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>$d$</td>
<td>4.5</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>$e$</td>
<td>$3.8 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>$f$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$g$</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>$h$</td>
<td>28</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$i$</td>
<td>0.03</td>
<td>0.02</td>
<td>0.007</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>$6.4 \times 10^{-3}$</td>
<td>$6.4 \times 10^{-3}$</td>
<td>$6.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R$ (m)</td>
<td>21.5</td>
<td>10.7</td>
<td>5.4</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>$1.67 \times 10^{-7}$</td>
<td>$1.67 \times 10^{-7}$</td>
<td>$1.67 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>$\varepsilon_3$</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The following empirical observations could be made regarding the relationships of conductivity, temperature and time:

a) The conductivity $\mu_3$ of the dewatering slurry was found to increase linearly with temperature (Figures 6 & 14).

b) The conductivity $\mu_2$ of the consolidated bed was found to decrease linearly with temperature. This may be explained in terms of the enhanced formation of steam and gas in the porous bed at higher temperatures (Figures 7 & 15).
c) The heat transfer characteristics of both vessels were such that an exponential relationship was observed between the temperature $T_3$ of the dewatering slurry and time (Figures 4 & 12).

d) Under the conditions used the temperature $T_2$ of the dewatered sludge bed was observed to increase linearly with time (Figures 5 & 13).

TABLE 3 Parameters and conditions for experiment 2:
Kimberlite slurry B in vessel 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$R=0.055$ m</th>
<th>$R=0.04$ m</th>
<th>$R=0.03$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_0$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>$a$</td>
<td>$3.2 \times 10^{-1}$</td>
<td>$3.2 \times 10^{-1}$</td>
<td>$3.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$c$</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>$d$</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$e$</td>
<td>$3.8 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>$f$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$3.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$g$</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>$h$</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$i$</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>$1.8 \times 10^{-2}$</td>
<td>$1.8 \times 10^{-2}$</td>
<td>$1.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\Phi (I_0)$</td>
<td>52.8</td>
<td>52.8</td>
<td>52.8</td>
</tr>
<tr>
<td>$I$ (A)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$1.1 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\varepsilon_3$</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
</tr>
</tbody>
</table>

These empirical observations may be summarised by the following expressions, which could be used in Equations [6] and [12]:

Region II

$$\mu_2 = a - b T_2$$

$$T_2 = c + d t$$

Region III

$$\mu_3 = e + f T_3$$

$$T_3 = g + h(1 - e^{-t})$$

Equations (13) and (14), and (15) and (16) are combined to express conductivity as a function of time. This allows the calculation of the derivative of $\mu_3$ as used in Equation (6) and the prediction of the voltage drop profile according to Equation (12). No expressions could be found in the literature to simulate the temperature dependence of conductivity for slurries or multiphase systems. In view of the variability of the characteristics of mineral particles, it is recommended that new $\mu$-T relationships should be determined for different slurries.

Tables 2 to 4 give values for the empirical parameters $a$ to $i$ which were obtained by fitting Equations (13) to (16) to the data illustrated in Figures 4 to 7 and 12 to 15. It was found that the conductivity - temperature relationships of Kimberlite A were also valid for Kimberlite...
B. The temperature - time relationships for kimberlite B in Table 3 were determined in the same fashion as those for kimberlite A.

**TABLE 4** Parameters and conditions for experiment 3: Coal slurry in vessel 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>I=0.8 A</th>
<th>I=0.4 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$a$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$c$</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>$d$</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>$e$</td>
<td>$7.6 \times 10^{-2}$</td>
<td>$7.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$f$</td>
<td>$3.8 \times 10^{-3}$</td>
<td>$3.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>$g$</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>$h$</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$i$</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>$6.4 \times 10^{-3}$</td>
<td>$6.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\beta(I_0)$</td>
<td>1.7</td>
<td>0.85</td>
</tr>
<tr>
<td>$R$ (m)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$3.13 \times 10^{-7}$</td>
<td>$3.13 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\epsilon_3$</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>$\epsilon_2$</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

It is clear that the proposed model fits the dewatering data of all three experiments most satisfactorily, whereas the prediction of the voltage drop was slightly more problematic. This may be attributed to the difficulty of measuring the conductivity of the consolidated sludge bed under the same conditions as prevailing in the electro-osmotic cell. The build-up of gas below the top electrode was sometimes erratic and contributed much to the fluctuations in the measured voltage drop. The sharp increase in the voltage drop towards the end of a run was clearly due to the rise in temperature and therefore the decrease in conductivity.

![Fig.2 Experimental and calculated dewatering results for kimberlite A ($\epsilon_1=\epsilon_2=0.96$) in Vessel 1 with R=2cm and A=64cm$^2$. Constant currents = 0.5A, 1A and 2A. (Experiment 1).](https://scholar.sun.ac.za)
Fig. 3 Experimental and calculated voltage drops for kimberlite A ($\epsilon_1=\epsilon_3=0.96$) in Vessel 1 with $R=2$cm and $A=64$cm$^2$. Constant currents = 0.5A, 1A and 2A. (Experiment 1).

Fig. 4 Measured temperature vs. time for kimberlite A dewatering slurry ($\epsilon_1=\epsilon_3=0.96$) in Vessel 1 with $R=2$cm and $A=64$cm$^2$. Constant currents = 0.5A, 1A and 2A. (Experiment 1).

It was observed that the fraction of water in region III did not change much during an experiment. This implies that most dewatering occurred in the untreated slurry in region I. The non-linearity of the $V - t$ and $V_t - t$ graphs indicates that temperature, the flow resistance of the consolidated solids, and accumulation of gas had a pronounced effect on the dewatering process. As expected, an increase in the applied current in Experiments 1 and 3 enhanced the rate of dewatering, but also increased the voltage drop owing to the higher resistance of region II. An increase in the distance between the electrodes in Experiment 2 did not affect the rate of dewatering, but increased the voltage drop as expected.

For a specific kimberlite or coal slurry in Experiments 1 to 3 the same $\alpha$ could be used under different operating conditions. The value of $\Phi$ increased linearly with an increase in
current density, as shown in Tables 2 and 4. This could be explained in terms of an enhanced gas build-up in the dewatered sludge bed, which impedes the flow of slurry from region 1. The extremely low values of $\Phi$ could be explained in terms of the formation of channels through the sludge bed according to the geometry of the upper electrode.

![Figure 5](image)

Fig. 5 Measured temperature vs. time for kimberlite A dewatered slurry in Vessel 1 ($\epsilon_2=0.81$) with $R=2\text{cm}$ and $A=64\text{cm}^2$. Constant currents = 0.5A, 1A and 2A. (Experiment 1).

![Figure 6](image)

Fig. 6 Measured conductivity vs. temperature for kimberlite A dewatering slurry ($\epsilon_1=\epsilon_3=0.96$) in Vessel 1 with $R=2\text{cm}$ and $A=64\text{cm}^2$. (Experiment 1).

**CONCLUSIONS**

The model proposed here gives reasonable predictions of the rate of electro-osmotic dewatering of kimberlite and coal slurries between fixed electrodes, and the corresponding voltage drop. A simple linear model would not have been sufficient to account for the pronounced effects of temperature and the flow resistance of the dewatered solids. Although
these influences on model parameters are not completely understood, this semi-empirical model provides a meaningful basis for the simulation of practical dewatering under non-isothermal conditions.

Fig. 7 Measured conductivity vs. temperature for kimberlite A dewatered slurry ($\varepsilon_2=0.81$) in Vessel 1 with $R=2cm$ and $A=64cm^2$. (Experiment 1).

Fig. 8 Experimental and calculated dewatering results for kimberlite B ($\varepsilon_1=\varepsilon_3=0.97$) in Vessel 2 with constant current $=1.5A$ and $A=182cm^2$. Fixed spacings $R=30mm$, $R=40mm$ and $R=55mm$. (Experiment 2).

ACKNOWLEDGEMENTS

The financial and technical assistance of De Beers Diamond Research Laboratories is gratefully acknowledged. Thanks are also extended to Mr. D.P.N. Gunston for laboratory assistance.
Fig. 9 Experimental and calculated voltage drops for kimberlite B in Vessel 2 with constant current =1.5A and A=182cm$^2$. Fixed spacings R=30mm, R=40mm and R=55mm. (Experiment 2).

Fig. 10 Experimental and calculated dewatering results for the coal slurry ($\epsilon_1=\epsilon_3=0.63$) in Vessel 1 with R=2cm and A=64cm$^2$. Constant currents =0.4A and 0.8A. (Experiment 3).

Fig. 11 Experimental and calculated voltage drops for the coal slurry ($\epsilon_1=\epsilon_3=0.63$) in Vessel 1 with R=2cm and A=64cm$^2$. Constant currents =0.4A and 0.8A. (Experiment 3).
Fig. 12 Measured temperature vs. time for the dewatering coal slurry ($\epsilon_1=\epsilon_3=0.63$) in Vessel 1 with $R=2\text{cm}$ and $A=64\text{cm}^2$. Constant currents =0.4A and 0.8A. (Experiment 3).

Fig. 13 Measured temperature vs. time for the dewatered coal slurry ($\epsilon_2=0.10$) in Vessel 1 with $R=2\text{cm}$ and $A=64\text{cm}^2$. Constant currents =0.4A and 0.8A. (Experiment 3).

Fig. 14 Measured conductivity vs. temperature for the dewatering coal slurry ($\epsilon_1=\epsilon_3=0.63$) in Vessel 1 with $R=2\text{cm}$ and $A=64\text{cm}^2$. (Experiment 3).
Fig. 15 Measured conductivity vs. temperature for the dewatered coal slurry ($\epsilon_2=0.10$) in Vessel 1 with $R=2$ cm and $A=64$ cm$^2$, (Experiment 3).

**NOMENCLATURE**

a-i Constants used in the conductivity-temperature and temperature-time relationships Equations [13] to [16].

A Electrode area (m$^2$)

D Dielectric constant of liquid (s.m$^{-1}.\Omega^{-1}$)

E Zeta potential (V)

$E_3$ Electric field intensity of region III (V.m$^{-1}$)

I Current density based on the cross-sectional area of the vessel (A.m$^{-2}$)

$P_c$ Pressure drop across the solids in region III (Pa)

Q Volumetric flow rate of clear liquid recovered from the bottom electrode (m$^3$.s$^{-1}$)

R Distance between electrodes (m)

t Time (s)

$T_{1,2,3}$ Temperature of region I, II or III ($^0$C)

$U_o$ Electro-osmotic dewatering velocity (m.s$^{-1}$)

$V_c$ Cumulative volume of clear liquid recovered from the bottom electrode (m$^3$)

$V_o$ Total volume of slurry initially added to vessel (m$^3$)

$Z_e$ Total voltage drop between the electrodes (Volt)

Greek

$\alpha$ Electro-osmotic coefficient (m$^2$.V$^{-1}$.s$^{-1}$)

$\epsilon$ Volumetric fraction of water in the slurry in region I, II or III

$\mu$ Conductivity in region I, II or III ($\Omega^{-1}$.m$^{-1}$)

$\sigma$ Density of liquid (kg.m$^{-3}$)

$\sigma_s$ Density of solids (kg.m$^{-3}$)

$\Gamma$ Viscosity of liquid (kg. m$^{-1}$. s$^{-1}$)

$\Phi$ Specific cake resistance as a function of $I_o$ (m.kg$^{-1}$)

Subscripts

1,2,3 Refers to a particular region I, II or III
REFERENCES


The effect of milling environment on the selective flotation of chalcopyrite from a complex sulphide ore

by J.S.J. VAN DEVENTER1, V.E. ROSS2 and R.C. DUNNE3

INTRODUCTION

The Black Mountain complex sulphide ore body is located in the north western Cape Province of South Africa. At the time of the research project, sequential flotation was practised to recover copper, lead and zinc sulphides [1-2]. The crushed ore was ground to a particle size of 70% - 75 mm in a rod-mill/ball-mill circuit, and zinc sulphate and Dow Z-200 (isopropyl ethylthionocarbamate) were added at that stage. The cyclone overflow was conditioned with more particle size thionocarbamate) were added as collectors. A 6.5% Methyl isobutylcarbinol (MIBC) frother was added, and a copper rougher concentrate was recovered. The tailings from the copper circuit were conditioned with lime to a pH of 8.5, with both zinc sulphate and sodium cyanide being added. Sodium ethyl xanthate and R242 (sulphates of aryl dihydroporphoric acid) were added as collectors, and the lead rougher concentrate obtained, was cleaned further. The lead rougher tailings were conditioned with CuSO4 and lime to a pH value of 10.5. Dow Z-200 was added as collector and a zinc rougher concentrate was recovered, which proceeded to cleaning.

Although the flotation of sulphide has been practised for many years, the interaction between the flotation variables remains largely unclear. Many investigators have undertaken basic work on pure minerals [3-6], and to a much lesser extent on ores [4-7-8]. In order to gain an understanding of the various mechanisms involved in the flotation of lead, zinc and copper sulphide. Of special interest are investigations into the depressing influence of the sulphite ion in the flotation of galena [9], and the influence of the level of dissolved oxygen and the redox potential on the differential flotation of chalcopyrite and galena from complex ores [8].

Pulp potentials and the subsequent flotation of galena were studied by investigators who correlated these results at Mount Isa, Australia [10]. The measurement of rest potentials was used to characterise the reactions occurring at the surface of various sulphide minerals in xanthate solutions [3]. The same technique was used to show that isopropyl ethylthionocarbamate (Z-200) reacts with chalcopyrite but not with galena, although the mechanism remains unclear [11].

Guy and Trahar [12] observed that the floatability of galena was dependent on the oxidation-reduction conditions in the pulp in both grinding and flotation. Grinding in steel mills adversely affects the flotation of pyrrhotite, and galvanic coupling of pyrrhotite with active metals resulted in the formation of hydroxide or oxide and sulphate species of iron on the pyrrhotite surface [13]. Galvanic interactions between grinding media and minerals in a mill influence the corrosive wear of the media as well as the surface properties of the ground mineral [14]. Nakazawa and Iwasaka [15] found that galvanic contact between pyrrhotite and pyrite enhanced the floatability of pyrrhotite, but adversely affected that of pyrite. Galvanic contact between nickel arsenide and pyrrhotite improved the floatation of nickel arsenide, but adversely affected the floatability of pyrrhotite [16]. Rao and Finch [17] observed that the combination potentials of pyrite-galena and pyrite-sphalerite couples were lower than the rest potentials of the pyrite on its own. The adsorption of xanthate on pyrite was also lower in pyrite-sphalerite mixtures compared to pyrite on its own. Galena was preferentially floated with air from galena-pyrite mixtures, but with nitrogen, pyrite was preferentially floated [17].

Despite all these studies on the effects of galvanic interactions, little is understood about the effect of milling environment on the flotation of real ores. Many studies have been conducted on isolated minerals, or in solutions only, and these artificial conditions bear little relevance to the complex interactions in real ores. Moreover, overall flotation results are usually given without any analysis of the solids/water ratio or the behaviour of the froth. As explained by Ross [7], transport phenomena in the froth phase are complex and depend inter alia on the surface chemistry of the flotation species.

The purpose of this paper is therefore to investigate the effect of galvanic interaction between metallic iron powder and minerals, during grinding in a ceramic mill, on the subsequent flotation behaviour of the Black Mountain ore. Different aeration conditions will also be used. The results will be related to the electrochemical study of Ross and van Deventer [14] on the same ore, in which rest potential measurements were used to characterise the reagent species on the surfaces of chalcopyrite and galena.

EXPERIMENTAL

In view of the fact that the experimental procedures have been described in detail by Ross18, only selected aspect thereof will be outlined in this paper. The ore samples used were rod mill feed obtained from the Black Mountain concentrator, and contained about 6.5% Pb, 2.2% Zn and 0.35% Cu. A mineralogical analysis by Miniek showed that the ore contained about 63% magnetite, 24% other non-sulphide minerals such as quartz, rutile, muncovite, biotite, chlorite and pyroxene, and pyrrhotite and pyrite as gangue sulphide minerals.

Before being floated, the ore was ground to 70% - 75 μm under an atmosphere of nitrogen in a ceramic mill. The mill load was as follows: 1 000 g of ore, ceramic
balls, and 500 ml of deoxygenated tap water. Different amounts of powdered metallic iron (purity 2N+) were added to the ore before milling in the ceramic mill. After being milled, the ore was transferred to the flotation cell, and deoxygenated tap water was added to bring the pulp density to 33 % solids.

Pre-aeration of pulp in the 3-litre Wemco flotation cell (with induced aeration) was done only on the ore that had been milled in the absence of metallic iron, i.e. for a period of 15 minutes at an air flow rate of 3 L/min. In these cases, the dissolved oxygen concentration of the pulp remained constant at 8.2 ppm throughout the 8 minutes of flotation. Ore that had been milled in the presence of iron was floated directly after milling. The initial level of dissolved oxygen varied between 0.3 ppm and 2 ppm at iron additions of 10 and 2 kg/ton ore respectively. The concentration of dissolved oxygen in the pulp was measured with a Schott CG 867 dissolved-oxygen electrode.

After aeration, the pulp was conditioned for 3 minutes with sodium sulphite as a pH regulator in some experiments. Subsequently, the pulp was conditioned with a collector such as sodium ethyl xanthate (NaEtX) and/or Dow Z-200 (isopropyl ethylthionocarbanilate) for another minute, which was followed by the addition of a triethoxybutane (TEB) as frother, and conditioning of the pulp for a further minute. Table 1 summarises the experimental conditions relevant to these tests.

After conditioning and pre-aeration, the pulp pH was measured with a Beckman pH 70 pH meter. The ore was agitated for 8 minutes. Samples of the concentrate were collected at intervals of 1 minute by manual scraping, and analysed for Cu, Pb, Zn, Fe and S. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0.2 in extreme cases. An aeration rate of between 1.5 and 3.0 L/min (table 1) was used in order to prevent the froth from overflowing the cell lip in an uncontrolled fashion. If iron was added before milling, an aeration rate of 10 L/min. could be used without producing an uncontrolled froth. The initial froth height in the flotation cell was 4 cm, and this increased during a run.

Rest potential measurements were conducted as described earlier [4]. Both the chalcopyrite and galena electrodes were rubbed in a fine iron powder (purity 2N+) before immersion in a xanthate solution or pulp. These experiments were done in order to simulate milling conditions in a steel mill.

RESULTS AND DISCUSSION

Tables 2(a) and 2(b) summarise the % recovery of chalcopyrite, galena, solids, water, total sulphur and iron, as well as the grades of sulphur and iron after 8 minutes of batch flotation. The index numbers of experiments correspond to those listed in table 1. In experiments 2, 6, 8, 10 and 11, different amounts of metallic iron were added to the ore before milling. The kinetics of recovery of chalcopyrite and galena for these experiments are depicted in figures 1 and 2 respectively.

As can be seen from tables 2(a) and 2(b), significant recoveries of chalcopyrite were obtained only during those flotation tests where metallic iron was present during milling. Copper recoveries are not given for experiments 1, 3, 4, 5, 7 and 9 as the Cu assays of these concentrates were less than 0.2 %.

TABLE 1

<table>
<thead>
<tr>
<th>Exp. no</th>
<th>Milling gas</th>
<th>Fe (kg/t)</th>
<th>Time (L/min)</th>
<th>Pre-aeration</th>
<th>Aeration (L/min)</th>
<th>Reagents</th>
<th>Ph</th>
<th>g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2</td>
<td>15</td>
<td>3</td>
<td>3</td>
<td>TEB</td>
<td>10</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>N2</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>TEB</td>
<td>10</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N2</td>
<td>15</td>
<td>3</td>
<td>3</td>
<td>TEB</td>
<td>100</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>N2</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
<td>NaEtX</td>
<td>20</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>O2</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
<td>Z-200</td>
<td>20</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>O2</td>
<td>6</td>
<td>-</td>
<td>2.4</td>
<td>TEB</td>
<td>10</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>N2</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
<td>NaEtX</td>
<td>20</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>N2</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>Na2SO3</td>
<td>50</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>N2</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
<td>NaEtX</td>
<td>20</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>N2</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>Na2SO3</td>
<td>100</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>N2</td>
<td>2</td>
<td>-</td>
<td>2.4</td>
<td>Z-200</td>
<td>20</td>
<td>8.2</td>
<td></td>
</tr>
</tbody>
</table>

+ Sulphurous acid was used as pH regulator in all the flotation tests conducted at a value of 6.1.

The presence or absence of iron during milling had a drastic effect on the characteristics of the froth phase. When iron was added to the ceramic mill, or when the ore was milled in a steel mill, the froth had plenty of "body" and revealed a dark-green colour due to the high recovery of chalcopyrite. If no iron was added, the froth was very brittle and bubbles collapsed almost as soon as they were formed. Initially, the froth was very mobile and had a dark colour owing to the high recovery of iron-bearing minerals, but it later changed to a greyish, foamy texture as most of the iron minerals had been removed. When iron was added before milling, the average bubble diameter was 1.9 mm, while the corresponding value was 0.4 mm when no iron was added.

Tables 2(a) and 2(b) reveal high ratios of cumulative solids/cumulative H2O recovered in the concentrate when no metallic iron was present during milling. This indicates...
poor drainage of gangue particles from the froth back to the pulp phase. It is well-known that high concentrations of hydrophobic particles in the froth could destabilize the froth structure [7], which is manifested in the brittle froths observed in experiments 1, 3, 4, 5, 7 and 9. As expected, low ratios of cumulative solids/cumulative H₂O were observed when iron was added before milling. These low ratios correspond to the relatively low recovery of iron minerals such as magnetite, pyrite and pyrrhotite in experiments 2, 6, 10, and 11. The high recoveries of water in the latter experiments where larger bubble sizes were observed, correspond to the fact that the laminar thickness of a bubble increases with increasing bubble size. The drainage of the froth was also greatly improved, as indicated by the lower recoveries of solids in comparison with experiments with no iron added.

It is clear from table 2(a) and 2(b) that the sulphur grades for experiments in which iron was added before milling were significantly higher than the sulphur grades obtained in the absence of iron. Except for experiment 6, the recoveries of sulphur did not change as much as the grades. In experiment 6, the ore was milled in an oxygen-flushed mill with an iron addition of 6 kg/ton ore. This increased exposure of the ore to oxygen in the presence of iron increased significantly the recovery and grade of sulphur, as well as the recoveries of chalcopyrite and galena, in spite of the increase in the recovery of both the total solids and water. These results imply that a high percentage of sulphide minerals, especially sphalerite, was floatable under these circumstances; the sphalerite recovery was 69% after 8 minutes of flotation.

In general, an increase in the recovery and grade of sulphur was accompanied by a significant decrease in the recovery and grade of iron, which indicates that the drainage of gangue particles such as magnetite was greatly improved after the ore was milled in the presence of iron. It appears as if the flotation of iron-bearing minerals is especially successful, as indicated by the relatively low recoveries of iron for the experiments described in table 1. Furthermore, the recovery and grade of iron in experiment 11 were significantly higher than those in experiment 10, but the opposite was true for sulphur recoveries and grades. A dosage of 20 g Z-200/ton ore would be required to achieve these conditions.
was necessary to increase the recovery of chalcopyrite in experiment 11, which was still lower than that in experiment 10.

Rest potential measurements [4] suggested that dixanthogen could be formed on both chalcopyrite and galena surfaces in the pulp after the ore had been milled in the absence of iron, which probably accounted for the poor copper-lead selectivity which was obtained by flotation under these conditions. However, no dixanthogen could be formed on either chalcopyrite or galena when these minerals were in galvanic contact with pure iron. Galvanic contact between steel and gangue minerals such as magnetite, pyrite and pyrrhotite undoubtedly accounted for the absence of iron. which probably accounted for the poor copper-lead selectivity when the ore was milled in the absence of iron subjected to extensive pre-aeration. Whereas milling in a ceramic mill without the addition of iron resulted in a flat and brittle froth with small bubbles, a stable and well-drained froth with larger bubbles was formed when iron was added before milling.

CONCLUSIONS

Under the aeration conditions studied, poor copper grades and copper-lead selectivity were obtained when the ore was milled in a ceramic mill under an atmosphere of nitrogen. Milling in the presence of metallic iron, followed by pre-aeration, greatly improved copper grades and copper-lead selectivity when sulphurous acid was used as pH regulator. Even without pre-aeration, the copper grades obtained after milling with an iron addition of 6 kg/t ore were significantly higher than those obtained when the ore was milled in the absence of iron subjected to extensive pre-aeration. Whereas milling in a ceramic mill without the addition of iron resulted in a flat and brittle froth with small bubbles, a stable and well-drained froth with larger bubbles was formed when iron was added before milling.

ACKNOWLEDGEMENTS

The financial sponsorship and technical support received from the Council for Mineral Technology (Mintek) in South Africa, as well as the supply of ore samples by the Black Mountain Mineral Development Co. are greatly appreciated. Thanks are also extended to Mr W.P. van Reenen for constructing the experimental equipment.

REFERENCES

THE EFFECT OF GALVANIC INTERACTION ON THE BEHAVIOUR OF THE FROTH PHASE DURING THE FLOTATION OF A COMPLEX SULPHIDE ORE

J.S.J. VAN DEVENTER§, V.E. ROSS* and R.C. DUNNE†

§ Dept. of Metallurgical Engineering, University of Stellenbosch, Stellenbosch, 7600, South Africa
† Newcrest Mining Ltd, 179 Great Eastern Highway, Belmont, WA 6104, Perth, Australia
* Present address: De Beers Diamond Research Laboratories, PO Box 916, Johannesburg 2000, South Africa
(Received 26 April 1993; accepted 7 June 1993)

ABSTRACT

A literature review has shown that the chemical effects of grinding media on the flotation of real ores, especially those containing pyrite, are still not understood adequately. Many studies have been conducted on isolated minerals or in solutions only, and transport phenomena in the froth phase have generally been ignored in studies on galvanic interactions. A complex ore containing galena, sphalerite, chalcopyrite and significant quantities of magnetite, pyrrhotite and pyrite was used in batch flotation tests to study this problem. Metallic iron powder was added in different quantities to a ceramic ball mill in order to simulate the use of mild steel grinding media in flotation tests aimed at selectively floating chalcopyrite.

An oxygen-saturated pulp milled in the presence of iron yielded the best recovery of chalcopyrite and copper-lead selectivity. Milling under a nitrogen atmosphere in the absence of metallic iron resulted in poor copper-lead selectivity. The galvanic interaction caused by the presence of iron yielded a stable, well-drained froth with low ratios of solids/water recovery and larger bubbles in the froth. However, milling in the absence of iron caused an extremely brittle froth with very fine bubbles, high recoveries of iron and low grades of sulphur. In contrast with the improvement in the copper recovery and copper-lead selectivity obtained when the pulp was pre-aerated after milling in the presence of iron, no significant increase in the copper grade was observed after extensive pre-aeration when milling occurred in the absence of iron. The unsatisfactory flotation results in the absence of iron could be explained by the enhanced floatability of iron-bearing gangue minerals, which rupture films and suppress froth stability owing to bubble-overloading.

Keywords
Grinding media; galvanic interaction; flotation; froth; sulphides

INTRODUCTION

Despite the fact that froth flotation has been used for many years to beneficiate complex sulphide ores, the interaction between the flotation variables remains largely unclear. Numerous fundamental studies have been undertaken on the flotation of pure minerals [1-4], and to a much lesser extent on ores [4-7], in order to gain an understanding of the various mechanisms involved in the flotation of lead, zinc and copper sulphides. Of special interest in the present study is the depressing effect of the sulphite ion on the flotation of galena [5]. The level of dissolved oxygen and the redox potential appear to have a major effect on the differential flotation of chalcopyrite and galena from complex ores [5,7,8,9].
In many cases the nature of the adsorbed species and the reactions occurring at the surface of various sulphide minerals in xanthate solutions could be characterised by the measurement of rest potentials for individual minerals \([1,5,9]\). The same technique was used to show that isopropyl ethylthionocarbamate (Z-200) reacts with chalcopyrite but not with galena, although the mechanism remains unclear \([10]\). For the same chemical system used in the present study, Ross and Van Deventer \([5]\) showed that dixanthogen formed on chalcopyrite in the pulp and in xanthate solutions at pH values lower than about 7. Dixanthogen appeared to form on galena surfaces in the pulp, but lead xanthate was presumably formed on galena in solutions at pH values higher than about 4. Johnson et al. \([11]\) correlated pulp potentials and the flotation of galena at Mount Isa in Australia. From an extensive survey, Ralston \([8]\) concluded that the pulp potential is a controversial but useful parameter, and could be related to the nature of the surface species. Our earlier paper \([5]\) showed that the pulp and rest potentials differed by a constant value which was specific to the type of mineral.

Consequently, any factor such as galvanic interaction that affects the rest potential of a mineral also affects the nature of adsorbed species and thus the hydrophobicity and floatability of a mineral. Numerous papers have appeared and will undoubtedly still appear on the effect of galvanic interaction on flotation response. For example, the floatability of galena was found to be dependent on the redox conditions in the pulp in both grinding and flotation \([12]\). Nakazawa and Iwasaki \([13]\) found that galvanic contact between pyrrhotite and pyrite enhanced the floatability of pyrrhotite, but adversely affected that of pyrite. Galvanic contact between nickel arsenide and pyrrhotite improved the flotation of nickel arsenide, but adversely affected the floatability of pyrrhotite \([14]\). Rao and Finch \([15]\) observed that the combination potentials of pyrite-galena and pyrite-sphalerite couples were lower than the rest potential of the pyrite on its own. The adsorption of xanthate on pyrite was also lower in pyrite-sphalerite mixtures compared with pyrite on its own. Galena was preferentially floated with air from galena-pyrite mixtures, but with nitrogen pyrite was preferentially floated \([15]\). Yelloji Rao and Natarajan \([16]\) confirmed that galvanic interaction between a "noble" mineral such as chalcopyrite and "active" minerals such as sphalerite or galena affects the floatability of the noble mineral significantly, while the effect on the active mineral is minimal.

Adam et al. \([17]\) observed that grinding in steel mills adversely affected the flotation of pyrrhotite, and galvanic coupling of pyrrhotite with active metals resulted in the formation of hydroxide or oxide and sulphate species of iron on the pyrrhotite surface. Similarly, the X-ray photoelectron spectroscopic analyses by Yelloji Rao and Natarajan \([18]\) showed that the decrease in the floatability of sphalerite owing to galvanic interaction with steel grinding balls can be ascribed to the formation of iron oxy-hydroxide species caused by the anodic dissolution of the steel. Ahn and Gebhardt \([19]\) observed that stainless steel was more easily passivated than high-carbon steel, and the collectorless floatability of chalcopyrite was significantly higher after grinding with stainless-steel. In addition to any effect on the surface properties of the ground mineral, the corrosive wear of the grinding media is also affected by galvanic interactions between the minerals and the grinding media in a mill \([20]\).

In an interesting review of the chemical effect of the type of grinding medium on the flotation of sulphides, Martin et al. \([4]\) stated that this phenomenon is "now reasonably well understood" and even accepted in economic evaluations. They concluded that, in general, stainless steel or autogenous grinding vis-à-vis mild steel grinding leads to improved flotation of unactivated sphalerite, galena, pyrrhotite, chalcopyrite and pentlandite. However, contradictory results have been obtained on the effect of media type on pyrite flotation. Moreover, the effect of the type of grinding medium on the flotation of other minerals becomes less pronounced when ores contain a large proportion of pyrite \([4]\).

Complex sulphide ores usually contain pyrite and other iron minerals such as magnetite, the effect of which has not been considered in any study on galvanic interactions. Therefore, despite all the meticulous research on the chemical effects of grinding media, the effect of galvanic interaction on the flotation of real ores is still not understood adequately. Many studies have been conducted on isolated minerals, or in solutions only, and these artificial conditions bear little relevance to the complex interactions in the froth flotation of real ores.
In all the publications surveyed above, only factors affecting the floatability of minerals in the pulp phase have been considered, and no mention has been made of phenomena in the froth phase. Moreover, overall flotation results are usually given without any analysis of the solids/water ratio or the behaviour of the froth. As explained by Ross [6], transport phenomena in the froth phase are complex and depend inter alia on the surface chemistry of the flotation species. Johansson and Pugh [21] showed that particles of high hydrophobicity can rupture films and suppress froth stability, while particles of lower hydrophobicity remain dispersed in the lamellae and appear to have little effect on froth stability.

Consequently, galvanic interactions that enhance floatability may not necessarily enhance flotation recovery owing to a destabilisation of the froth. This phenomenon has not been studied before in relation to galvanic interaction, and is the subject of the present paper. Here, a complex sulphide ore containing chalcopyrite, galena and sphalerite is floated with the purpose to selectively recover the chalcopyrite. The effect of galvanic interaction between grinding media and ore particles is simulated by adding metallic iron powder to a ceramic mill in some tests.

EXPERIMENTAL

The Black Mountain complex sulphide ore mine is located in the North Western Cape Province of South Africa. Sequential flotation is practised at that plant to recover copper, lead and zinc sulphides [22]. It was decided to emulate plant conditions in the copper circuit for most of the runs in the present study. However, for experimental purposes some conditions and reagent additions will differ from those on the plant.

The experimental procedures used in the present work are similar to those described previously [5,9,23], so that only some aspects will be emphasised here. Rod mill feed obtained from the Black Mountain concentrator was stored in air-tight containers and used as experimental material. XRF analyses showed that it contained 6.3 mass % Pb as galena, 2.4 mass % Zn as sphalerite and 0.32 mass % Cu as chalcopyrite. Quantitative XRD showed that the ore contained about 42 mass % magnetite, about 13 mass % pyrrhotite and pyrite as gangue sulphide minerals, and other non-sulphide minerals such as quartz, rutile, muscovite, biotite, chlorite and pyroxene.

In order to simulate plant conditions, the ore was ground to 70% -75 μm immediately before being floated. An atmosphere of nitrogen or oxygen in a ceramic mill was used, so that the oxidation of the ore and galvanic interaction with the grinding medium could be controlled. The mill load consisted of 1.00 kg of ore, ceramic balls, 500 ml of deoxygenated tap water and different amounts of powdered metallic iron. After milling, the ore was transferred to the 3-litre Wemco flotation cell (with induced aeration), and deoxygenated tap water was added at 22°C to bring the pulp density to 35 mass % solids. Ore that had been milled in the absence of metallic iron was pre-aerated in the flotation cell for a period of 12 minutes at an air flowrate of 2.5 L/min. In these cases, the dissolved oxygen concentration of the pulp remained constant at 8.5 p.p.m. throughout the 8 minutes of flotation. When the ore was milled in the presence of iron powder, it was conditioned and floated directly after milling so as to avoid excessive oxidation of the iron. The level of dissolved oxygen varied between 0.3 p.p.m. and 2 p.p.m. initially at iron additions of 10 and 2 kg/ton ore respectively, but increased gradually during flotation to 8.5 p.p.m. A Schott CG 867 oxygen electrode was used to measure the level of dissolved oxygen in the pulp.

Sulphurous acid (H₂SO₃) was normally used as a pH regulator. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0.2 in extreme cases. In some experiments sodium sulphite (Na₂SO₃) was added as a modulator and the pulp was then conditioned for 3 minutes. The pulp was subsequently conditioned with sodium ethyl xanthate (NaEtX) and/or Dow Z-200 (isopropyl ethylthionocarbamate) as collector for another minute, which was followed by the addition of tri-ethoxybutane (TEB) as frother, and conditioning of the pulp for a further minute. Table 1 summarises the experimental conditions governing the eleven runs discussed in this paper.
**TABLE 1 Experimental milling and flotation conditions**

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Milling</th>
<th>Pre-aeration</th>
<th>Aeration</th>
<th>Reagents</th>
<th>pH*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Iron (kg/t)</td>
<td>Time (min)</td>
<td>(L/min)</td>
<td>Type</td>
</tr>
<tr>
<td>1</td>
<td>N₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>N₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>N₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>O₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>O₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>N₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>N₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>N₂</td>
<td>-</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>N₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>N₂</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

+ Sulphurous acid was used as pH regulator

With no addition of iron, an aeration rate of less than 3.0 L/min. had to be used in order to prevent the froth from overflowing the cell lip in an uncontrolled fashion. When iron was added before milling, an aeration rate of up to 10 L/min. could be used without producing an uncontrolled froth, although only low aeration rates are shown in Table 1. The initial froth height in the flotation cell was 4 cm, and this increased during a run as the pulp became depleted. The conditioned pulp was floated for 8 minutes, and the concentrate was collected by manual scraping at intervals of one minute. The concentrate samples and the tailings were analysed for Cu, Pb, Zn, Fe and S using XRF spectroscopy. The froth surfaces were photographed and the bubble size distributions in the froth were estimated by measuring the bubble sizes visually from the enlarged photographic image at the intersections of an evenly spaced 20x20 grid.
RESULTS AND DISCUSSION

The index numbers of experiments given in Figures 1 to 12 correspond to those used in Table 1. In experiments 2, 6, 8, 10 and 11 different amounts of metallic iron powder were added to the ore before milling.

Figure 1 shows that significant recoveries of chalcopyrite were obtained only during those flotation tests where metallic iron was present during milling, and that the final copper recoveries for experiments 1, 3, 4, 5, 7 and 9 were less than 1.6%. The recoveries of galena illustrated in Figure 2 were also higher when iron was added before milling, although this effect was less severe than in the case of chalcopyrite. It is important to note that acceptable copper-lead selectivity could only be obtained when iron was added before milling, as depicted in Figure 3. Although not shown here, the grades of copper were also substantially higher when iron was added before milling.

% RECOVERY OF CHALCOPYRITE

EXPERIMENT NUMBER

IRON ADDITION
NO IRON ADDITION

Fig.1 Recovery of chalcopyrite by flotation with and without the addition of iron during milling.

This phenomenon can be explained mainly by the significant difference in behaviour of the froth phase caused by the different milling conditions. If no metallic iron was added before milling, the froth was very brittle and bubbles collapsed almost as soon as they were formed, as illustrated in Figure 4. Initially, the froth was very mobile and had a dark colour owing to the high recovery of iron-bearing minerals, but it later changed to a greyish, foamy texture as most of the iron minerals had been removed. When iron was added to the ceramic mill, or when the ore was milled in a steel mill, the froth had plenty of "body" and revealed a dark-green colour due to the high recovery of chalcopyrite, as illustrated in Figure 5. The bubble size distributions at the surface of the froth phase in Figure 6 show that, when iron was added before milling, the bubbles were significantly larger than when no iron was added.

The laminar thickness of a bubble increases with increasing bubble size, which explains why Figure 7 reveals higher recoveries of water in those experiments where iron was added and larger bubble sizes were observed. Figure 8 reveals very high ratios of cumulative solids/cumulative water recovered in the concentrate when no metallic iron was present during milling. This indicates poor drainage of gangue particles from the froth back to the pulp phase. It is well-known that high concentrations of hydrophobic particles in the froth could destabilise the froth structure owing to bubble-overloading [21], which is manifested in the brittle froths observed in experiments 1, 3, 4, 5, 7 and 9. As expected, low ratios of cumulative solids/cumulative water were observed when iron was added before milling. These low ratios
correspond to the relatively low recovery of iron minerals such as magnetite, pyrite and pyrrhotite in experiments 2, 6, 8, 10 and 11, as shown in Figure 9. Despite the addition of iron in these experiments, Figure 10 illustrates that the grade of iron in the concentrate was much lower in these experiments. The drainage of the froth was also greatly improved, as indicated by the lower recoveries of solids in comparison with experiments with no iron added.

Fig. 2 Recovery of galena by flotation with and without the addition of iron during milling.

Galvanic contact between steel and gangue minerals such as magnetite, pyrite and pyrrhotite reduce the rest potential of these minerals [4,9,17,20], with a concomitant inhibition of their floatabilities. This may be attributed to the observation that the more hydrophobic dixanthogen forms at higher rest potentials,
while the less hydrophobic metal xanthate dominates at lower rest potentials [4,9]. This inhibiting effect of the addition of iron before milling appeared to be more severe in the case of non-valuable minerals, which yielded a net increase in the recovery of chalcopyrite. The inhibited flotation of the iron-bearing gangue minerals in the case of iron addition caused the improved froth characteristics, lower solid/water ratios and improved grades of copper. The difference in solid/liquid ratios between the experiments with and without iron addition indicates that galvanic contact between metallic iron and the various minerals influenced not only the hydrophobicity of minerals, but also the mass transport phenomena in the froth phase.

Fig. 4 Photograph of froth surface in experiment 9 with no addition of iron.

Fig. 5 Photograph of froth surface in experiment 11 with the addition of 2 kg of iron per tonne of ore.
Therefore, although the floatability of the iron-bearing minerals is decreased by galvanic contact with metallic iron, the associated enhanced stability of the froth phase enhances the flotation recovery of chalcopyrite. This ambivalent effect of galvanic interaction could be the reason why Martin et al. [4] reported contradictory results on the effect of grinding media on the flotation of pyrite.

Rest potential measurements [5] suggested that dixanthogen could be formed on both chalcopyrite and galena surfaces in the pulp after the ore had been milled in the absence of iron, which probably accounted for the poor copper-lead selectivity attained under these conditions. However, no dixanthogen could be formed on either chalcopyrite or galena when these minerals were in galvanic contact with pure iron [9], which yielded an enhanced copper-lead selectivity.

Except in the case of experiment 6, Figure 11 reveals that the recovery of total sulphur was not actually dependent on the addition of iron before milling. This could be explained by the substitution of base metal
Flotation of a complex sulphide ore

sulphides by pyrite and pyrrhotite in the flotation froth as iron was added prior to milling. Figure 12 shows that the sulphur grades for experiments in which iron was added before milling were significantly higher than the sulphur grades obtained in the absence of iron. In general, an increase in the recovery and grade of sulphur was accompanied by a significant decrease in the recovery and grade of iron, which indicates that the drainage of gangue particles such as magnetite was greatly improved after the ore was milled in the presence of iron. It appears as if the flotation of iron-bearing minerals prevented the recovery of valuable minerals after the ore had been milled in a ceramic mill, even at low aeration rates.

![Ratio of solids/water recovery](image1)

**Fig. 8** Ratio of solids to water recovery in the froth with and without the addition of iron during milling.

![Recovery % of Fe in conc.](image2)

**Fig. 9** Total recovery of iron-bearing minerals by flotation with and without the addition of iron during milling.
Fig. 10 Grade of iron in the flotation concentrate with and without the addition of iron during milling.

Fig. 11 Total recovery of sulphides by flotation with and without the addition of iron during milling.

By comparing experiments 10 and 11 in Table 1 and Figure 8, it can be seen that the ratio of cumulative solids/cumulative water recovered in the concentrate increases as the iron addition before milling is decreased. The froth obtained in experiment 11 had much less 'body' than the froth in experiment 10. Furthermore, the recovery and grade of iron in experiment 11 were significantly higher than those in experiment 10, and as could be expected, the opposite was true for the grade of sulphur (Figures 9, 10 and 12). A dosage of 20g Dow Z-200/ton ore was necessary to increase the recovery of chalcopyrite in experiment 11, which was still lower than in experiment 10 (Figure 1).
Except for experiment 6, the recoveries of sulphur (Figure 11) did not change as much as the grades (Figure 12) when iron was added, due to the much higher recovery of solids in the absence of iron. In experiment 6, the ore was milled in an oxygen-flushed mill with an iron addition of 6 kg/ton ore. This increased exposure of the ore to oxygen in the presence of iron increased significantly the recovery and grade of sulphur, as well as the recoveries of chalcopyrite and galena, in spite of the increase in the recovery of both the total solids and water (Figures 7 and 8). These results imply that a high percentage of sulphide minerals, especially sphalerite, was floatable under these conditions; the sphalerite recovery was 70% after 8 minutes of flotation.

![GRADE OF SULPHUR (%S)](image)

**Fig. 12 Grade of sulphur in the flotation concentrate with and without the addition of iron during milling.**

Moreover, the dissolved oxygen content of the pulp with no metallic iron being present was much higher than in experiments with iron. Earlier work [5,7] showed that an increased level of dissolved oxygen enhanced the selective flotation of chalcopyrite. As can be seen from the experiments conducted without the addition of iron, very low recoveries of galena were obtained after the pulp was subjected to extensive pre-aeration (Figure 2). Presumably, oxidised species on the surface of the galena rendered this mineral less hydrophobic.

**CONCLUSIONS**

Numerous studies have appeared on the effect of galvanic interaction on the flotation of minerals. Nevertheless, the effect of iron-bearing minerals such as pyrite and magnetite on the stability of the froth phase in flotation has not been studied with respect to galvanic interaction. In the present study it was found that milling in a ceramic mill without the addition of iron yielded extremely brittle froths with very fine bubbles and high solids/water ratios. This was caused by the high floatability of iron-bearing minerals which destabilised the froth phase owing to bubble-overloading, and resulted in poor grades of copper and sulphur and poor copper-lead selectivity. Furthermore, previous work suggested that dixanthogen formed on both chalcopyrite and galena in the pulp after the ore had been milled in the absence of iron, which probably also contributed to the poor copper-lead selectivity.

When milling occurred in the presence of metallic iron, galvanic interaction caused by the rubbing-off of iron onto both valuable and gangue minerals reduced the rest potentials of such minerals, and therefore
inhibited the formation of dixanthogen on the mineral surfaces. This inhibited the floatabilities of all minerals, especially the iron-bearing gangue minerals, which yielded more stable and well-drained froths with larger average bubble sizes and lower solid/liquid ratios. Consequently, greatly improved copper grades, copper recoveries and copper-lead selectivities were obtained, even without pre-aeration. An oxygen-saturated pulp milled in the presence of iron yielded the best recovery of chalcopyrite and copper-lead selectivity.

This study has shown that the flotation recovery of a specific mineral is not merely a function of galvanic interaction with that mineral, but also strongly dependent on the effect of galvanic interactions with associated minerals and their effect on the stability of the froth phase.

REFERENCES

THE BEHAVIOUR OF GOLD BEARING MINERALS DURING FROTH FLOTATION AS DETERMINED BY DIAGNOSTIC LEACHING

A.J. TEAGUE§, C. SWAMINATHAN§ and J.S.J. VAN DEVENTER†

§ Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology, 124 LaTrobe Street, Melbourne Vic 3000, Australia
† Department of Chemical Engineering, The University of Melbourne, Parkville Vic 3052, Australia. E-mail: jsj.van_deventer@chemeng.unimelb.edu.au

(Received 14 October 1997; accepted 16 March 1998)

ABSTRACT

The aim of the present paper is to explain the recovery of gold by flotation as a function of the floatability of liberated and precipitated gold and gold occluded in base metals sulphides, pyrrhotite, pyrite, and arsenopyrite. In contrast with many other studies, the current research determines the flotation recovery of each mineral as an integral part of the ore. A further feature of this study is the fact that a significant fraction of the gold is associated with pyrrhotite, so that flotation strategies are aimed at maximising the recovery of pyrrhotite, which is in contrast with the practice in many similar flotation processes. Quantitative XRD and diagnostic leaching are used to determine the distribution of gold between the host minerals as well as the flotation recovery of each mineral. Optimal sulphide recovery is attained by activation with copper sulphate, conditioning with potassium amyl xanthate and nitrogen, and flotation with air. The greatest recoveries of free gold occurred when oxygen was added during xanthate conditioning. The recovery of gold bearing sulphides, free gold and refractory gold will be discussed for each test where oxygen and nitrogen addition to the pulp was used.

© 1998 Published by Elsevier Science Ltd. All rights reserved

Keywords
Gold ores; Sulphide ores; Froth flotation; Leaching; Ore mineralogy

INTRODUCTION

Previous studies on the flotation of pyrite, pyrrhotite and arsenopyrite [1–7] have focussed on sulphide behaviour and not the possible relationships between gold recovery and individual sulphide recovery. Also, past research has not covered the effects of free gold being present in the pulp with the gold bearing sulphides [8–9]. When free gold has been studied, it has been as an individual species or as a component in artificial mixtures [10–11]. The present paper is aimed at providing new information towards this area. In many gold ores around the world most of the valuables are associated with pyrite and arsenopyrite, while pyrrhotite typically holds less gold and is usually disregarded. In this particular study, however, the

Presented at Minerals Engineering ‘97, Santiago, Chile, July–August 1997
refractory gold ore used not only has a high pyrrhotite content but also a high fraction of gold values associated with it, making the mineral very important to recover.

Pre-aeration effects on pyrrhotite before copper sulphate addition using oxygen and nitrogen have received little [1] or no attention from the research community. Chang et al. [1] published data which indicated that any exposure of pyrrhotite to oxygen before copper sulphate addition would cause depression of the mineral. This was due to ferrous or ferric hydroxide surface layers forming around the mineral and impeding the exchange reaction between copper and iron in the pyrrhotite lattice. Similar results were obtained by Bushell and Krauss [12], Forssberg and Jonsson [13] and Wang et al. [14]. Chang et al. [1] also found that nitrogen pre-aeration gave the greatest pyrrhotite recoveries compared to air and oxygen, but failed to make any major conclusions from this phenomenon. Rao and Finch [2] investigated the effect of using nitrogen instead of air during flotation where the tests were designed to depress pyrrhotite recovery and hence improve nickel grades. However, little work has been done on pyrrhotite rich refractory gold ores where the aim is to maximise pyrrhotite recovery. Therefore, the aims of the present work are to investigate the flotation behaviour of refractory pyrrhotite using oxygen and nitrogen and to examine how its flotation patterns influence the recovery of free gold, refractory gold and pyrite.

Batch flotation tests were performed on the Central ore type from Stawell in Victoria, Australia. Pre-aeration with nitrogen and oxygen was compared to no pre-aeration. Other tests were completed where there was no pre-aeration, but nitrogen and oxygen were added with potassium amyl xanthate (P.A.X.) to see if these gases had any effect on promoting dixanthogen formation and hence pyrrhotite and pyrite recoveries. It has been noted in past research that dixanthogen formation is required for optimum recovery of these minerals [2–4]. The results are presented in terms of individual mineral recoveries in comparison to total gold recovery. Diagnostic leaching is used to determine the recovery of gold in each host mineral in the concentrates.

**EXPERIMENTAL**

**Floatation Tests**

The refractory gold ore used in this study was taken from Stawell in Victoria where a typical XRD analysis on the feed is given in Table 1. Batch flotation tests were carried out in a 3 litre Denver Agitair cell. Carefully prepared ore samples of 1900 grams each were dry-milled individually to 80 weight % passing 106 μm and were transferred directly to the flotation cell where the slurry was made up to 45% solids by mass using dionised water. The reagents and amounts used were: activator-copper sulphate (100g/t), collector-potassium amyl xanthate (P.A.X.) (25 g/t), and frother-PPG 400 (60g/t). Flowrates of air, oxygen and nitrogen were kept at a constant rate of 2 L/min. A natural pH was used which varied from 7.5 to 8.1 throughout the tests, and redox potential was also monitored using a combination electrode.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrhotite</td>
<td>5.9</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.9</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>1.3</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.6</td>
</tr>
<tr>
<td>Gangue</td>
<td>91.3</td>
</tr>
</tbody>
</table>

The pulp was agitated at a rate of 1400 r.p.m. for a period of 10 minutes so that the pH and redox potential stabilised before any reagents were added. Pre-aeration tests involved adding oxygen or nitrogen directly into the impeller for 10 minutes before copper sulphate was added. For the tests where no pre-aeration was used, copper sulphate was added to the pulp and conditioned for 5 minutes, then either oxygen or nitrogen was added to the pulp with P.A.X. for 5 minutes before frother addition and flotation with air. After the
conditioning period, bulk concentrates were taken over a 15 minute period where scraping was performed every 20 seconds. Feed, tailings and concentrate samples were assayed for gold, and Siroquant XRD was used to determine individual mineral recoveries. Table 2 shows the conditioning sequences for the pre-aeration tests and the tests where no pre-aeration was used. The reproducibility of gold recovery during flotation was within an error of 4% on average, which was a result of very careful sample preparation, consistency of flotation tests and accurate analysis.

**TABLE 2 Conditioning sequences**

<table>
<thead>
<tr>
<th>Pre-aeration tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The slurry was agitated for 10 minutes at 1400 r.p.m.</td>
</tr>
<tr>
<td>2. Either O₂ or N₂ was added to the pulp at 2L/min for 10 minutes.</td>
</tr>
<tr>
<td>3. The gas was turned off, and CuSO₄ was added at 100g/t for 5 minutes.</td>
</tr>
<tr>
<td>4. P.A.X. and O₂ were then added to the pulp at 25g/t and 2L/min for 5 minutes.</td>
</tr>
<tr>
<td>5. The O₂ was turned off, and PPG 400 frother was added to the pulp at 60g/t for 1 minute.</td>
</tr>
<tr>
<td>6. Air was then added at 2L/min and flotation proceeded for 15 minutes with scraping every 20 seconds.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tests with no pre-aeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The slurry was agitated for 10 minutes at 1400 r.p.m.</td>
</tr>
<tr>
<td>2. CuSO₄ was added to the pulp at 100g/t for 5 minutes.</td>
</tr>
<tr>
<td>3. P.A.X. and either O₂ or N₂ was added to the pulp at 25g/t and 2L/min for 5 minutes.</td>
</tr>
<tr>
<td>4. The gas was turned off, and PPG 400 frother was added to the pulp at 60g/t for 1 minute.</td>
</tr>
<tr>
<td>5. Air was then added at 2L/min and flotation proceeded for 15 minutes with scraping every 20 seconds.</td>
</tr>
</tbody>
</table>

**Diagnostic Leaching**

Diagnostic leaching was performed on the feed and bulk concentrates generated from the above tests. The techniques employed were similar to that outlined by Lorenzen [15]. The samples were leached for 24 hours using NaCN. This was followed by two subsequent acid digestion/NaCN leach stages to destroy the important gold bearing sulphides and leach any gold liberated from them. The stages chosen in this work reflect the relative amounts of individual sulphides in the feed material in Table 1. Following the initial NaCN leach to dissolve any free gold, the pyrrhotite fraction was digested using hydrochloric acid at a high temperature (50–80°C). It was also at this stage where the greatest mass loss occurred. The pyrite/arsenopyrite fraction was then destroyed using nitric acid. The silicates left in the final residue were treated with aqua regia to dissolve any remaining gold values. The aqua regia residue was fire assayed and was found to contain no gold. This result indicated that the aqua regia was strong enough to produce complete liberation of any remaining gold not previously leached. All solutions were assayed for gold using...
atomic absorption spectroscopy and gold extractions were back calculated using solution volumes and solid masses.

RESULTS AND DISCUSSION

Figure 1 shows a typical profile of redox potential (S.H.E.) monitored during the first 15 minutes of conditioning. Pre-aeration with oxygen and nitrogen is compared during the initial 10 minute period before copper sulphate and P.A.X. are added to the pulp. As expected, nitrogen greatly reduces the redox potential from 10 mV to -99 mV by lowering the activity of oxygen in the pulp. This gives the pyrite and especially the pyrrhotite in the pulp the greatest chance of being activated when copper sulphate is finally added. By contrast, the oxygen pre-aeration increases the potential up to values of 245 mV which gives an oxygen-saturated pulp and possible tarnishing of sulphide surfaces. Investigations were carried out to see if the conditioning time used for the tests without pre-aeration had any additional effect on the redox potential of the slurry and ultimate flotation results. After agitating the slurry for periods of 10 and 20 minutes respectively, the potential stabilised to a value of 0 mV ± 10 mV versus S.H.E. No significant additional effect was observed on flotation results. This shows that it is the oxygen and nitrogen gas which are responsible for altering the potential of the sulphide minerals and hence floatability, and not the conditioning time. Table 3 shows a comparison of pyrrhotite recovery to pyrite and total gold recovery with variations in the aeration conditions used. Siroquant quantitative XRD was used to determine individual sulphide values. In this paper only a selected set of results on Stawell feed material using PAX is reported. Nevertheless, results and trends similar to those presented here have been obtained on cyclone overflow collected at a different time as well as using sodium ethyl xanthate as an alternative collector on the Stawell feed material. This bears testimony to the consistency of the observed trends.

![Graph showing variation in redox potential](https://example.com/graph1.png)

**Fig.1** Variation in redox potential after 15 minute conditioning period. Initial 10 minutes compares pre-aeration with oxygen and nitrogen.

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Pyrite Recovery (%)</th>
<th>Gold Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/P.A.X. and O₂</td>
<td>50</td>
<td>91</td>
<td>72</td>
</tr>
<tr>
<td>P.A.X. and O₂</td>
<td>78</td>
<td>72</td>
<td>84</td>
</tr>
<tr>
<td>N₂/P.A.X. and O₂</td>
<td>90</td>
<td>96</td>
<td>82</td>
</tr>
<tr>
<td>P.A.X. and N₂</td>
<td>100</td>
<td>100</td>
<td>84</td>
</tr>
</tbody>
</table>
Effect of oxygen and nitrogen pre-aeration on sulphide recoveries

Table 3 shows clearly that the greater the oxygen content of the pulp before copper sulphate addition, the lower is the pyrrhotite recovery. Recovery of pyrrhotite decreases from 90% when pre-aeration with nitrogen is used, to 50% when oxygen pre-aeration is used. When no gas is used, an intermediate recovery of 78% is determined. Figure 2a, 2b and 2c were taken during the pre-aeration tests and further

Fig.2a Flotation froth with oxygen pre-aeration.

Fig.2b Flotation froth with nitrogen pre-aeration.

Fig.2c Flotation froth with no pre-aeration.
confirm the effect of oxygen and nitrogen on pyrrhotite floatability. In Figure 2a oxygen pre-aeration yields an extremely brittle froth with small bubbles which indicates low sulphide loading. Here the iron hydroxide species which have been discussed by previous researchers [2-5] coat the pyrrhotite surface and impede the action of copper ions added to the pulp as CuSO₄. When pre-aeration with nitrogen is used as shown in Figure 2b, the oxygen already present in the pulp is removed, which gives the pyrrhotite a maximum chance of being activated before the protective layers can form and take effect. Here the froth is very stable with even sized bubbles indicating maximum sulphide loading. When no pre-aeration is used as in Figure 2c the froth stability indicates the sulphide loading is in between that of oxygen and nitrogen pre-aeration as there is still some oxygen present in the pulp which can interfere with copper activation.

Pyrite recovery seems to have no familiar pattern. As with pyrrhotite, pyrite recovery is a maximum when nitrogen pre-aeration is employed at 96%, but the mineral still floats very well with 91% recovered when pre-aeration with oxygen is used. This is where the two minerals behave differently. These results agree with work done by Bushell and Krauss [12] as the oxygen pre-aeration had no effect on the recovery of pyrite. It is known that pyrite will not become coated with the same protective layers which inhibit copper activation of pyrrhotite. Where there is no pre-aeration, again we see an average recovery of pyrite with 72% recovered.

Effect of oxygen and nitrogen addition with xanthate

The results for the tests where no pre-aeration was used but oxygen and nitrogen were added with P.A. X. are shown in Table 3. When oxygen was added with the collector, the pyrrhotite and pyrite recoveries were 78% and 72% respectively. In comparison, the use of nitrogen with collector gives 100% recoveries of both pyrrhotite and pyrite. These results were not expected. As oxygen levels were very minimal during nitrogen addition, this result suggests that dixanthogen formation during conditioning is not essential for flotation of these sulphides. This finding agrees with work done by Rao and Finch [2] to some extent, who state that xanthate alone should be enough to impart hydrophobicity to pyrrhotite. But it disagrees with other work done by Hodgson and Agar [16] who suggested that pyrrhotite is floated by a mixed film of xanthate and dixanthogen.

Gold recovery

Table 3 shows the effect of pyrrhotite recovery on total gold recovery to the concentrate for the pre-aeration tests. These data show that the recovery of gold bearing pyrrhotite has a major effect on the overall gold recovery. When oxygen pre-aeration is used, the gold recovery is at a low 72% corresponding to a poor pyrrhotite recovery. When no pre-aeration is used the pyrrhotite and gold values increase to 78% and 84% respectively. When nitrogen pre-aeration was used over 90% of the pyrrhotite was recovered but the overall gold recovery was a slightly lower 82%. The data in Table 3 show a relationship between pyrrhotite recovery and gold recovery. Because the pyrrhotite is a refractory gold bearing sulphide and it makes up a substantial part of the feed material (5-6%) any increase in its recovery increases the total gold recovery. The fact that a 12% increase in pyrrhotite recovery between no pre-aeration and nitrogen pre-aeration contributed to a gold decrease of 2% between the two tests indicates that some other gold hosts do not respond as well to nitrogen as does pyrrhotite. This was later confirmed with the diagnostic leaching data in Table 4 and Figure 3 which showed that the amount of free gold in the concentrates decreased when nitrogen was added to the pulp.

When oxygen was added with the collector, the pyrrhotite and pyrite recoveries of 78% and 72% gave a total gold recovery of 84%, where the use of nitrogen with collector gave 100% recoveries of both pyrrhotite and pyrite for the same gold recovery of 84%. This again indicates that nitrogen affects the flotation of free gold.
TABLE 4 Distribution of gold in concentrates using diagnostic leaching

<table>
<thead>
<tr>
<th>Lixiviant sequence</th>
<th>Aim</th>
<th>P.A.X. and O₂</th>
<th>P.A.X. and N₂</th>
<th>O₂/ P.A.X. and O₂</th>
<th>N₂/ P.A.X. and O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg</td>
<td>%</td>
<td>mg</td>
<td>%</td>
<td>mg</td>
</tr>
<tr>
<td>NaCN Free gold</td>
<td>1.82</td>
<td>73.39</td>
<td>1.49</td>
<td>66.22</td>
<td>1.54</td>
</tr>
<tr>
<td>HCl/NaCN Gold in pyrrhotite</td>
<td>0.25</td>
<td>10.08</td>
<td>0.24</td>
<td>10.67</td>
<td>0.11</td>
</tr>
<tr>
<td>HNO₃/NaCN Gold in pyrite</td>
<td>0.41</td>
<td>16.53</td>
<td>0.52</td>
<td>23.11</td>
<td>0.38</td>
</tr>
<tr>
<td>Aqua Regia Gold in silicates</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>2.48</td>
<td>100</td>
<td>2.25</td>
<td>100</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Diagnostic Leaching

The diagnostic leaching gold distributions shown in Table 4 and Figure 3 indicate that there is a significant proportion of gold associated with the refractory pyrrhotite ranging in value from 5% to almost 11%. The data also show that there is a slight drop in the amount of free gold present when comparing the use of oxygen and nitrogen both with no pre-aeration and when pre-aeration is used. When oxygen or nitrogen is added to the pulp with the P.A.X. this decrease is about 7%, and when oxygen or nitrogen has been used for pre-aeration, the decrease in free gold is approximately 4%. Oxygen pre-aeration has an effect on increasing the amount of free gold which has floated into the concentrate. In this case it is as high as 76% compared to 66–73% for the other tests.

While oxygen pre-aeration increases the proportion of free gold in the concentrate, it decreases the amount of gold associated with the pyrrhotite. The opposite can be said about the use of nitrogen either as pre-aeration or addition with the collector. In these tests the amount of gold associated with the sulphides is at...
a maximum value between 28–34% compared to 24% for oxygen pre-aeration. Another interesting point to note is that the amount of gold associated with pyrite is a maximum 23% when nitrogen is added with the P.A.X. compared with 16–20% for the other tests.

The diagnostic leaching results discussed indicate how much gold is associated with the host minerals in the ore, but to make suitable conclusions we need to know how much of the gold in the host minerals was recovered during each test. The results in Table 4 and Figure 3 do not tell us this information. Because there are intrinsic errors associated with sampling, sample preparation and analysis, this could mean that the calculated gold content in the host minerals is not the same. Hence it was necessary to perform a material balance smoothing similar to that explained by Wills [17] using the XRD data for each sample and the original gold associations.

The material balance procedure involved calculating a mean value of gold in each mineral, and then using this mean as an initial estimate of gold in mineral i. This value was then justified using an optimisation equation where the errors between the initial value and the gold associations in the remaining samples were minimised. An example is given in Appendix A with initial data for pyrite given in Table A1. The importance of this material balance smoothing exercise is to reconcile the diagnostic leaching results and the individual sulphide recoveries determined by quantitative XRD. It appears that this has not been discussed before in the literature. Once the new values for gold content in the host minerals were determined, it became possible to calculate the recovery of gold in each host mineral. This was done by using the XRD data to calculate how much gold in mineral A was present in the feed, concentrate and tailings. The recovery to the concentrate was calculated as the gold in the concentrate divided by that in the feed. The recoveries of gold associated with each refractory sulphide during the flotation tests are shown in Table 5.

<table>
<thead>
<tr>
<th>Mineral Type</th>
<th>P.A.X. + O_2, %</th>
<th>P.A.X. + N_2</th>
<th>O_2/P.A.X. + O_2</th>
<th>N_2/P.A.X. + O_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Gold</td>
<td>82.54</td>
<td>68.33</td>
<td>73.95</td>
<td>84.08</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>94.87</td>
<td>92.31</td>
<td>43.59</td>
<td>76.92</td>
</tr>
<tr>
<td>Pyrite/Arsenopyrite</td>
<td>75.95</td>
<td>97.47</td>
<td>74.68</td>
<td>94.94</td>
</tr>
</tbody>
</table>

The results in Table 5 indicate that there is a major proportion of gold recovered with the refractory pyrrhotite and pyrite. When oxygen is added with the P.A.X. during conditioning this increases the amount of free gold recovered to between 82 and 84% which is significantly higher than the 68% recovered when nitrogen is employed. Table 5 shows that the addition of nitrogen to the pulp during the xanthate conditioning period increases the recovery of sulphide associated gold, but this is off-set by the reduced amount of free gold recovered. When oxygen pre-aeration is used the amount of gold recovered with the pyrrhotite decreased to a low level of 44% because conditions were such that this sulphide was depressed. The same conclusions were found from discussion of the gold association results in Table 4. These data also show that pyrite contributes significantly to the overall gold values even when gold recovered with the pyrrhotite is low.

On the basis of quantitative XRD and diagnostic leaching, it can be said that there is a relationship between the recovery of the refractory sulphides and total gold recovery. The gold associations in Table 4 and Figure 3 and the recoveries shown in Table 5 explain why the total gold recovery during flotation varies as it does. They also indicate why the total gold recovery decreases during some tests when the maximum recovery of pyrrhotite and pyrite would suggest the opposite should happen. Unlike other ore types, the amount of pyrrhotite present in the Stawell Central ore and its gold association indicate that flotation strategies should be aimed at recovering this resource.
CONCLUSIONS

- Pre-aeration with oxygen before copper sulphate addition severely depresses the pyrrhotite but appears to have no effect on pyrite.

- Pyrrhotite recovery decreased with increasing levels of oxygen being present in the pulp prior to copper sulphate addition. Hence pre-aeration with nitrogen led to the greatest pyrrhotite recovery.

- Oxygen pre-aeration lowers the overall gold recovery because of its effect on depressing the pyrrhotite, but the proportion of free gold in the concentrate is much greater compared to that associated with the sulphides.

- The greatest sulphide recoveries were achieved when nitrogen was added with potassium amyl xanthate which suggests that dixanthogen production is not necessary for optimum sulphur recovery. However, diagnostic leaching confirmed that nitrogen has a depressing effect on the free gold.

- Diagnostic leaching showed that significant proportions of gold were locked within refractory pyrrhotite and pyrite. This corresponds with quantitative XRD results which described how the varying recovery of pyrrhotite and pyrite with various aeration techniques had an effect on the total recovery of gold.

ACKNOWLEDGEMENTS

The authors wish to express thanks to Stawell Gold Mines Pty Ltd and MPI Ltd for funding this research, and for providing gold analysis and ore samples. Also, Stafford McKnight at the Ballarat University School of Geology is thanked for the Siroquant XRD analysis.

REFERENCES


APPENDIX A

The following procedure was used to calculate the amount of gold associated with each refractory sulphide using a combination of initial diagnostic leach and XRD data.

Based on 1kg of material:

\[ X_{RD_{i}} = \text{mass of mineral}_i \text{ in 1kg} \]

\[ DL_{i} = \text{mass of gold in mineral}_i \text{ in 1kg} \]

where \( i = \text{FeS, FeS}_2, \text{free gold, gangue}. \)

Then for different flotation conditions \( (DL_{i})/(X_{RD_{i}}) = X_i \) \( (1) \)

And for all conditions and all samples it is expected that:

\[ \left[ \sum_{n=1}^{n} (DL_{i}/X_{RD_{i}}) \right] / n = \overline{X}_i \] \( (2) \)

The optimisation equation then becomes: \( \min \sum (\overline{X}_i)(X_{RD_{i}}) - DL_{i})^2 \Rightarrow 0 \)

for all concentrate and feed samples where \( \overline{X}_i \) is the value to be optimised.

Eg. For calculating the amount of gold in pyrite for the flotation tests:

Equation (1) is used for the initial diagnostic leach and XRD data shown in Table A1. so that \( X_i \) is calculated for each sample.

ie. Concentrates:

\[ \text{PAX} + O_2 = (3.733/0.162) = 23.043 \text{ mg Au/kg} \]
\[ \text{PAX} + N_2 = (2.933/0.207) = 14.205 \text{ mg Au/kg} \]
\[ O_2/PAX + O_2 = (3.1/0.225) = 13.778 \text{ mg Au/kg} \]
\[ N_2/PAX + O_2 = (3.733/0.218) = 17.124 \text{ mg Au/kg} \]
\[ \text{Feed} = (0.473/0.025) = 18.92 \text{ mg Au/kg} \]

and from equation (2) \( \overline{X}_i = 17.414 \text{ mg Au/kg} \)
TABLE A1 Initial diagnostic leach and XRD data for pyrite.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Diagnostic Leach Result (total mg Au)</th>
<th>Mass of mineral by XRD (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A.X. + O₂ concentrate</td>
<td>3.733</td>
<td>0.162</td>
</tr>
<tr>
<td>P.A.X. + N₂ concentrate</td>
<td>2.933</td>
<td>0.207</td>
</tr>
<tr>
<td>O₂/P.A.X. + O₂ concentrate</td>
<td>3.100</td>
<td>0.225</td>
</tr>
<tr>
<td>N₂/P.A.X. + O₂ concentrate</td>
<td>3.733</td>
<td>0.218</td>
</tr>
<tr>
<td>Feed</td>
<td>0.475</td>
<td>0.025</td>
</tr>
</tbody>
</table>

From equation (3) the data can then be optimised to find the justified value of \( \bar{X}_i \), which in this case for FeS₂ comes to 16.694 mg Au/kg.

The justified value of \( \bar{X}_i \) is then multiplied again by the original XRD, to produce a new set of values for DL₁.

Because these data show the amount of gold in mineral, in 1kg, they have to be divided by a certain factor to calculate back to the original sample mass. For this case the sample masses were 150 grams except for O₂/P.A.X.+O₂ which was 100 grams. Using the original XRD data and gold assays for each sample, the recovery of gold held in each refractory sulphide can be calculated.

Correspondence on papers published in *Minerals Engineering* is invited, preferably by e-mail to bw@minerals.avel.co.uk, or by Fax to +44-(0)1326-318352
A CONCEPTUAL MODEL FOR GOLD FLOTATION

A.J. TEAGUE¹, J.S.J. VAN DEVENTER¹ and C. SWAMINATHAN¹

¹Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology, 124 LaTrobe St., Melbourne 3000, Australia.

¹Department of Chemical Engineering, The University of Melbourne, Parkville 3052, Australia.

ABSTRACT

This paper is aimed at producing a conceptual model for gold flotation based on the discussion of a number of experimental results where the behaviour of free and refractory gold has been studied under different chemical and physical conditions. A review of the literature suggests that there have been numerous studies on the flotation of free gold particles and refractory sulphides, but these investigations have typically focused on the individual flotation behaviour of each gold bearing species in synthetic mixtures and not when they are present together in "real" ores in the same pulp. The model discussed here shows that the flotation of refractory gold follows a similar trend to the recovery of refractory pyrite and pyrrhotite and is mainly affected by chemical conditions in the pulp such as redox potential, aeration conditions, copper activation, reagent synergism and galvanic interaction. Refractory gold is usually recovered by true flotation that is hydrophobic particle-bubble attachment, unless under certain conditions the physical transport of water and gangue provides a washing effect and detaches some of the sulphide material from the air bubbles. The flotation recovery of free gold is largely affected by physical constraints like the shape and size of the particles, the degree of water and gangue transport to the froth, the stability of the froth, and the extent of bubble loading of sulphide particles which can provide a barrier towards the hydrophobic bubble attachment of free gold. In each individual study the results suggest that the recovery of free gold follows a proportional trend with regard to water and gangue recovery. However, there is an inverse relationship between the true flotation of free and refractory gold due to the fact that free gold particles cannot attach to air bubbles properly in the presence of physical barriers.

Keywords

Froth Flotation, Gold Ores, Sulphide Ores, Copper Sulphate, Pyrrhotite.
INTRODUCTION

The flotation of sulphide ores containing base metals and gold has been utilised in the mineral processing industry since the beginning of the century, and in this time many novel applications and fundamental studies have been produced to gain a more thorough understanding of the chemical and physical phenomena that occur within the solid-water pulp matrix. However, regardless of all the information that has been acquired during this time, the flotation behaviour of gold bearing minerals, especially free gold particles and refractory gold bearing sulphides, remains largely unclear. There have been numerous studies on the flotation of free gold particles as far back as 1934 by Leaver and Woolf [1] and more recently by Aksoy and Yarar [2], but these investigations have focused on the flotation behaviour of gold in synthetic mixtures and not when it is a component of a real ore containing other gold bearing sulphide minerals and silicaceous gangue. Also, some research has been documented on the flotation of gold bearing pyrites [3] and arsenopyrite [4], however these studies have not included free gold particles.

One of the first studies on the flotation of free gold was performed by Leaver and Woolf [1]. From this investigation it became apparent that a number of variables like adsorption of collector (viz. hydrophobicity), activation using copper sulphate, particle size and the addition of sulphidising reagents could affect the flotation of free gold. In general it was suggested that free gold floats well in the presence of xanthate collectors and frothers but not if its particle size is too great or if reagents such as CaO or sodium sulphide are added to the pulp. It was found that activation with copper sulphate did not increase the recovery of free gold but increased the rate of recovery. In this case the copper may have had more of a mass transport effect on the gold particles than a chemical activation effect. Immediately it could be recognised from this early work that free gold is affected by both chemical and physical conditions during flotation. Taggart [5] provided further evidence that the flotation of native gold particles can be affected by physical constraints such as pulp viscosity and the condition of the gold particle surface. He states clearly that native gold is made more difficult to float when it is coated, and also when very fine grinding imbeds other constituents into the surface of the gold particles so that their hydrophobicity and flotation response are reduced. Also, the flotation response of free gold is best in pulps of high-density. Lange [6] also found that high pulp densities are beneficial for free gold flotation which suggests that a significant proportion of the gold may be recovered along with any entrained water and gangue material.
There are a few references in the literature by Allison et al. [7] and Aksoy and Yarar [2] that suggest the recovery of free gold may be affected by its inability to attach to air bubbles due to competition by other species. Allison et al. [7] explain that the recovery of fine gold from a particular ore might be expected to be strongly influenced by the presence of large amounts of partly hydrophobic gangue fines such as pyrophyllites. In general there is an increased competition for bubble surface sites reducing the rate of recovery of fine gold. In the fine size range the selectivity between particles is decreased as differences in the relative degree of hydrophobicity between particles is reduced. The fine partly hydrophobic material does not drain out of the froth as readily, making cleaning more difficult. Aksoy and Yarar [2] found that ferric ions in the form of hydrated oxides acted as physical barriers between the air bubbles and the gold surfaces during flotation. Humic acid also produced the same effect. This phenomenon hindered the flotation of free gold but could be reversed simply by washing with water. It was also found that native gold flakes have highly rough flat surfaces and the greater the roughness, the less hydrophobic the flakes became so that bubble attachment and floatability decreased. Since there is a substantial amount of debate as to the degree of hydrophobicity of gold particles and the fact that they usually exist as flattened plates where the surface heterogeneity affects their bubble attachment and floatability, it is necessary to clarify the way in which free gold is transported from the pulp to the froth during flotation.

Refractory gold bearing constituents have long been recognised as being associated with the sulphide component of a particular ore [6,8] but they have only recently become increasingly important to treat as the amounts of oxidised free-milling ores around the world are being depleted. In general the recovery of refractory gold follows the same trend as the sulphide minerals it is locked in, i.e. pyrite, pyrrhotite and arsenopyrite. O'Connor and Dunne [8] state that some gold bearing ores are refractory due to the smallness of the gold grains and concentration of the sulphide minerals by flotation is required, followed by either roasting, bacterial leaching or pressure oxidation to liberate the gold prior to cyanidation. There have not been many studies documented on the flotation of refractory gold bearing minerals with the exception of a few papers produced by Allison et al. [7], Botelho de Sousa et al. [3] and O'Connor et al. [4]. Allison et al. [7] found that the addition of copper sulphate increased the rate of pyrite flotation which also led to an improved gold recovery because of its gold association, and the presence of fine slimes in the flotation feed inhibited the rate of pyrite flotation. Also, the use of amine collectors instead of xanthates could be effective for the recovery of pyrite and gold in alkaline flotation circuits. These results indicate that the recovery
of refractory gold bearing minerals can be affected by both chemical and physical conditions. O'Connor et al. [4] provided further evidence that the recovery of a refractory gold bearing sulphide would enhance gold recoveries by investigating the flotation of refractory arsenopyrite using mixtures of dithiophosphate and dithiocarbamate. In this study it was found that the synergism produced by using a mixture of sodium cyclohexyl and n-propyl dithiocarbamate gave a recovery of 75 % arsenopyrite and 84 % gold.

In all the literature that has been produced up until the present period, one outstanding phenomenon has always been disregarded, that is the flotation behaviour of free and refractory gold under the same conditions within the same pulp. In this study a complex sulphide ore containing large amounts of refractory pyrrhotite, pyrite and free gold from Stawell in Central Victoria, Australia, is used to investigate a number of chemical and physical variables during flotation. In particular, the effect of different aeration conditions, sequence of copper sulphate addition, reagent synergism, galvanic interaction and pulp temperature are investigated with regard to the flotation behaviour of free and refractory gold.

EXPERIMENTAL

The practical work in this paper was carried out as a number of individual studies on the batch flotation behaviour of the Stawell Central ore type. The individual tests consisted of investigating the effect of oxygen and nitrogen aeration, sequence of copper sulphate addition, reagent synergism, galvanic interaction and pulp temperature during flotation. For each particular study a similar ore preparation and flotation technique was used except where changes needed to be made to analyse each variable. A description of the basic flotation technique follows.

Batch flotation tests were completed on the Stawell Central orebody in a 3 litre Agitair cell. Carefully prepared ore samples of 1900 grams each were dry-milled individually to 80 weight % passing 106 µm and were transferred directly to the flotation cell where the slurry was made up to 45 % solids by mass using deionised water. Potassium amyl xanthate (P.A.X.) was used as the collector at a dosage of 25 g/t, copper sulphate (CuSO₄) as the activator was added at a dosage of 100 g/t, and the frother (PPG 400) was kept constant at 60 g/t. Regulated air was added directly into the impeller and was maintained at a rate of 2.0 litres per minute during the different tests.
The pulp was agitated at a rate of 1400 r.p.m. for a period of 10 minutes so that any differences in pH and redox potential between each test would be negligible. CuSO₄ was then added to the pulp and conditioned for 5 minutes, before P.A.X. was added and conditioned for a further 5 minutes. Frother was then conditioned for 1 minute before the air entered the pulp and flotation was carried out for 15 minutes. Scraping of the froth was performed every 20 seconds at a constant depth so that a bulk concentrate was recovered over the 15 minute period, and the water recovery to the concentrate was determined. In most cases the flotation performance of the Stawell Central mill feed and cyclone overflow materials was compared for each variable. The two materials are from the same orebody except the cyclone overflow has undergone previous gravity treatment to remove much of the free gold.

Leaching of the concentrates was completed using sodium cyanide so that the recovery of free and refractory gold could be determined. The concentrates generated from the aeration condition tests were analysed by a diagnostic leaching procedure similar to that outlined by Lorenzen [9]. All of the samples produced by flotation were analysed for gold by atomic absorption spectroscopy and also by quantitative X.R.D. Changes to the basic flotation technique that were implemented to study each variable are given below.

**Aeration Conditions**

These tests were completed to investigate the effect of pre-aeration before any reagent addition and also aeration during xanthate addition, using oxygen and nitrogen. The pre-aeration tests involved adding oxygen or nitrogen directly into the impeller at 2.0 litres per minute for 10 minutes before copper sulphate was added. For the tests where no pre-aeration was used, copper sulphate was added to the pulp and conditioned for 5 minutes, then either oxygen or nitrogen was added to the pulp with P.A.X. or S.E.X. for 5 minutes before frother addition and flotation with air. Copper adsorption tests were also completed on two batches of the Stawell Central mill feed during this series of experiments where nitrogen pre-aeration was compared with no pre-aeration. Five solution samples were taken from the pulp at 1 minute intervals during the copper sulphate conditioning stage for each different aeration condition and they were analysed on the A.A.S. Since the amount of copper added to the slurry was known at the beginning of each test, the percentage of copper adsorbed from solution could be calculated.
Sequence of Copper Sulphate Addition

In these tests the copper sulphate was added in amounts of 0, 100, and 300 g/t and the regulated air was maintained at rates of 0.5, 1.0, 2.0, 3.0 and 4.0 litres per minute. By varying the aeration rates the water recovery was manipulated which in turn governed the entrainment of hydrophilic species. Consequently, it was possible to construct graphs according to the method proposed by Warren [10]. The tests were completed in three sets of five, with one set of five different air flow rates being used for each dosage of copper sulphate. The same tests were completed using copper sulphate addition before and after xanthate conditioning. When no CuSO₄ was used during conditioning, a 5 minute agitation period was still maintained so that the conditioning time was kept constant during each test. When CuSO₄ was added after the P.A.X. the conditioning time and addition sequence of the other reagents remained the same.

Reagent Synergism

In these tests P.A.X. and a thiacarbamate type collector (denoted GX) were added together in different conditioning sequences and also individually. After 100 g/t copper sulphate was conditioned in the slurry for 5 minutes, either 25 g/t P.A.X. or 25 g/t GX was added and conditioned for a further 5 minutes. Flotation was carried out for 8 minutes and scraping of the concentrate was performed every 20 seconds. After the 8 minute period, 25 g/t of the other collector was added to the pulp and conditioned for 5 minutes and then flotation continued for a further 7 minutes so that a total flotation time of 15 minutes had elapsed and a bulk concentrate was taken. When the two collectors were used in the same test, only 25 g/t of each was added so that the results could be compared directly to the tests where 50 g/t of each collector was added by itself.

Galvanic Interaction

In this set of tests the ore samples were dry milled individually to 80 weight % passing 106 μm in a ceramic mill with ceramic balls. Different dosages of zero, 300 g/t and 5 kg/t of metallic iron powder were added with the ore before grinding to simulate milling in a mild steel environment which would normally occur under plant conditions. After copper sulphate addition, either 50 g/t of potassium amyl xanthate (P.A.X.) or GX was added and conditioned for a further 5 minutes. When a combination of P.A.X. and GX was used, the P.A.X. was
conditioned first and flotation was carried out for 7 minutes, then the GX reagent was added and conditioned for 5 minutes and flotation continued for a further 8 minutes.

Pulp Temperature

In these tests three different temperatures were used: Room temperature (25°C), 15°C and 35°C. After the ore had been ground, special preparation procedures needed to be used for the tests at 15°C and 35°C to ensure that the slurry was at the correct temperature before flotation conditioning commenced. Once flotation conditioning commenced, the standard flotation procedure was used as for the other tests. For the test carried out at 15°C, the slurry was made up in the 3 litre cell and was placed in a refrigerator set at 8°C for one hour so that the temperature of the slurry was reduced to 10°C. The temperature was measured using the TPS MC-80 Microprocessor with a temperature probe which was accurate to one decimal place. After one hour the flotation cell was transferred to the Denver Agitair flotation apparatus and was agitated for 10 minutes before conditioning commenced so that the redox potential, pH and temperature stabilised. During this agitation period the temperature increased from 10°C to 13.5°C. After conditioning and during flotation the temperature changed only slightly from 13.5°C to 15°C, so that the maximum temperature reached was 15°C. A similar procedure was used for maintaining the flotation temperature at 35°C except when making up the flotation slurry, the deionised water was pre-heated to a temperature of 50°C before the required mass was weighed out and added to the 1900 grams of ore. During agitation the temperature of the slurry decreased to 37°C and after conditioning and flotation the temperature decreased from 37°C to 35°C.

DESCRIPTION OF MODEL

The model which is shown in Figure 1 and is described here, is given under two sub-headings. These two broad sections are used so that the findings of each individual study can be related separately to both free and refractory gold. The discussion is backed up by experimental results that were produced from each investigation. There is some overlap between each discussion because in most cases the flotation of free gold is greatly affected by the nature of the refractory sulphide recovery.
The Effect of Chemical Conditions on Refractory Gold Flotation

To begin with, it is necessary to discuss the chemical interactions that occur in the pulp phase when refractory pyrite and pyrrhotite are present together with free gold, under the same conditions of aeration, xanthate and copper addition, reagent synergism and galvanic interaction. In general, the findings from this work indicate that the recovery of refractory gold relates well with the recovery of the gold bearing sulphides pyrite and pyrrhotite. These minerals have similar gold associations of between 12 and 14 grams per tonne as outlined by Teague [11] hence, when the flotation conditions are changed so that the sulphide recovery changes, the refractory gold also follows the same pattern.

When xanthate collectors such as sodium ethyl xanthate and potassium amyl xanthate are added to the Stawell mill feed or cyclone overflow materials they impart hydrophobicity to the two major gold bearing sulphides present, which are pyrite and pyrrhotite. Xanthates adsorb readily onto iron sulphide surfaces but the resulting Fe-X surface layer is partially soluble and is less hydrophobic than a copper-xanthate surface layer [12, 13], which means that without copper activation the attachment of these minerals to air bubbles would be reduced. Hence, when copper is added before the xanthate during pulp conditioning, the stronger Cu-X species form on the iron sulphide minerals which show a stronger tendency to attach to air bubbles and rise through the pulp to the froth by true flotation where they are collected. An illustration of this effect is given in Table 1 where the sequence of copper and xanthate addition was compared for the Stawell Central mill feed and cyclone overflow. In this table it can be seen that there is a 34 % increase in pyrrhotite recovery and a 22 % increase in pyrite recovery during flotation of the mill feed material when copper is added before the xanthate conditioning. When the cyclone overflow material is used, the increase in pyrrhotite recovery is 14 % and the pyrite is about 32 %. Also, because these sulphides contain gold, under the same conditions it was found that the recovery of refractory gold is nearly twice as high when copper is added before the xanthate compared with adding it after the P.A.X. These results are shown in Figures 2 and 3.

Even though potassium amyl xanthate has the strength to float most of the pyrite and pyrrhotite under normal plant operating conditions, it is rarely successful in floating all of the pyrrhotite because this mineral is very susceptible to oxidation products coating its surface. Pyrite is not affected in this way [14] and usually has a recovery of greater than 90 % as shown in Table 2. If there is any oxygen present in the slurry, or if there is any significant rise in the redox potential
prior to copper addition, hydroxide or hydroxyl species will coat the pyrrhotite and inhibit copper activation and subsequent collector adsorption and flotation [15-17]. The rise in redox potential can even occur if the pH of the slurry becomes greater than 9. To combat this effect, using a gas such as nitrogen as a pre-conditioning step before copper activation ensures that any dissolved oxygen in the slurry is kept to a minimum, and there is no inhibition of copper activation of the pyrrhotite surfaces. This effect has been discussed by Teague et al. [18] and is also illustrated in Figure 4 where copper adsorption work on the Stawell Central mill feed showed that after nitrogen pre-aeration over 64% of the copper was removed from solution compared with about 25% when no pre-aeration was used. This value of 25% may seem very low for a 10% sulphide ore, but considering that between 7 and 8 per cent is made up of pyrrhotite, it becomes clear that this can have a dominating effect on the slurry. Aeration with nitrogen gives a higher recovery of pyrrhotite than the other aeration conditions, and it was found that both the pyrrhotite and pyrite recoveries are high and the recovery of refractory gold is optimised. Even though pyrite recovery is usually favoured by oxidising conditions, some of the results given in Table 2 and the model shown in Figure 1 suggest that it can also be recovered in the presence of nitrogen. This could occur because of the increase in pyrrhotite floatability during nitrogen aeration which provides a positive effect on the overall froth stability. An example of the froth stability is shown in Figures 5a and 5b where it can be seen that pre-aeration using nitrogen gives evenly sized bubbles and a stable metallic froth compared with oxygen pre-aeration. As well as the effect of nitrogen pre-aeration on the recovery of pyrrhotite being discussed here, Chang et al. [15] also found the same phenomenon occurred during their fundamental investigation into the flotation characteristics of pyrrhotite. Unfortunately, the authors did not draw any conclusions with regard to the mechanisms responsible for nitrogen pre-aeration enhancing pyrrhotite recovery. It was also found by Teague [11] that other reductants such as sodium hydrosulphide (NaHS) can be added to the slurry as an alternative pre-conditioning step in place of nitrogen which results in a similar effect.

Aeration with oxygen and nitrogen has an effect on the type of xanthate product that is formed at the surfaces of the sulphide minerals, that is, whether a metal-xanthate or a dixanthogen complex is formed. Dixanthogen is noted as being a much stronger collector than the metal-xanthate species [12] and it is present at the sulphide surfaces when oxygen is added during the xanthate conditioning or when significant amounts of copper sulphate have been used during conditioning. Copper, along with other heavy-metal ions of lead, has been known for some time as being an oxidant for xanthate [12,19,20] so when it is added during xanthate conditioning in
increasing amounts, it will oxidise greater amounts of xanthate to dixanthogen. Although dixanthogen is a very strong collector, it loses selectivity due to its strength [12] and if formed in significant amounts, it can affect the frothing characteristics of the pulp whether it is dissolved or suspended in the pulp [20]. Finkelstein and Poling [21] also found that if more dixanthogen is formed the amount of fine particles entrained into the concentrate may increase. This may be due to an increase in froth stabilisation. The data given in Table 3 which represent some of the results from the aeration tests support this theory where it was found that adding oxygen during xanthate conditioning resulted in an increase in water and gangue recovery. Also, Figure 6 shows that when 300 g/t CuSO₄ is added before xanthate conditioning there is a greater entrainment of the refractory sulphide material compared with when 100 g/t CuSO₄ was used as shown in Figure 2. With respect to this work and the above discussion, it can be postulated that when dixanthogen formation is enhanced, the entrainment of water and gangue into the concentrate increases due to froth stabilisation. On the other hand, when nitrogen is added with the xanthate, the presence of dixanthogen at the mineral surface is very low [19] so that the majority of hydrophobic species is made up of metal xanthate species, being Fe-X or Cu-X, depending on whether copper has been added or not. These metal-xanthates are more selective so that more pyrite and pyrrhotite are recovered by true particle-bubble attachment, while less water and gangue material is recovered by entrainment. The water and gangue recoveries given in Table 3 illustrate this phenomenon clearly. When nitrogen is added with either sodium ethyl or potassium amyl xanthate, the water and gangue recoveries are consistently lower than the same tests where oxygen addition has been used and the pyrite and pyrrhotite recoveries are higher.

Other chemical conditions such as synergism created by the addition of more than one collecting reagent can have a positive effect on the recovery of refractory sulphide material. During flotation of the Stawell Central mill feed, greater pyrrhotite and pyrite recoveries are obtained when the GX collector is added to the slurry before P.A.X. For example in Table 4 it can be seen that a pyrrhotite recovery of 84 % was obtained under these conditions which compares favorably with using P.A.X. on its own which gave a recovery of 62 % and the GX collector on its own which gave a recovery of 49 %. When the GX collector is added before the P.A.X. it behaves much like a substitute for nitrogen pre-aeration since it is supposed to ignore the oxidation products on the pyrrhotite and enable the mineral to be floated. When both reagents are used together the pyrite recoveries are also maintained at about 70 %, which is an indication that the synergism between the collectors has a positive effect on the recovery of the refractory
gold bearing minerals. Out of all the tests that were completed to investigate the effect of reagent synergism on the flotation of the Stawell ore, the greatest gold recoveries were achieved when the two collectors were used together.

The presence of metallic iron during grinding of the Stawell Central ore causes galvanic interaction to occur between iron and pyrite, pyrrhotite and other trace sulphide minerals. The most obvious galvanic effects occur between the iron and pyrite or pyrrhotite. When a xanthate collector such as P.A.X. is used or a combination of P.A.X. and GX trithiocarbonate, the iron reduces the rest potential of the pyrrhotite so that the extent of oxide and hydroxide film formation on the mineral surface is reduced. Hence the pyrrhotite recovery increases because it has a greater chance of being activated with copper. The results for the tests where P.A.X. was used during flotation after milling in the presence and absence of metallic iron are given in Table 5. It can be seen from this table that when there is no metallic iron addition prior to milling the pyrrhotite recovery is about 45 % but this increases to 47 % when 300 g/t of iron is added and to 69 % when 5 kg/t of iron is added. The effect noticed here is similar to that of nitrogen pre-aeration. The opposite effect is observed when the GX collector is used on its own which is mainly because of the reduced extent of galvanic interaction between the metallic iron and pyrrhotite in the presence of this reagent.

It was noticed that when P.A.X. and combinations of P.A.X. and GX were used, as the level of metallic iron addition increases, the recovery of refractory pyrrhotite increases and the total gold recovery increases. These results are given in Tables 5 and 6. The iron addition also facilitates an increase in the bubble size in the froth and the overall froth stability, which contributes to an increase in refractory sulphide recovery whereas milling in the absence of iron yields an extremely brittle froth and poor sulphide recoveries. The difference between milling with 5 kg/t of iron and with no iron is illustrated in Figures 7 and 8. Van Deventer et al. [22] observed the same froth behaviour when they studied the effect of galvanic interaction on the froth phase during flotation of a complex sulphide ore. Galvanic contact with metallic iron reduces the rest potential of pyrite [11], which should give a reduction in flotation recovery as observed in Table 6. However, the enhanced froth stability could be the reason for the enhanced recovery observed in Table 5.
The Effect of Physical Conditions on Free and Refractory Gold Flotation

The previous section outlined the flotation behaviour of the refractory gold bearing sulphides and how this related to the overall gold recovery, but it must be realised that the Stawell sulphide ore has a substantial free gold component which can contain between 85 to 90 per cent of the total gold in some cases. Due to the unusual shape and structure of the free gold particles and the fact that they have to compete for attachment sites on air bubbles along with the sulphide minerals, in many cases the conditions which suit the flotation of the refractory sulphides do not suit the flotation of free gold and vice versa.

Free gold is naturally hydrophilic but becomes hydrophobic during the conditioning steps in flotation where it readily adsorbs organic material [23]. The gold particles are shaped like plates [24-26] and usually have rough surfaces consisting of pits and valleys as illustrated in the S.E.M. micrograph of Figure 9 [26]. The unusual shape and rough texture of the gold makes it difficult for the gold to attach to the air bubbles, especially when physical barriers exist, such as sulphide mineral particles that may have already loaded onto the air bubbles. Aksoy and Yarar [2] proved that other physical barriers such as ferric ions and humic acid could hinder the flotation of gold particles. It was also pointed out that the greater the roughness of the gold plates, the more likely they would exhibit a decrease in hydrophobicity. Also, Taggart [5] observed that native gold is difficult to float when it is coated or imbedded with other particles. In the current model, it can be suggested that if the bubbles are fully loaded with sulphide minerals, then the free gold tries to attach by its edge since its flat surface is rough and non-uniform. Under conditions of high sulphide loading, if the gold plates are successful in attaching to the air bubbles, the resulting particle-bubble interface is unstable since there is only a small section of the gold surfaces attached, therefore it is likely that the free gold will be entrained in the pockets of water that exist between the air bubbles, or if it is relatively coarse, it will not be recovered and will drain back to the pulp. This effect was noticed during the tests that were designed to investigate the importance of the sequence of copper sulphate addition on the transport and recovery of free and refractory gold. Figure 2 shows that when 100 g/t CuSO₄ is added prior to P.A.X. conditioning there is a high true flotation of sulphide material of about 44 % and a low degree of entrainment of 0.6. In comparison, the degree of entrainment of free gold is much higher at 1.7 because there is not sufficient space on the air bubbles for its attachment.
In the previous section it was explained how the conditioning of xanthate with oxygen and nitrogen affected the amount of sulphide material recovered by true flotation. Also, Teague et al. [18] suggested that nitrogen addition depressed the flotation of free gold while oxygen addition activated the flotation of free gold. From the present discussion it is clear that the reason why nitrogen depresses the flotation of free gold is because of the nature of the bubble loading and the reduction in water and gangue recovery as given in Table 3. When nitrogen is conditioned with xanthate the sulphide (mostly pyrrhotite) bubble loading is very high which makes it difficult for the free gold to float by true flotation under these conditions, and because the water and gangue recoveries are also low, the entrainment of free gold decreases. The results given in Table 2 indicate that conditioning with oxygen does not float as much sulphide material, so there would be more room on the bubbles for the free gold to attach, and if there is considerable froth stabilisation provided by the dixanthogen, this may enhance the entrainment of water, gangue and free gold.

Hence, under all conditions, whenever the true flotation of sulphide material is high then the true flotation of free gold should decrease and it will show a greater level of entrainment. When the true flotation of sulphide material decreases, there should be an increase in the true flotation of free gold. All of the findings from the investigations documented in this paper provide support towards this model.

The tests that were completed to investigate the effect of copper addition sequence on the recovery of free and refractory gold provide further evidence of how the level of entrainment and the bubble load can affect the flotation behaviour of the two gold bearing types. It was found that when greater dosages of copper were added before the xanthate there would be an increased level of entrainment of the refractory gold bearing sulphides which meant that less sulphide material would be attached to the air bubbles. When this occurred, the true flotation of the free gold would increase due to a decrease in the sulphide bubble loading. The copper has an effect of increasing the entrainment of solids and water in the froth and the greater flux of water upwards from the pulp could wash some of the sulphide material off the bubbles, therefore decreasing the bubble load. This effect is illustrated if one compares the data shown in Figures 2 and 6. This is the reason why many of the results in this paper seem to suggest that the free gold recovery has a proportional relationship with the water recovery. The X.R.D. analyses given in Table 7 provide proof that when 300 g/t CuSO₄ is used a greater gangue recovery of 5.00 % is
realised because of the greater level of entrainment that is occurring compared with only 3.90 % when 100 g/t CuSO₄ is added.

When the copper is added to the slurry after the xanthate, it does not have much of a chance to adsorb onto the sulphide minerals so that the strongly hydrophobic Cu-X species do not form. As a result, the sulphides display a weaker tendency to attach to the air bubbles. It may be likely that a substantial amount of copper still complexes with the xanthate adsorbed onto the minerals so that the amount of copper in solution diminishes, but there would be less elemental exchange of Cu²⁺ and Fe²⁺ ions that typifies copper activation of iron sulphide surfaces. Under these conditions there is more copper available to stabilise the froth so that the degree of entrainment of free gold increases dramatically. The recovery of refractory gold decreases linearly with water recovery when copper is added after the xanthate because the sulphides tend to scale off the bubbles more easily when more water is entrained into the froth. This effect is shown in both Figures 3 and 10. In these tests it was noticed that at air flow rates of 2.0 L/min and above, the total gold recovery became about 7 % greater when copper was added after the xanthate, compared with adding it before the xanthate. This is because up to 10 % more free gold is being recovered into the concentrates which is due to the increase in entrainment and true flotation of the free gold (refer to Figure 11).

Further flotation studies that were completed on the Stawell Central mill feed show how the temperature and viscosity of the pulp can affect the recovery of free and refractory gold. The results for these tests are given in Table 8. From this table it can be seen that an increase in the pulp temperature from 15 to 35 degrees and hence a decrease in pulp viscosity, decreases the water recovery from 19.9 to 16.4 % and reduces the amount of gangue recovered from 5.9 to 0.8 %. The X.R.D. analyses show that as the temperature increases so does the amount of pyrite and pyrrhotite that are recovered to the concentrate. As discussed before the free gold recovery increases with water recovery. At high temperatures the pulp viscosity is reduced and the sulphide bubble loading is increased. The low viscosity of the pulp enables a greater amount of water drainage to occur from the concentrate back to the pulp and this produces a cleaning effect on the concentrate where most of the gangue material drains back to the pulp with the water. The free gold has no room to attach to the bubbles due to the high sulphide loading and it is also carried back down to the pulp with the draining water. This is why the free gold recovery decreases as temperature increases. At low temperatures and high pulp viscosities there is greater entrainment of water and gangue material so that some of the sulphide material is washed.
off the bubbles which results in a lower bubble loading. Hence there is more free gold recovered by true flotation and entrainment under these conditions.

Most of the results that were generated from the reagent synergism testwork also suggest there is a direct relationship between water, gangue and free gold recovery. During the flotation of cyclone overflow material the addition of both xanthate and trithiocarbonate collectors increases the recovery of water, gangue and free gold. These results are given in Table 9. The synergistic effect between the two reagents may be responsible for inducing greater entrainment of material in the froth. The same patterns are evident when floating the Central mill feed material, although the synergistic effect does not seem to be as strong with regard to the entrainment of water and gangue.

Galvanic interaction between metallic iron, gold and the sulphide minerals in the Stawell Central ore during grinding and flotation provides a froth stabilisation effect similar to that seen when different dosages of copper are added to the flotation slurry. The data generated during the work completed for the galvanic interaction tests show that the water and gangue recoveries during flotation are usually directly proportional. Also, during the flotation tests using P.A.X. and a combination of P.A.X. and the GX collector, the recovery of free gold is also proportional to the water and gangue recoveries, which is the same trend that has been established in an extensive series of other tests [11]. This is illustrated in Figure 12. The only exception to this was the set of tests completed where the GX collector was used by itself. When a high dosage of metallic iron powder of 5 kg/t is added prior to milling an increase in the ratio of gangue to water recovered is observed and this provides greater entrainment of gangue in the froth. These tests also show that regardless of the type of collector used, the higher dosage of metallic iron provides an increase in gold recovery which is probably due to the larger bubble size and the increase in the stabilisation of the froth phase.

These results and others confirm the linear relationship between the recovery of water, gangue and free gold. If more evidence is needed as to the existence of these trends it may be pointed out that as far back as 1927, Taggart [5] already suggested that the recovery of free gold during flotation was enhanced by high pulp densities which probably increased the proportion of gangue and water being entrained into the concentrate, and this was also proven to be true by Leaver and Woolf [1] and Lange [6]. All the available literature on the flotation characteristics of free gold supports the patterns observed in this study.
It can be said that with regard to true flotation, the recovery of free and refractory gold shows an inverse relationship so that if the sulphide particles take up the bulk of the bubble surface area, in most cases a large proportion of the free gold can only be recovered by entrainment. In this instance it must be remembered that free gold is hydrophobic and will always try to float by true flotation if it is not restricted in any way by physical barriers.

CONCLUSIONS

The conceptual model for gold flotation that has been developed in this study shows that the flotation of refractory gold follows a similar trend to the recovery of refractory pyrite and pyrrhotite and is mainly affected by chemical conditions in the pulp such as redox potential, aeration conditions, copper activation, reagent synergism and galvanic interaction. In particular, it was found that the flotation of refractory pyrrhotite could be enhanced when the redox potential of the slurry is reduced prior to copper activation and flotation. This effect was observed when nitrogen pre-aeration and metallic iron addition were used before flotation. Under these conditions, the protective oxide and hydroxyl films that may form on pyrrhotite in the presence of oxygen are reduced, so that the pyrrhotite is not prevented from being activated with copper. The galvanic interaction that was implemented by metallic iron addition during milling of the ore also had an effect of increasing the froth stability during flotation. This had a positive influence on the recovery of pyrrhotite, pyrite and free gold. Other test results indicated that the reagent synergism between P.A.X. and GX increased the recovery of refractory pyrrhotite and pyrite and this also increased the total gold recovery compared with when the collectors were used individually.

The flotation recovery of free gold is largely affected by physical constraints like the shape and size of the particles, the degree of water and gangue transport to the froth, the stability of the froth, and the extent of bubble loading of sulphide particles which can provide a barrier towards the hydrophobic bubble attachment of free gold. In each individual study the results suggest that the recovery of free gold follows a proportional trend with regard to water and gangue recovery. However, there is an inverse relationship between the true flotation of free and refractory gold. The results show that when the true flotation of sulphide material increases, a greater proportion of free gold is recovered by entrainment because there is not enough room on the air bubbles for
the free gold to attach. This effect is observed when copper sulphate is added at a dosage of 100 g/t before the xanthate collector prior to flotation. An opposite trend is noticed when the copper sulphate is added after the xanthate collector. In this case the true flotation of sulphide material is reduced because there is a decrease in the hydrophobicity of the sulphide particles, and as a result the true flotation of the free gold increases. The addition of copper sulphate after the collector also increases the entrainment of the free gold because there is a greater recovery of water and gangue under these conditions.

ACKNOWLEDGEMENTS

The assistance of Stawell Gold Mines Pty Ltd for funding this research, providing ore samples and gold analysis is gratefully acknowledged. Also, Stafford McKnight at the University of Ballarat is thanked for the Siroquant X.R.D. analysis.

REFERENCES


LIST OF TABLES

1. The effect of copper addition sequence on sulphide and gold recoveries for Central mill feed and cyclone overflow material
2. Sulphide and gold recoveries under different aeration conditions using P.A.X.
3. Water and gangue recovery during flotation using P.A.X. and S.E.X.
4. Sulphide and gangue recoveries for reagent synergism tests
5. Flotation results for the galvanic interaction tests using P.A.X.
6. Flotation results for the galvanic interaction tests using P.A.X. and GX
7. Mineral recoveries for flotation tests using copper activation before xanthate conditioning at 2 L/min
8. Experimental results for flotation tests at different pulp temperature
9. Water, gangue and free gold recoveries for the reagent synergism tests using cyclone overflow
TABLE 1  The effect of copper addition sequence on sulphide and gold recoveries for Central mill feed and cyclone overflow material

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Pyrite Recovery (%)</th>
<th>Gold Recovery (%)</th>
<th>Water Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central Mill Feed</td>
<td>78.60</td>
<td>90.70</td>
<td>74.50</td>
<td>18.58</td>
</tr>
<tr>
<td>CulP.A.X.</td>
<td>45.2</td>
<td>69.00</td>
<td>81.30</td>
<td>19.27</td>
</tr>
<tr>
<td>Cyclone overflow</td>
<td>85.80</td>
<td>56.90</td>
<td>76.8</td>
<td>19.95</td>
</tr>
<tr>
<td>CulP.A.X.</td>
<td>100.00</td>
<td>88.50</td>
<td>71.10</td>
<td>19.20</td>
</tr>
<tr>
<td>P.A.X./Cu</td>
<td>85.80</td>
<td>56.90</td>
<td>76.8</td>
<td>19.95</td>
</tr>
</tbody>
</table>

TABLE 2  Sulphide and gold recoveries under different aeration conditions using P.A.X.

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Pyrite Recovery (%)</th>
<th>Gold Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2/P.A.X. and O2</td>
<td>50</td>
<td>91</td>
<td>71</td>
</tr>
<tr>
<td>P.A.X. and O2</td>
<td>78</td>
<td>72</td>
<td>84</td>
</tr>
<tr>
<td>N2/P.A.X. and O2</td>
<td>90</td>
<td>96</td>
<td>82</td>
</tr>
<tr>
<td>P.A.X. and N2</td>
<td>100</td>
<td>100</td>
<td>82</td>
</tr>
</tbody>
</table>
### TABLE 3  Water and gangue recovery during flotation using P.A.X. and S.E.X.

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Flotation Using P.A.X.</th>
<th>Flotation Using S.E.X.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Recovery (%)</td>
<td>Mass of Gangue (g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂/X and O₂</td>
<td>20.18</td>
<td>69.38</td>
</tr>
<tr>
<td>X and O₂</td>
<td>19.31</td>
<td>71.87</td>
</tr>
<tr>
<td>N₂/X and O₂</td>
<td>17.50</td>
<td>67.30</td>
</tr>
<tr>
<td>X and N₂</td>
<td>17.86</td>
<td>67.01</td>
</tr>
</tbody>
</table>

### TABLE 4  Sulphide and gangue recoveries for reagent synergism tests

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Pyrite Recovery (%)</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Gangue Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>100 Cu/50 P.A.X.</td>
<td>54.8</td>
<td>61.9</td>
</tr>
<tr>
<td>T2</td>
<td>100 Cu/25 GX</td>
<td>69.4</td>
<td>83.9</td>
</tr>
<tr>
<td></td>
<td>+25 P.A.X.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>100 Cu/25 P.A.X.</td>
<td>48.1</td>
<td>65.3</td>
</tr>
<tr>
<td></td>
<td>+25 GX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td>100 Cu/50 GX</td>
<td>48.9</td>
<td>48.5</td>
</tr>
</tbody>
</table>

### TABLE 5  Flotation results for the galvanic interaction tests using P.A.X.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Refractory gold recovery (%)</th>
<th>Total gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A.X./zero Fe</td>
<td>79.7</td>
<td>45.1</td>
<td>70.3</td>
<td>45.5</td>
<td>61.8</td>
</tr>
<tr>
<td>P.A.X./300g Fe/t</td>
<td>85.9</td>
<td>46.8</td>
<td>68.3</td>
<td>69.5</td>
<td>68.6</td>
</tr>
<tr>
<td>P.A.X./5kg Fe/t</td>
<td>87.0</td>
<td>68.8</td>
<td>63.9</td>
<td>74.2</td>
<td>71.7</td>
</tr>
</tbody>
</table>
### TABLE 6  Flotation results for the galvanic interaction tests using P.A.X. and GX

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Refractory gold recovery (%)</th>
<th>Total gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A.X.+ GX</td>
<td>100.0</td>
<td>40.6</td>
<td>73.0</td>
<td>65.2</td>
<td>66.1</td>
</tr>
<tr>
<td>zero Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.A.X.+ GX</td>
<td>76.0</td>
<td>57.5</td>
<td>69.3</td>
<td>61.5</td>
<td>68.2</td>
</tr>
<tr>
<td>300g Fe/t</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.A.X.+ GX</td>
<td>80.4</td>
<td>74.3</td>
<td>76.5</td>
<td>59.1</td>
<td>71.5</td>
</tr>
<tr>
<td>5kg Fe/t</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 7  Mineral recoveries for flotation tests using copper activation before xanthate conditioning at 2 L/min

<table>
<thead>
<tr>
<th>Test</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Gangue recovery (%)</th>
<th>Total gold recovery (%)</th>
<th>Water recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 g/t Cu</td>
<td>87.50</td>
<td>72.70</td>
<td>3.90</td>
<td>68.90</td>
<td>18.13</td>
</tr>
<tr>
<td>25 g/t P.A.X.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 g/t Cu</td>
<td>73.60</td>
<td>66.40</td>
<td>5.00</td>
<td>69.60</td>
<td>18.70</td>
</tr>
<tr>
<td>25 g/t P.A.X.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 8  Experimental results for flotation tests at different pulp temperature

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite Recovery (%)</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Total Gold Recovery (%)</th>
<th>Free Gold Recovery (%)</th>
<th>Refractory Gold Recovery (%)</th>
<th>Water Recovery (%)</th>
<th>Gangue Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>71.9</td>
<td>46.0</td>
<td>70.2</td>
<td>81.2</td>
<td>8.3</td>
<td>19.9</td>
<td>5.9</td>
</tr>
<tr>
<td>25°C</td>
<td>88.7</td>
<td>81.2</td>
<td>74.9</td>
<td>77.7</td>
<td>36.7</td>
<td>18.0</td>
<td>4.7</td>
</tr>
<tr>
<td>35°C</td>
<td>93.8</td>
<td>94.3</td>
<td>59.8</td>
<td>66.2</td>
<td>40.0</td>
<td>16.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>
TABLE 9  Water, gangue and free gold recoveries for the reagent synergism tests using cyclone overflow

<table>
<thead>
<tr>
<th>Test</th>
<th>Conditions</th>
<th>Water Recovery (%)</th>
<th>Gangue Recovery (%)</th>
<th>Ratio (Gangue/Water)</th>
<th>Free Gold Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>100 Cu/50 P.A.X.</td>
<td>17.40</td>
<td>3.96</td>
<td>0.228</td>
<td>73.1</td>
</tr>
<tr>
<td>T2</td>
<td>100 Cu/25 GX +25 P.A.X.</td>
<td>26.20</td>
<td>6.15</td>
<td>0.235</td>
<td>83.0</td>
</tr>
<tr>
<td>T3</td>
<td>100 Cu/25 P.A.X. +25 GX</td>
<td>28.96</td>
<td>6.75</td>
<td>0.233</td>
<td>86.5</td>
</tr>
<tr>
<td>T4</td>
<td>100 Cu/50 GX</td>
<td>23.17</td>
<td>5.26</td>
<td>0.227</td>
<td>74.4</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Fig. 1 A conceptual model for gold flotation.

Fig. 2 Correlation between the recovery of free and refractory gold with water for 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 3 Correlation between the recovery of free and refractory gold with water for 25 g/t P.A.X. and 100 g/t CuSO₄.

Fig. 4 Copper adsorption versus time for nitrogen pre-aeration and no pre-aeration.

Fig. 5a Flotation froth with oxygen pre-aeration [18].

Fig. 5b Flotation froth with nitrogen pre-aeration [18].

Fig. 6 Correlation between the recovery of free and refractory gold with water for 300 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 7 Froth image taken at 1 minute of flotation with 5 kg/t metallic iron addition and 50 g/t P.A.X.

Fig. 8 Froth image taken at 1 minute of flotation with zero iron addition and 50 g/t P.A.X.

Fig. 9 S.E.M. photomicrograph of gold flakes [26].

Fig. 10 Correlation between the recovery of free and refractory gold with water for 25 g/t P.A.X. and 300 g/t CuSO₄.

Fig. 11 Free gold and total gold recovery versus air flow rate using different sequences of 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 12 The recovery of free gold versus water for the galvanic interaction tests.
Fig. 1 A conceptual model for gold flotation.
Fig. 2 Correlation between the recovery of free and refractory gold with water for 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 3 Correlation between the recovery of free and refractory gold with water for 25 g/t P.A.X. and 100 g/t CuSO₄.
Fig. 4 Copper adsorption versus time for nitrogen pre-aeration and no pre-aeration.
**Fig. 5a** Flotation froth with oxygen pre-aeration [18].

**Fig. 5b** Flotation froth with nitrogen pre-aeration [18].
Fig. 6  Correlation between the recovery of free and refractory gold with water for 300 g/t CuSO₄ and 25 g/t P.A.X.
Fig. 7 Froth image taken at 1 minute of flotation with 5 kg/t metallic iron addition and 50 g/t P.A.X.
Fig. 8 Froth image taken at 1 minute of flotation with zero iron addition and 50 g/t P.A.X.
Fig. 9 S.E.M. photomicrograph of gold flake [26].
Fig. 10 Correlation between the recovery of free and refractory gold with water for 25 g/t P.A.X. and 300 g/t CuSO₄.
Fig. 11 Free gold and total gold recovery versus air flow rate using different sequences of 100 g/t CuSO₄ and 25 g/t P.A.X.
Fig. 12 The recovery of free gold versus water for the galvanic interaction tests.

\[ y = 1.5714x + 39.526 \]

\[ R^2 = 0.6829 \]
The effect of galvanic interaction on the behaviour of free and refractory gold during froth flotation

A.J. Teagut, J.S.J. Van Deventer* and C. Swaminathan†

†Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology, 124 LaTrobe Street, Melbourne Vic 3000 (Australia)

*Department of Chemical Engineering, The University of Melbourne, Parkville Vic 3052 (Australia)

ABSTRACT

This paper provides new information towards the effect of galvanic contact between metallic iron and free gold, and gold locked in refractory iron sulphide minerals such as pyrite and pyrrhotite. Galvanic interaction between pyrite, pyrrhotite and other sulphide minerals has been studied before and is well documented in the literature but there is no evidence that the effect of galvanic interaction on the recovery of free and refractory gold has been investigated. In this study, milling in a mild steel environment has been simulated by adding different dosages of metallic iron powder to a ceramic mill during grinding, and flotation has been performed using three different collector regimes. The results show that the overall gold recovery increases as more metallic iron is added to the ore prior to milling regardless of whether potassium amyl xanthate, a trithiocarbonate or a combination of the two collectors is used. When potassium amyl xanthate is used by itself or in combination with a trithiocarbonate collector, a greater dosage of metallic iron added prior to milling causes the rest potential of the pyrrhotite to decrease and its flotation recovery increases. The decrease in the pyrrhotite rest potential means that there would be a reduction in the extent of oxide and hydroxide film formation on the mineral surface which typically prevents copper activation and flotation of the pyrrhotite. In most cases the greatest amount of sulphide material is recovered when 5 kg/t of metallic iron is added to the ore prior to milling which is mainly a result of an increase in froth stability. Due to this increase in froth stability, it was found that more water and solids could be entrained and in most cases a greater recovery of free gold was obtained.
INTRODUCTION

Galvanic interaction between grinding media and sulphide minerals is a common occurrence in mineral processing operations. The control of redox conditions in a flotation slurry can become very difficult due to galvanic contact between a number of sulphide minerals which can be typically pyrite, pyrrhotite, galena and sphalerite, as well as contact between the minerals and the steel media. A number of studies have been completed which have investigated the interaction between different ferrous materials including metallic iron, and sulphide minerals (Learmont and Iwasaki, 1984; Adam et al., 1984; van Deventer, 1998; Martin et al., 1991; Rao and Finch, 1988).

Of particular interest in the current work is the effect of galvanic interaction between metallic iron, pyrrhotite and other sulphide minerals and how this affects the recovery of free and refractory gold. The Stawell Central ore used in this study is unique in the amount of pyrrhotite present, usually between 5 and 6 per cent, and the existence of significant quantities of free gold and other refractory gold bearing sulphides. A review of past work in flotation shows that the galvanic interaction between pyrite and pyrrhotite is well documented (Nakazawa and Iwasaki, 1986; Adam et al., 1984; Nakazawa and Iwasaki, 1985; Adam and Iwasaki, 1984) but there have been no studies that have concentrated on the effect of galvanic interaction on gold flotation, in particular free gold and refractory gold bearing minerals.

Nakazawa and Iwasaki (1985) studied the effect of pyrite-pyrrhotite contact. It was found that the galvanic contact decreased the formation of hydroxide or oxide and sulphate species of iron on pyrrhotite so that its floatability increased, whereas such formations were increased on pyrite and its floatability decreased. The pyrite behaves as the cathode and draws electrons from the pyrrhotite. Another study of galvanic interaction by Adam and Iwasaki, (1984) found that pyrrhotite is similarly affected when it is in contact with sulphide minerals with lower rest potentials. The formation of hydroxide or oxide and sulphate species of iron through the oxygen reduction reaction at the cathodically polarised surface of pyrrhotite was shown to be the mechanism responsible for the reduced floatability of pyrrhotite. Nakazawa and Iwasaki (1986) came to the same conclusions when they studied the galvanic contact between pyrrhotite and the less stable nickel arsenide.

Few if any past studies in flotation have investigated the galvanic interaction that can occur between grinding media, sulphide minerals and gold particles. Lorenzen and van Deventer (1992) found that chalcopyrite, pyrite and galena cause a decrease in the rate of gold dissolution in cyanide solutions because of the passive films that form on the gold surface and the galvanic interaction between the gold and the sulphides. It would be expected that the same interactions may have a significant effect during the flotation of free and refractory gold.
Much of the past work that has been completed on galvanic interaction during flotation has focused on the chemical effects in the pulp phase, and usually the transport phenomena in the froth phase have been ignored. An exception to this is the paper by van Deventer et al. (1993) who investigated the effect of galvanic interaction on the froth phase during flotation of a complex sulphide ore. It was found in this study that the galvanic interaction caused by the presence of iron yielded a stable, well-drained froth with low ratios of solids/water recovery and larger bubbles in the froth. However, milling in the absence of iron caused an extremely brittle froth with very fine bubbles.

In all the previous papers produced on galvanic interaction during flotation, xanthates have been the predominant collectors used. There has been no direct reference to the use of reagent synergism by the addition of a number of collectors and there has been no evidence of trithiocarbonate reagents being used to gain more of an understanding towards galvanic effects. With this in mind, it is little wonder that all the models that have been developed for galvanic interaction between sulphide minerals have been based on xanthate-sulphide adsorption behaviour. In this paper, potassium amyl xanthate (P.A.X.), a trithiocarbonate and a combination of the two reagents are used to provide more of an understanding towards galvanic effects in complex sulphide ores.

EXPERIMENTAL METHODS

Batch flotation tests were completed on the Stawell Central mill feed material in a 3 litre Agitair cell. Carefully prepared ore samples of 1900 grams each were dry milled individually to 80 weight % passing 106 μm in a ceramic mill with ceramic balls. Different dosages of zero, 300 g/t and 5 kg/t of metallic iron powder were added with the ore before grinding to simulate milling in a mild steel environment. The addition of 5 kg/t is much higher than the steel consumption under normal plant conditions, but this was an attempt to determine the consistency of a trend. After grinding, the material was transferred to the flotation cell and a pulp of 45 % solids by mass was made up using deionised water. Agitation of the slurry was carried out for 10 minutes to ensure that the pulp potential and pH stabilised before any reagents were added. Copper sulphate (CuSO₄) was then added to the slurry at 100 g/t and was allowed to condition for 5 minutes, before either 50 g/t of potassium amyl xanthate (P.A.X.) or a trithiocarbonate (denoted GX by supplier Chemfit Mining Chemicals, South Africa) was added and conditioned for a further 5 minutes. The frother PPG 400 was added next at a dosage of 60 g/t and was conditioned for one minute before the air entered the impeller at 2 litres per minute and flotation was carried out for 15 minutes with scraping of the froth every 20 seconds. When a combination of P.A.X. and GX was used, the P.A.X. was conditioned
first and flotation was carried out for 7 minutes, then the GX reagent was added and conditioned for 5 minutes and flotation continued for a further 8 minutes.

The concentrates were leached with sodium cyanide to determine the amount of free and refractory gold that was recovered to the concentrate and all samples were analysed for gold by atomic absorption spectroscopy. Samples of the concentrates and tailings were subjected to Siroquant quantitative X.R.D. analysis, which gave the recoveries of pyrite and pyrrhotite. Due to extreme care taken during experimentation and chemical analysis it was found that flotation results were reproducible with a standard deviation of less than 5%, so that small differences in recovery were statistically significant. Instead of giving grade-recovery curves, the recoveries of the major components such as free and refractory gold, pyrite, pyrrhotite and gangue (the remaining material) will be discussed, which essentially constitutes the same information.

Electrochemical measurements of rest and combination potentials were performed using mineral electrodes with reference to the saturated calomel electrode (S.C.E.) in separate solutions of $10^{-3}$ M potassium amyl xanthate and GX trithiocarbonate at a pH of 7. The same measurements were also taken in separate slurries of the Stawell Central mill feed in the presence of the same quantity of P.A.X. and GX. The electrodes consisting of pyrrhotite, pyrite, arsenopyrite, gold and iron were fabricated by compacting the specimens in a polymer resin and an electrical contact with the copper wire was maintained using mercury. The sulphide mineral specimens were obtained from Stawell Gold Mines and an analysis by S.E.M. shows their elemental composition: pyrite (51.5 % S, 42.6 % Fe, 5.9 % impurities), pyrrhotite (38.7 % S, 58.7 % Fe, 2.6 % impurities) and arsenopyrite (44.5 % arsenic, 18.2 % S, 34.0 % Fe, 3.3 % impurities). The gold was obtained as a button of 99.99 % bullion and was cleaned in acetone before being subjected to experimentation. The Kent Instruments EIL 7055 potential meter was used for all the rest potential measurements.

RESULTS AND DISCUSSION

Rest potentials

During the rest potential tests, a measure of reproducibility was achieved by continuously taking readings in solution or slurry before and after cleaning the surface of the electrodes with a polishing disc. This was done at least five times for each electrode and in every case the potentials stabilised to plus or minus five millivolts of the original value. Table I shows that the rest potential obtained for pyrite in xanthate solution compares well with other studies done by Rao and Finch (1991) and Tolley et al. (1996). The rest potentials for the other minerals in xanthate solution are slightly lower
than the values obtained by Allison et al. (1972) but this may be due to the difference in the type and concentration of the xanthate used as well as differences in mineral composition. In general it can be seen that the mineral rest potentials in the presence of GX are somewhat lower than in the presence of P.A.X. in both clear solution and the mineral slurry. Also, where a more noble mineral has been combined with a more active metal like iron, the rest potential has become obviously lower. It can be seen that the rest and combination potentials measured in the mineral slurry are usually between 60 to 80 mV greater than in the clear solutions. The same phenomenon was observed by Ross and van Deventer (1985) when they studied the rest potentials of galena and chalcopyrite in solutions and mineral pulps. In that study it was found that the rest potentials for galena and chalcopyrite were some 90 to 100 mV greater in Black Mountain pulps than in solutions of sodium sulphate. Fig. 1 and Fig. 2 show the relationship between the rest potentials measured in the mineral slurry and the rest potentials measured in clear solutions of 10⁻³ M P.A.X. and GX. It was important to monitor the rest potentials in the actual mineral slurry that was used during flotation as well as in clear solutions because the two systems give very different measurements and this could affect the interpretation of the results in this investigation.

Fig. 1 and Fig. 2 show a linear relationship between the mineral rest potential in clear solutions of P.A.X. and GX, and the mineral rest potential in the slurry. The trends indicate that the electrochemical behaviour of the minerals is very similar in the different media although the magnitude of the potential increases significantly in the slurry, and this increase in magnitude usually remains constant for each mineral. The recovery of arsenopyrite has been left out of the tables in the following sections because it is usually only present up to 0.1 % in the Stawell Central ore, and because it has similar flotation characteristics to pyrite, it has been assumed that it would normally behave in the same way during flotation. So when the flotation recovery of pyrite is henceforth mentioned in this paper the reader should interpret this as including a minor amount of arsenopyrite.

**The effect of galvanic interaction during flotation using P.A.X.**

In this section results of sulphide and gold recovery are given and discussed for the flotation tests using P.A.X. where the ore was ground in a ceramic mill and metallic iron powder was added during the grind in dosages of zero, 300 g/t and 5 kg/t. The bulk flotation results for the tests using 50 g/t P.A.X. are given in Table II. The sulphide recoveries were determined by Siroquant quantitative X.R.D. The data in Table II show that the recovery of pyrite increases slightly when 300 g/t or 5 kg/t of iron powder is added to the grind. With no iron addition the recovery of pyrite is

5
about 80% and when the different amounts of iron are added the recovery remains constant between 86 and 87%. The pyrrhotite behaves in a similar way. Initially when no iron is added, the pyrrhotite recovery is only 45% but this increases to 47% when 300 g/t iron powder is added and to 68% when a dosage of 5 kg/t is used. The galvanic contact between the pyrrhotite and the iron in the mineral slurry reduces the rest potential of the pyrrhotite from -0.044 V to -0.065 V. In these tests, the reduction of the pyrrhotite rest potential by iron prior to copper activation and flotation means that the surface of the mineral is less active and will probably be less responsive to the formation of oxidation products. The significance of this is that many researchers including Chang et al. (1954), Wang et al. (1989) and Teague et al., (1998) have shown that pyrrhotite prefers a reducing environment to enhance its interaction with copper sulphate and subsequent floatability. These researchers have indicated that in oxidising conditions the pyrrhotite can become coated with oxide or hydroxide films which form an impenetrable barrier towards copper activation, and the formation of the insoluble copper-xanthate species at the mineral surface is reduced. Similar conclusions were drawn by Teague (1998). In this work it was found that pre-aeration with nitrogen reduced the redox potential of the slurry and this enhanced the adsorption of copper at the mineral surfaces and increased the pyrrhotite recovery.

A different interpretation has been documented by Adam et al. (1984) which argues that when pyrrhotite is in galvanic contact with more active minerals or metals like iron, it behaves as a cathode and draws electrons from the iron which induces an oxidation product of hydroxide or oxide and sulphate species to form on the pyrrhotite surface. This oxidation product can lead to selective depression of pyrrhotite during flotation. Although the authors have good experimental evidence to back up their findings, their flotation work was carried out on a sample of pure pyrrhotite by itself in a Hallimond tube instead of on a “real” ore containing substantial quantities of other sulphide minerals, and copper sulphate was not used as an activator. This means that not only were the chemical conditions different, but also the complex galvanic effects of iron, pyrrhotite, gold, and other sulphide and gangue minerals would have been disregarded. In the current work it can be suggested that whether or not the phenomenon discussed by Adam et al. (1984) occurs during flotation of the Stawell ore, the reduction of the pyrrhotite rest potential and subsequent hydroxide film formation on the mineral surface prior to copper activation have a governing effect on the recovery of the pyrrhotite.

Nakazawa and Iwasaki (1985) found that when pyrrhotite is in contact with a more noble mineral like pyrite, the floatability of pyrite would be retarded and that of pyrrhotite would increase. However, these findings cannot be applied to the current work because the ore has been well liberated prior to flotation so it would be expected that the contact between the pyrite and pyrrhotite
The galvanic contact between the iron and pyrite in the slurry is almost non-existent. Hence the effects of galvanic contact in this work are due to the iron addition alone.

The galvanic contact between the iron and pyrite in the slurry causes the rest potential of the pyrite to decrease from -0.031 to -0.052 V. In most cases this would be expected to decrease the floatability of pyrite since it has been observed in past work (Wang and Forssberg, 1991) that when the rest potential of pyrite decreases, the amount of dixanthogen formed at the mineral surface is reduced. It has been known for some time that dixanthogen is usually the predominant collecting species for pyrite (Fuerstenau et al., 1968; Fuerstenau and Mishra, 1980) and its formation and hence pyrite floatability are usually favoured by oxidation. However, in Table II it can be seen that the pyrite recovery increases instead of decreasing. Similar contradictory results for the recovery of pyrite during galvanic contact with other materials have also been observed by Martin et al. (1991), and Petruk and Hughson (1977). Rao et al. (1976) offered an explanation that pyrite exhibited an increased hydrophobicity when in galvanic contact with abraded iron due to the formation of elemental sulphur on the pyrite surface. However, a common problem with all these papers as explained by van Deventer (1998) is that they only focused on the factors affecting the floatability of minerals in the pulp phase, while the froth phase has generally been ignored. In the current tests, it may be suggested that the increased recovery of pyrrhotite which occurs due to the greater dosage of iron helps to create a stable froth, and it may be the increase in froth stability which enhances the recovery of pyrite. Ross (1988) suggested that the transport phenomena in the froth phase are complex and depend *inter alia* on the floatability of each flotation species. The difference in froth stability during flotation using P.A.X. with zero Fe and 5 kg/t Fe is given in Fig. 3 and Fig. 4 and it can be seen from these pictures that the addition of iron during grinding creates a more stable froth with larger bubbles.

The reason why there is such a difference in the pyrrhotite and pyrite recoveries when the ore is ground in a ceramic mill without any iron addition is because of the oxidation occurring during the grind and the different effect this has on the two major sulphides. By comparison, under “normal” conditions of grinding in a steel mill (which gives some liberation of iron) as documented by Teague et al. (1998), the recovery of pyrrhotite is 78 % and that of pyrite is 72 % during flotation of the same ore. This is further evidence that a reducing environment enhances the floatability of pyrrhotite. A number of studies on the factors influencing the copper activation of pyrite and pyrrhotite (Chang et al., 1954; Bushell and Krauss, 1962) have found that activation of pyrrhotite is affected by the oxidation products forming on its surface because the exchange reaction between Cu$^{2+}$ and Fe$^{2+}$ ions cannot proceed, but the same surface products do not form on pyrite and hence the copper activation of pyrite is not affected. In fact, Tolley et al. (1996) made it clear that
"oxidation increases pyrite floatability". Fig. 5 illustrates the difference in pulp potential in the 10 minute agitation period prior to copper conditioning for the different tests where zero iron, 300 g/t and 5 kg/t of iron were added to the ceramic mill. It can be seen from this graph that when no iron powder is added during the grind the pulp potential increases to about +150 mV prior to conditioning with copper sulphate compared with -146 mV when 300 g/t is added and -204 mV when 5 kg/t of iron powder is added. In Fig. 5 there is a further decrease in pulp potential with time, because during agitation of the pulp, the mineral and iron particles consume the oxygen which is present in solution and there also may be further contact between the iron particles and minerals which reduces the potential of the pulp. The oxidised nature of the ore after grinding in the ceramic mill with zero iron powder means that a high proportion of pyrrhotite may be coated with a thin layer of oxide or hydroxide film and the amount of copper adsorption would most likely be very low, resulting in a reduced flotation recovery. In the studies completed by Teague (1998) it was explained that a greater copper adsorption enhanced the flotation recovery of pyrrhotite because the Cu-X surface species provide greater hydrophobicity towards the FeS than the Fe-X compounds.

A case study by van Deventer (1998) showed that the effect of galvanic interaction on the recovery of a particular mineral can also be dependent on the stability of the froth phase. Interestingly, the data in Table II indicate that the greatest sulphide recoveries are achieved when more metallic iron is added prior to milling. Similar to the work done by van Deventer et al. (1993) the tests documented in this paper show that when no iron was added to the grind a very weak and brittle froth results which could be caused by a reduction in the hydrophobic attachment of sulphide material and a slight increase in gangue recovery compared with the test where 300 g/t iron is used. An example of this froth structure is shown in Fig. 3 and was taken using a video camera during the flotation test. The low pyrrhotite recovery may have also contributed to the poor froth structure as explained by Teague et al. (1998). In comparison, when 300 g/t of iron was added prior to the grinding stage, the flotation froth became very stable with larger bubbles and a lower recovery of gangue, although when 5 kg/t of iron was added the recovery of gangue and water increased. A photo which shows the effect of adding 5 kg/t of iron is given in Fig. 4.

These data and froth images show that the addition of metallic iron not only affects the potential of the sulphide particles but also affects the froth phase, as observed by van Deventer et al. (1993). With this in mind, it would be unusual if the addition of iron did not also affect the recovery of free and refractory gold since it has been suggested by Teague (1998) that the flotation of free gold can be influenced by the transport of material from the pulp to the froth phase.

The free gold, refractory gold and total gold recoveries for the first set of flotation tests using P.A.X. are listed in Table II. It can be seen that the total gold recovery increases from 62 % when
no iron is added to the ceramic mill to 69 % when 300 g/t iron is added. When 5 kg/t of iron is added prior to milling, the gold recovery increases by 3 % to 72 %. The values determined for the recovery of free and refractory gold show how the two different gold types influence the total gold recovery. From Table III, it can be seen that when there is zero iron addition, there is a greater recovery of water and gangue to the concentrate compared with 300 g/t Fe addition, and the free and refractory gold recoveries are 70 % and 45.5 % respectively. The investigations completed by Teague (1998) showed that there is a relationship between the recovery of water and the recovery of free gold and in general there is an inverse trend between the true flotation of free and refractory gold due to the competition between the species for attachment at the bubble surfaces. When 300 g/t iron is added the recovery of water and gangue decreases slightly and the free gold recovery decreases to 68 % while the refractory gold increases from 45.5 % to 69.5 %. In this test it is the increase in the mass of refractory gold that is providing the increase in total gold recovery.

The decrease in the amount of free gold that is recovered can also be explained in terms of the galvanic interaction between the metallic iron and the gold particles. In Table I it is observed that the combination potentials between gold and iron are lower than the rest potentials of gold alone in solution and in the mineral slurry, which indicates that a cathodic current exists. Teague (1998) found that free gold is activated by oxidising conditions in the presence of xanthate solutions so that its floatability is enhanced. The same trends have been observed by Clark and Newell (1995) when they performed test work for their patent to improve the recovery of precious metals from ores. In the current tests the interaction between the metallic iron and gold particles reduces the rest potential of the gold and hence its activation and flotation response are reduced.

When 5 kg/t of iron is added prior to milling there is a further decrease in the free gold recovery from 68 % to 64 % which is probably because the greater dosage of iron creates a greater galvanic interaction with the gold particles which reduces its flotation recovery even more than when 300 g/t Fe is used. However, the refractory gold recovery increases from 69 % to 74 %. This result is expected since the greatest recoveries of pyrite and pyrrhotite occurred during this test and it is expected that the majority of refractory gold would be derived from these minerals. Also, it has been proven by Teague (1998) that when the true flotation of free gold decreases, it is most likely that there is a greater degree of refractory sulphide bubble attachment and a higher sulphide recovery.
The effect of galvanic interaction during flotation using trithiocarbonate

Tests were completed using a new trithiocarbonate collector (denoted GX). The same milling conditions were used as for the P.A.X. tests where dosages of zero, 300 g/t and 5 kg/t of iron powder were added prior to grinding in a ceramic mill.

Table IV shows the results for pyrite and pyrrhotite recovery during the different tests using the GX collector. It can be seen that when milling is performed without any iron addition both the pyrite and pyrrhotite recoveries are low at about 57 % and 33 % respectively. The low pyrrhotite recovery occurs because the same oxidising conditions are prevalent during milling in the ceramic mill as for the previous tests using P.A.X. The formation of oxide and hydroxide films on the pyrrhotite surface retards copper activation and flotation as explained previously. The pyrite recovery in this test is much lower than the corresponding test using P.A.X. which gave a recovery of 80 %. This can be explained in terms of the electrochemical nature of the GX collector. Unfortunately in the current literature there has been no documentation of the adsorption mechanisms and electrochemistry of trithiocarbonate reagents, but some work has been done on dithiocarbamates by O'Connor et al. (1990) and Finkelstein and Poling (1977). The only difference between the two reagents is that an extra sulphur atom is present in the trithiocarbonate in place of the nitrogen atom that exists in the dithiocarbamate. For the purpose of this discussion it may be assumed that the electrochemical nature of the reagents is very similar since they form part of the same chemical group.

In a review of dithiolate collectors for sulphide minerals Finkelstein and Poling (1977) state that dithiocarbamates are more powerful collectors than xanthates although they are somewhat less readily oxidised, however oxygen is a prerequisite for flotation just as it is with xanthates. In general, the standard reduction potentials given for a series of thiocarbonates by Finkelstein and Poling (1977) are about 80 to 90 mV more positive than their corresponding xanthate homologues. This means that during flotation with these reagents a significant increase in the sulphide rest potential has to occur before the thiocarbonate is oxidised to its dimer. Pyrite flotation with xanthates usually requires oxidising conditions so that a significant proportion of dixanthogen formation and adsorption can take place. In Table I the mineral rest potentials show that in the mineral slurry with GX, the pyrite rest potential is negative 0.040 V. In the presence of P.A.X. this rest potential is high enough to oxidise xanthate to dixanthogen at the pyrite surface, but in the presence of the GX collector, the pyrite rest potential is not high enough for this oxidation to occur. This statement can be verified by using the same calculation technique as Ross and van Deventer (1985) where they determined the minimum reduction potential for the dixanthogen/xanthate couple.
using the Nernst equation shown as equation [1]. The calculation was carried out using a
temperature of 25°C, a standard potential $E^0$ of -0.06 V and a P.A.X. concentration of $1\times10^{-3}$M.

$$E_{X/X^+} = E^0 + 0.0128 \ln(a_{x-})^2$$  \[1\]

The minimum reduction potential for these conditions was calculated as $+117$ mV. To compare
the pyrite rest potential of $-0.040$ V to the calculated reduction potential it needs to be converted to a
figure versus the standard hydrogen electrode. If a value of 245 mV is used to convert the calomel
electrode reading, then the pyrite rest potential becomes $+205$ mV which is significantly greater
than the minimum reduction potential of $+117$ mV.

Under the same conditions in the presence of GX it may be expected that the pyrite rest potential
would have to be at least $+210$ mV before its oxidation product could begin to form. Hence, the
oxidation product of the GX does not adsorb onto the pyrite surface and the floatability of the pyrite
is reduced. This may be the reason for the low pyrite recovery under the oxidising environment of
the ceramic mill.

Even though the addition of 300 g/t and 5 kg/t Fe prior to milling lowers the pyrite rest potential
by 15 mV in the presence of GX, its flotation recovery increases slightly to 59 % and then more
significantly to 89 %. The increase in pyrite recovery cannot be a result of electrochemical
interactions as discussed above because the pyrite rest potential decreases, but it may be due to the
physical effect of the iron addition on the froth phase. Fig. 6 and Fig. 7 show how the addition of 5
kg/t Fe prior to milling has a significant froth stabilisation effect during flotation compared with
zero iron addition. Also, because the pyrrhotite exhibits a poor flotation recovery during these tests,
this may provide more room on the bubbles for the hydrophobic attachment of pyrite.

The pyrrhotite recovery shows an unusual trend. It decreases from 33 % when no iron is added
to about 29 % when 300 g/t and 5 kg/t Fe is added prior to milling. Based on previous discussions
in this paper it is not clear why the pyrrhotite would behave like this, but it may be possible that
there is a reduced galvanic interaction in the mineral slurry between pyrrhotite and iron in the
presence of the GX collector compared with in the presence of P.A.X. Table I shows that the
pyrrhotite rest potential is only reduced by 8 mV in the presence of GX compared with 21 mV in the
presence of P.A.X. As discussed previously in this work the flotation of pyrrhotite usually responds
well to a reduction in rest potential prior to copper activation because there is less chance that the
mineral will form oxide and hydroxide films on its surface which create a barrier to the ionic
exchange of Cu$^{2+}$ and Fe$^{2+}$. Hence, because the iron addition does not seem to have the same
reducing influence on the pyrrhotite rest potential in the presence of the GX collector, it is likely
that some form of oxide and hydroxide may coat the pyrrhotite surface so that its recovery remains low at 29%.

The data for the different types of gold being recovered during the GX flotation tests are given in Table IV. It can be seen from this table that the total gold recovery increases from 64% when no iron is added before milling to 70% when 300 g/t iron is added and 75% when 5 kg/t iron is added. These results show the same trend as the previous tests which were completed using P.A.X. In both cases the gold recovery increased as more metallic iron was added prior to milling in the ceramic mill although the highest gold recovery achieved when using P.A.X. was about 3% lower.

When no iron is added to the milling the free gold recovery is 71% and the refractory gold is about 41%. The difference observed in the recovery of the two gold types was expected since the pyrite and pyrrhotite recoveries were quite low, and a lower sulphide particle-bubble attachment means that there is more room on the bubble surface for the free gold to attach. When 300 g/t of iron is added the free gold recovery increases to about 80% and the refractory gold recovery increases to 50% which leads to a higher total gold recovery. When 5 kg/t of iron is added the refractory gold recovery increases by about 13% probably due to the increase in pyrite recovery, but the free gold recovery decreased by about 3%. This decrease in free gold recovery may have been a result of the higher proportion of sulphide material that was recovered so that the bubble attachment of the free gold was reduced. Teague (1998) postulated that because of its shape and surface texture, the free gold cannot attach to the air bubbles properly if the majority of bubble sites are already taken up by sulphide particles. This phenomenon could be occurring during this test. Even though the free gold recovery decreases by 3% when 5 kg/t or iron is added to the mill, the 13% increase in refractory gold recovery maintains an overall increase in gold recovery of 5%.

**The effect of galvanic interaction during flotation using a combination of P.A.X. and trithiocarbonate**

In this section the results are discussed for the flotation tests where a combination of P.A.X. and the GX trithiocarbonate collector was used after the Stawell Central ore had been milled in a ceramic mill. Before milling, amounts of zero, 300 g/t and 5 kg/t of metallic iron powder were added to the feed material in the same way as for the previous tests.

The pyrite and pyrrhotite recoveries are given in Table V and it can be seen that there is a similar trend to the results in Table II with regard to the effect of galvanic interaction of iron on the behaviour of the two major sulphides. The pyrrhotite recovery is low initially because of the oxidising conditions present in the ceramic mill as discussed previously in this paper, but when 300
g/t of iron is added the recovery increases from 41 % to 58 % and when 5 kg/t of iron is added the recovery increases to 74 %. The increase in pyrrhotite recovery with greater dosages of iron can be attributed to the reduction of the pyrrhotite rest potential (refer to Table I) so that the oxide and hydroxide films do not form on its surface.

The pyrite shows the opposite trend. Initially the pyrite recovery is very high at 100 % because of its increased floatability in the presence of the synergistic collector combination of P.A.X. and GX and because it is known to float well in oxidising conditions (Fuerstenau and Mishra, 1980; Teague et al., 1998). However, when 300 g/t of iron is added to the milling stage, the galvanic interaction between the iron and pyrite particles causes the pyrite rest potential to decrease so that its interaction with xanthate decreases (Rao and Finch, 1988) and it is less likely that dixanthogen would form at its surface (Martin et al., 1989). When 5 kg/t of iron powder is added prior to milling, the pyrite recovery increases by 4 % to 80 %. It is surprising that the pyrite recovery did not continue to decrease as the trend and hypotheses predict, but because the large dosage of iron powder induces significant stabilisation of the froth as shown in Fig. 8 and Fig. 9, it may be possible that some pyrite particles are carried into the concentrate with the other entrained material so that instead of decreasing, the pyrite recovery increases slightly. This suggests that the net effect of iron is a compromise between the negative effect of a lower potential and hence less formation of dixanthogen, the negative effect of the formation of oxy-hydroxides, and the positive effect of froth stabilisation.

The recovery of free gold, refractory gold and total gold for these tests is given in Table V. The total gold recovery shows a similar trend to the previous two sets of data in that it increases when more iron powder is added prior to milling. When 300 g/t of iron is added the gold recovery increases slightly from 66 % to 68 %, and when 5 kg/t of iron is added the recovery increases to 72 %. When no iron powder is added to the grind, the free gold recovery is about 73 % and the refractory gold recovery is 65 %. The high free gold recovery is expected since there is slightly greater entrainment of water and gangue when no iron addition is compared with an iron dosage of 300 g/t. The recovery of refractory gold is also higher than usual in this test which is probably due to the high recovery of pyrite.

When 300 g/t of iron is added prior to milling the flotation results show that there is a 4 % decrease in the amount of free gold being recovered and the refractory gold also decreases by about 4 %. The decrease in free gold recovery may be because of the galvanic interaction between the gold and iron which lowers the rest potential of the gold particles so that their floatability is reduced. It has been discussed previously in this work that free gold prefers an oxidised environment where it is activated and its floatability increases. Also, in this test there is less water.
being recovered which is given in Table III and it has been proven by Teague (1998) that the recovery of free gold is usually proportional to the water recovery. Hence the trend identified here is consistent with that of previous research. The reason why the refractory gold recovery also decreases is most likely because of the decrease in pyrite recovery by 24 %.

The addition of 5 kg/t of iron prior to milling makes the free gold recovery rise to 77 % and the refractory gold recovery decreases slightly to 59 %. The high dosage of iron induces substantial froth stabilisation so that the recovery of water and solids increases. The difference in froth stability can be seen in Fig. 8 and Fig. 9 and this effect was consistent with each type of collector used. The froth stabilisation and the increased recovery of water both contribute to the significant rise in free gold recovery. Since the galvanic and froth stabilisation effects induced by the high dosage of iron powder gave a high recovery of pyrite and pyrrhotite, it is unusual that the recovery of refractory gold did not increase as well. However, sometimes the leachability of the gold can be affected by the sulphide minerals that it is in electrochemical contact with (Lorenzen and van Deventer, 1992) so that the amount of refractory gold that is recovered does not always correspond exactly to the recovery of the refractory host minerals.

The recovery of water, gangue and free gold

Teague (1998) hypothesised that the recovery of free gold may be proportional to the recovery of water and gangue during flotation. Substantial experimental evidence was given that supported this hypothesis and it was explained how an increase in water recovery could decrease the amount of sulphide material loaded onto the bubbles so that there was enough room on the bubbles for the hydrophobic gold particles to attach. The high water and gangue recovery meant that significant entrainment was taking place in the froth and if any of the gold particles could not attach to the air bubbles due to high sulphide loading then it was likely that they would be entrained with the other material.

The results in this paper are no different. The recovery of water, gangue and free gold is given in Table V and a ratio of gangue to water recovery is also shown. In all the tests completed in this investigation it can be seen that the water and gangue recoveries follow the same trend. Also, for the flotation tests where P.A.X. was used by itself and where the combination of P.A.X. and GX was used, the recovery of free gold versus water recovery gives a straight line relationship as shown in Fig. 10. The exception to this relationship was the set of tests using the GX collector on its own which showed the opposite trend. However, this reagent has been developed only recently, so that its effect on chemical and physical conditions during the flotation of sulphide ores is not completely
understood and there may be other interactions occurring in the pulp between the collector and the metallic iron which could alter the behaviour of the free gold.

Table III shows that in each of the three sets of tests the ratio of gangue to water is usually constant between no iron addition and 300 g/t of iron addition. This value is usually between 0.15 and 0.16. The fact that the addition of 5 kg/t of iron powder gives an average increase in the ratio of gangue to water of about 0.03 indicates that the metallic iron is providing a froth stabilising effect during flotation and there is a greater entrainment of gangue in the froth. This phenomenon is similar to that seen when copper was added in high dosages during the tests discussed by Teague (1998) and a similar effect was found by van Deventer et al. (1993) when they investigated the effect of galvanic interaction on the behaviour of the froth phase during flotation of a complex sulphide ore.

In general flotation operators attempt to minimise the entrainment of undesirable particles. Evidently the recovery of a species will increase if entrainment increases, but this decreases grades, which is usually unacceptable. On some flotation plants where the recovery of fine free gold is important, operators will compromise grades by using froth stabilisation to enhance the recovery of gold by entrainment. This is consistent with the observations made in this paper.

CONCLUSIONS

There are a number of findings in this study which may contribute to a more thorough understanding of the nature of galvanic interaction between metallic iron, iron sulphide minerals which contain gold, free gold particles, and the influence of metallic iron on the froth stability and the transport of gangue material from the pulp to the froth during flotation. When one considers the complexity of the chemical interactions between iron and the sulphide minerals and the physical effects that iron addition can have on the flotation froth as discussed in this paper, it is surprising that more investigations in this area have not been carried out.

The major conclusions from this work can be summarised as follows:

- The total gold recovery increased as more metallic iron was added to the ore prior to milling regardless of whether P.A.X., GX or a combination of the two collectors was used. In most cases the greatest amount of sulphide material was recovered when 5 kg/t of metallic iron was added to the ore prior to milling which was mainly the result of an increase in froth stability.
When P.A.X. was used by itself or in combination with the GX collector, a greater dosage of metallic iron added prior to milling caused the rest potential of the pyrrhotite to decrease and its flotation recovery increased. The decrease in the pyrrhotite rest potential meant that there would be a reduction in the extent of oxide and hydroxide film formation on the mineral surface which typically prevents copper activation and flotation of the pyrrhotite.

In most cases it was found that the flotation of pyrite seemed to be more dependent on the physical conditions in the froth such as the stability caused by the iron addition and the degree of flotation of other sulphide species such as pyrrhotite. The addition of metallic iron prior to milling reduced the rest potential of the pyrite, but as observed by other researchers, the pyrite recovery did not decrease but either remained constant or increased.

It was found that the recovery of pyrite increased and the pyrrhotite recovery remained low when the ore was milled in the presence of metallic iron and flotation was carried out using the GX collector. The low pyrrhotite recovery was attributed to a reduction in the extent of galvanic interaction between the mineral and metallic iron in the presence of the trithiocarbonate compared with when P.A.X. was used.

In each of the three sets of tests it was found that the ratio of gangue to water increased when 5 kg/t of iron was added prior to milling. The iron was found to increase the stability of the froth during flotation so that more water and solids could be entrained and in most cases a greater recovery of free gold was obtained.

Similar to the results obtained by other researchers, in most cases the free gold recovery followed the same trend as the water recovery while the refractory gold recovery was usually reflected in the proportion of sulphide material that was recovered during each test.

ACKNOWLEDGEMENTS

The assistance of Stawell Gold Mines Pty Ltd for funding this research, providing ore samples and gold analysis is gratefully acknowledged. Also, Stafford McKnight at the University of Ballarat is thanked for the Siroquant X.R.D. analysis.
REFERENCES


LIST OF TABLES

I  Rest and combination potentials for pyrite, pyrrhotite, arsenopyrite and gold in separate clear solutions and mineral slurries containing $10^{-3}$ M P.A.X. and GX at pH 7

II  Flotation results using P.A.X.

III  Recovery of water, gangue and free gold for flotation tests

IV  Flotation results using GX

V  Flotation results using P.A.X. and GX
Table I  Rest and combination potentials for pyrite, pyrrhotite, arsenopyrite and gold in separate clear solutions and mineral slurries containing $10^{-3}$ M P.A.X. and GX at pH 7

<table>
<thead>
<tr>
<th>Mineral or Combination</th>
<th>Potential V (vs. SCE) in a clear solution of $10^{-3}$ M P.A.X.</th>
<th>Potential V (vs. SCE) in a clear solution of $10^{-3}$ M GX</th>
<th>Potential V (vs. SCE) in a slurry with $10^{-3}$ M P.A.X.</th>
<th>Potential V (vs. SCE) in a slurry with $10^{-3}$ M GX</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrite</td>
<td>-0.090</td>
<td>-0.120</td>
<td>-0.031</td>
<td>-0.040</td>
</tr>
<tr>
<td>Pyrite and gold</td>
<td>-0.110</td>
<td>-0.125</td>
<td>-0.039</td>
<td>-0.051</td>
</tr>
<tr>
<td>Pyrite and iron</td>
<td>-0.121</td>
<td>-0.148</td>
<td>-0.052</td>
<td>-0.055</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>-0.112</td>
<td>-0.130</td>
<td>-0.044</td>
<td>-0.056</td>
</tr>
<tr>
<td>Pyrrhotite and gold</td>
<td>-0.126</td>
<td>-0.134</td>
<td>-0.050</td>
<td>-0.060</td>
</tr>
<tr>
<td>Pyrrhotite and iron</td>
<td>-0.133</td>
<td>-0.155</td>
<td>-0.065</td>
<td>-0.064</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>-0.096</td>
<td>-0.124</td>
<td>-0.033</td>
<td>-0.045</td>
</tr>
<tr>
<td>Arsenopyrite and gold</td>
<td>-0.107</td>
<td>-0.128</td>
<td>-0.045</td>
<td>-0.055</td>
</tr>
<tr>
<td>Arsenopyrite and iron</td>
<td>-0.121</td>
<td>-0.150</td>
<td>-0.056</td>
<td>-0.061</td>
</tr>
<tr>
<td>Gold</td>
<td>-0.140</td>
<td>-0.200</td>
<td>-0.084</td>
<td>-0.114</td>
</tr>
<tr>
<td>Gold and iron</td>
<td>-0.156</td>
<td>-0.213</td>
<td>-0.109</td>
<td>-0.137</td>
</tr>
</tbody>
</table>

Table II  Flotation results using P.A.X.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Refractory gold recovery (%)</th>
<th>Total gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A.X./zero Fe</td>
<td>79.7</td>
<td>45.1</td>
<td>70.3</td>
<td>45.5</td>
<td>61.8</td>
</tr>
<tr>
<td>P.A.X./300g Fe/t</td>
<td>85.9</td>
<td>46.8</td>
<td>68.3</td>
<td>69.5</td>
<td>68.6</td>
</tr>
<tr>
<td>P.A.X./5kg Fe/t</td>
<td>87.0</td>
<td>68.8</td>
<td>63.9</td>
<td>74.2</td>
<td>71.7</td>
</tr>
</tbody>
</table>
### Table III  Recovery of water, gangue and free gold for flotation tests

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Water recovery (%)</th>
<th>Gangue recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Ratio gangue/water</th>
</tr>
</thead>
<tbody>
<tr>
<td>GX</td>
<td>20.33</td>
<td>3.2</td>
<td>70.6</td>
<td>0.157</td>
</tr>
<tr>
<td>GX/300g Fe/t</td>
<td>19.62</td>
<td>3.0</td>
<td>79.7</td>
<td>0.153</td>
</tr>
<tr>
<td>GX/5kg Fe/t</td>
<td>22.68</td>
<td>4.3</td>
<td>76.8</td>
<td>0.189</td>
</tr>
<tr>
<td>P.A.X.</td>
<td>20.16</td>
<td>3.2</td>
<td>70.3</td>
<td>0.159</td>
</tr>
<tr>
<td>P.A.X./300g Fe/t</td>
<td>19.29</td>
<td>3.0</td>
<td>68.3</td>
<td>0.156</td>
</tr>
<tr>
<td>P.A.X./5kg Fe/t</td>
<td>22.16</td>
<td>4.3</td>
<td>63.9</td>
<td>0.194</td>
</tr>
<tr>
<td>P.A.X. + GX</td>
<td>19.65</td>
<td>3.4</td>
<td>73.0</td>
<td>0.173</td>
</tr>
<tr>
<td>300g Fe/t</td>
<td>18.16</td>
<td>2.8</td>
<td>69.3</td>
<td>0.154</td>
</tr>
<tr>
<td>P.A.X. + GX</td>
<td>21.63</td>
<td>4.4</td>
<td>76.5</td>
<td>0.203</td>
</tr>
</tbody>
</table>

### Table IV  Flotation results using GX

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Refractory gold recovery (%)</th>
<th>Total gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GX/zero Fe</td>
<td>56.5</td>
<td>32.5</td>
<td>70.6</td>
<td>41.2</td>
<td>63.7</td>
</tr>
<tr>
<td>GX/300g Fe/t</td>
<td>58.7</td>
<td>28.7</td>
<td>79.7</td>
<td>50.0</td>
<td>70.2</td>
</tr>
<tr>
<td>GX/5kg Fe/t</td>
<td>88.6</td>
<td>29.1</td>
<td>76.8</td>
<td>63.5</td>
<td>74.9</td>
</tr>
</tbody>
</table>

### Table V  Flotation results using P.A.X. and GX

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Free gold recovery (%)</th>
<th>Refractory gold recovery (%)</th>
<th>Total gold recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A.X.+ GX</td>
<td>100.0</td>
<td>40.6</td>
<td>73.0</td>
<td>65.2</td>
<td>66.1</td>
</tr>
<tr>
<td>Zero Fe</td>
<td>76.0</td>
<td>57.5</td>
<td>69.3</td>
<td>61.5</td>
<td>68.2</td>
</tr>
<tr>
<td>P.A.X.+ GX</td>
<td>80.4</td>
<td>74.3</td>
<td>76.5</td>
<td>59.1</td>
<td>71.5</td>
</tr>
</tbody>
</table>

Stellenbosch University  https://scholar.sun.ac.za
LIST OF FIGURES

Fig. 1 Potential in a clear solution of P.A.X. vs potential in a mineral slurry.

Fig. 2 Potential in a clear solution of GX vs potential in a mineral slurry.

Fig. 3 Froth image taken at 1 minute of flotation using no iron addition and 50 g/t P.A.X.

Fig. 4 Froth image taken at 1 minute of flotation with 5 kg/t iron addition and 50 g/t P.A.X.

Fig. 5 A comparison of pulp potential during the initial 10 minute agitation period before conditioning for zero, 300 g/t and 5 kg/t iron addition.

Fig. 6 Froth image taken at 1 minute of flotation with 50 g/t GX and zero iron.

Fig. 7 Froth image taken at 1 minute of flotation with 50 g/t GX and 5 kg/t iron.

Fig. 8 Froth image taken at 1 minute of flotation with 25 g/t P.A.X., 25 g/t GX and zero iron.

Fig. 9 Froth image taken at 1 minute of flotation with 25 g/t P.A.X., 25 g/t GX and 5 kg/t iron.

Fig. 10 The recovery of free gold versus water during flotation.
Fig. 1 Potential in a clear solution of P.A.X. vs potential in a mineral slurry.

Fig. 2 Potential in a clear solution of GX vs potential in a mineral slurry.
Fig. 3  Froth image taken at 1 minute of flotation using no iron addition and 50 g/t P.A.X.

Fig. 4  Froth image taken at 1 minute of flotation with 5 kg/t iron addition and 50 g/t P.A.X.
Fig. 5 A comparison of pulp potential during the initial 10 minute agitation period before conditioning for zero, 300 g/t and 5 kg/t iron addition.
Fig. 6 Froth image taken at 1 minute of flotation with 50 g/t GX and zero iron.

Fig. 7 Froth image taken at 1 minute of flotation with 50 g/t GX and 5 kg/t iron.
Fig. 8 Froth image taken at 1 minute of flotation with 25 g/t P.A.X., 25 g/t GX and zero iron.
Fig. 9 Froth image taken at 1 minute of flotation with 25 g/t P.A.X., 25 g/t GX and 5 kg/t iron.
Fig. 10 The recovery of free gold versus water during flotation.

\[ y = 1.5714x + 39.526 \]

\[ R^2 = 0.6829 \]
The effect of copper activation on the behaviour of free and refractory gold during froth flotation

A.J. Teague¹, J.S.J. Van Deventer¹ and C. Swaminathan¹

¹Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology, 124 LaTrobe Street, Melbourne Vic 3000 (Australia)

*Department of Chemical Engineering, The University of Melbourne, Parkville Vic 3052 (Australia)

ABSTRACT

This study is aimed at explaining the effect of copper activation in flotation systems which contain free gold and gold locked in pyrrhotite and pyrite. Unlike other studies, the effect of the sequence and amount of copper added to the slurry in relation to the xanthate conditioning period is investigated and the results are discussed in terms of how the two gold bearing types respond to true particle-bubble attachment and entrainment during flotation. The results indicate that increasing the dosage of copper sulphate increases the entrainment of refractory gold when the copper is added before the P.A.X., because there is a greater flux of water upwards to the froth which results in a decrease in the amount of sulphide material that is attached to the air bubbles. When the true flotation of refractory gold decreases, it has a higher degree of entrainment and the true flotation of free gold increases since there is a larger proportion of non-mineralised surface sites on the bubbles where attachment can take place. When copper sulphate is added after the collector the recovery of free gold increases dramatically so that there is an overall increase in total gold recovery of up to 6% compared with the usual sequence of adding the copper first.

INTRODUCTION

It is well known that activation of iron sulphide flotation systems with Cu(II) will provide an increase in sulphide grades and recoveries (Chang et al., 1954; O'Connor et al., 1988; O'Connor and Dunne, 1994). In most cases, when these sulphides such as pyrite, pyrrhotite and arsenopyrite contain gold, activation with copper sulphate will also result in greater gold recoveries. Even though this is common knowledge, the role of copper activation during the flotation of gold bearing
material still remains unclear with many plants around the world using copper sulphate solely to enhance froth stability (O’Connor and Dunne, 1994).

The majority of research into copper activation during flotation has concentrated on individual sulphide minerals like those in the iron sulphide group (Chang et al., 1954; O’Connor et al., 1988; Bradshaw and O’Connor, 1994), galena (Popov and Vucinic, 1990) and sphalerite (Girczys and Laskowski, 1985) and not on the possible effect of copper activation on free gold and refractory gold. Unlike other deposits around the world the ore used in this study contains free gold and substantial amounts of gold contained in refractory pyrrhotite and pyrite. In previous research (Chang et al., 1954; O’Connor et al., 1988) the sequence of copper addition in relation to xanthate conditioning has been kept constant except when investigating the flotation of pyrite using mixtures of thiol collectors (Bradshaw and O’Connor, 1994). In this case the authors found that adding copper sulphate after the collectors had a similar or slightly better (1 %) effect than adding it before the collectors. Even so, no one has shown whether adding copper sulphate after a xanthate collector will have a different effect on gold recovery compared with the usual sequence of adding it before the xanthate. In 1988, a survey of twelve South African pyrite flotation plants found that five added copper sulphate before the collector and five added it after the collector (O’Connor et al., 1988). The question remains as to why one sequence would be better than the other, and under what conditions. This is an area which this paper addresses.

Also, no work has been done to examine how different dosages of copper may affect the relative amounts of free gold and refractory gold being recovered by entrainment compared with true flotation. True flotation relates to hydrophobic particle-bubble attachment and the subsequent rise of the mineralised bubble through the pulp to the froth, while entrainment is generally used to describe hydrophilic or very fine hydrophobic material that becomes caught in the liquid films existing between the bubbles. If one could calculate or estimate how much of these gold bearing constituents were recovered in these ways, this would greatly enhance our knowledge of the role of copper activation in the flotation of refractory gold ores. This work provides new information towards these areas, and attempts to elucidate the effect of copper activation on the way free gold and refractory gold are transported from the pulp phase to the froth phase during flotation. Different amounts of copper sulphate and various air flow rates were used during batch flotation tests of the Central mill feed material from Stawell in Victoria. The sequence of addition of the copper in relation to the xanthate conditioning period was investigated and P.A.X. adsorption experiments were also carried out.
EXPERIMENTAL METHODS

Batch flotation tests were conducted on the Stawell Central ore in a 3 litre Agitair cell. The ore contained by weight 6.0% pyrrhotite, 3.5% pyrite, 0.5% arsenopyrite and 0.5% chalcopyrite. The mill feed contained 2.2 gA/uLt, while the pyrrhotite contained on average 13.5 gA/uLt and the pyrite contained on average 14gA/uLt. Carefully prepared ore samples of 1900 grams each were dry-milled individually to 80 weight % passing 106 µm and 49.5 weight % passing 38 µm. These samples were transferred directly to the flotation cell where the slurry was made up to 45 % solids by mass using deionised water. Potassium amyl xanthate (P.A.X.) was used as the collector at a dosage of 25 g/t, copper sulphate (CuSO₄) as the activator was added in amounts of 0, 100, and 300 g/t during the tests, and the frother (PPG 400) was kept constant at 60 g/t. The regulated air was introduced directly into the impeller and was maintained at rates of 0.5, 1.0, 2.0, 3.0 and 4.0 litres per minute during the different tests. By varying the aeration rates the water recovery was manipulated which in turn governed the entrainment of hydrophilic species. Consequently, it was possible to construct graphs according to the method proposed by Warren (1985). The tests were completed in three sets of five, with one set of five different air flow rates being used for each dosage of copper sulphate. The tests were performed using copper sulphate addition before and after xanthate conditioning.

In each test the pulp was agitated at a rate of 1400 r.p.m. for a period of 10 minutes so that any differences in pH and redox potential between each test would be negligible. The natural pH varied between 7.5 and 8.1 during the tests. After 10 minutes but before any addition of reagents the pulp potential stabilised to approximately zero ± 10 mV. CuSO₄ was then added to the pulp and conditioned for 5 minutes before P.A.X. was added and conditioned for a further 5 minutes. Frother was then conditioned for 1 minute before the air entered the pulp and flotation was carried out for 15 minutes. Scraping of the froth was performed every 20 seconds at a constant depth so that a bulk concentrate was recovered over the 15 minute period. When no CuSO₄ was used during conditioning, a 5 minute agitation period was still maintained so that the conditioning time was kept constant during each test. When CuSO₄ was added after the P.A.X. the conditioning time and addition sequence of the other reagents remained the same. After flotation, the concentrates and tailings were filtered and dried so that water recovery could be calculated. All samples were carefully digested and analysed for total gold content by atomic absorption spectroscopy. Samples of the concentrates and tailings were also taken for quantitative X.R.D. analysis.

The bulk concentrates from each test were sampled and prepared for cyanide leaching to determine the relative amounts of free gold and refractory gold that were recovered. Samples of 50
grams each were leached for 24 hours in 600 ml beakers with 3000 ppm NaCN. After addition of the concentrate to each leaching vessel the slurry was made up to 400 ml using deionised water and lime was added so that a stable pH of 11.0 was maintained during the leaching period. The high level of NaCN was needed because of the high gold content and the refractory nature of the concentrates generated during flotation. After leaching, the residues were filtered, dried and prepared for gold analysis by A.A.S. The gold remaining in the cyanide leach residues was determined to be the percentage of refractory gold in the flotation concentrates and the amount of gold extracted was assumed to be free gold. The recoveries of free gold and refractory gold for each test could then be calculated since the amounts in the original feed sample were already known.

The P.A.X. adsorption work was carried out on the Cary 1C U.V-Visible Spectrophotometer. Clear solutions were taken during the P.A.X. conditioning stage at times of 1, 3 and 5 minutes. Three peaks were identified at 301.34 nm, 226.56 nm and 204.96 nm. The 301.34 nm peak represents the xanthate molecule which has been verified by Rao and Finch (1991). The two other peaks which are closer together represent two types of dixanthogen which were also present in the solutions.

The ore used in this study had undergone very careful bulk sampling preparations prior to this work so that any errors due to variations in mineralogical composition and free gold distribution were minimised. As a result of this, the reproducibility of gold recovery during flotation was within an error of 4 %, while deviations in mass and water balances were less than 0.2 %. Because of the consistency maintained during the flotation tests with reference to conditioning sequences, test duration, scraping interval and depth of froth removal, it was expected that any significant change in bubble size between each test was due to the addition level of copper sulphate and/or the air flow rate.

RESULTS AND DISCUSSION

Initial flotation tests

In this section results are given for some initial flotation tests where the sequence of copper addition was investigated for Central mill feed and Central cyclone overflow material from Stawell. These initial flotation tests were completed before it was decided to investigate the effect of the sequence of copper sulphate addition on the transport characteristics of free and refractory gold. The standard flotation procedure as described in the experimental section was used to compare the
sequence of copper sulphate addition on gold and sulphide recoveries during batch flotation of the Stawell Central mill feed and Central cyclone overflow material. The results of gold and sulphide recovery determined by X.R.D. are given in Table I.

From these data it can be seen that during the flotation of both materials the overall gold recovery is much greater when copper sulphate is added after the P.A.X. compared with adding it before the P.A.X. For the Central mill feed the difference is close to 7% and for the Central cyclone overflow it is about 6%. Although free gold determination was not carried out for these initial experiments, the water recovery for each test gives an indication as to the trends the free gold recovery may have shown, if we assume that there is a proportional relationship between water recovery and free gold recovery like that suggested by Teague (1998). Table I shows that when copper is added after the P.A.X. during the flotation of both materials, the water recoveries increase slightly as does the gold recovery, but the individual sulphide recoveries decrease. This seemed to be a very unusual occurrence, but the inverse relationship noticed here between the recovery of water and the sulphide minerals is consistent with the trends outlined by Teague (1998), and also with the rest of the experimental work carried out in this investigation.

The increased recovery of gold by adding the copper after the P.A.X. was too high to be dismissed as an experimental error, and it was confirmed for two different materials. Therefore, a more detailed set of experiments was planned to investigate in detail the transport of free and refractory gold during flotation. These tests are discussed in the following sections.

**Flotation using no copper sulphate**

The figures given in the following sections were graphed according to the model developed by Warren (1985) which enabled the relative amounts of mineral floating by true flotation and entrainment to be determined, and is described by the straight line equation:

\[ R_M = F_M + e_M R_{\text{water}} \]  \[ 1 \]

where \( F_M \) is the intercept of the extrapolated line on the mineral recovery axis and designates the degree of true flotation, while \( e_M \) is the entrainment factor or slope of the line which gives the degree of entrainment of the recovered mineral \( R_M \), and \( R_{\text{water}} \) is the recovery of water.
Table II shows the X.R.D. results for the flotation test where no copper was used during conditioning and the flow rate of air was 2.0 litres per minute. The results indicate that without copper activation the recovery of pyrite and pyrrhotite is very low at about 45%. Fig. 1 shows the recovery of free gold and refractory gold versus water recovery for the same tests where no copper was added prior to conditioning with P.A.X. Here, the data for each test at the different air flow rates are used. It can be seen that the refractory gold has a true flotation value of approximately zero whereas the free gold is at about 37%, but the degree of entrainment of the refractory gold is slightly higher than that of the free gold. These results are as expected. As there is no copper sulphate addition prior to collector addition, the true flotation of the sulphide material would decrease because the iron-xanthate surface species do not impart the same level of hydrophobicity towards the iron-sulphide minerals as a copper-xanthate complex does. The solubility of the iron-xanthate species is much greater than that of copper-xanthate (Fuerstenau and Mishra, 1980) and this means that the attachment of the minerals to the air bubbles would be reduced. If less of the refractory gold bearing sulphides are recovered by true flotation, this explains why the recovery of refractory gold in this way is low. Therefore, recovery of refractory gold in the absence of copper is mainly by entrainment.

Fig. 2 shows an image of the froth taken with a video camera during the flotation test when no copper was added before the P.A.X. Compared with the images which are shown later, this froth looks much darker and more unstable and this corresponds well to the X.R.D. data that show that there is a poor sulphide recovery under these conditions. All the froth images presented in this paper were taken 1 minute from the beginning of flotation.

Free gold is naturally hydrophilic but becomes hydrophobic during the conditioning steps in flotation where it readily adsorbs any amount of organic material (Tennyson, 1980). The gold particles are shaped like plates (Dana, 1932; Monte et al., 1997) and usually have a rough surface consisting of pits and valleys (Aksoy and Yarar, 1989). The unusual shape and rough texture of the gold make it difficult for the gold to attach to the air bubbles, especially when physical barriers are present such as sulphide mineral particles that may have already loaded onto the air bubbles. Aksoy and Yarar (1989) made special reference to this effect when they demonstrated that ferric ions and humic acid could act as physical barriers between the air bubbles and gold surfaces thereby hindering flotation. It was also pointed out in this work that the greater the roughness of the gold plates, the more likely they would exhibit a decrease in hydrophobicity. In the current work, it can be suggested that if the bubbles are fully loaded with sulphide minerals, then the free gold tries to attach by its edge since its flat surface is rough and non-uniform. If the gold plates are successful in
attaching to the air bubbles, the resulting particle-bubble interface is unstable since there is only a small section of the gold surfaces attached to the bubbles. Therefore a large fraction of the free gold is recovered by entrainment instead of true flotation. In Fig. 1 the free gold shows a relatively high level of true flotation because the sulphide particle-bubble attachment is weak and consequently there is a greater availability of non-mineralised surface sites on the bubbles for the gold to adhere to.

Flotation with copper sulphate added before P.A.X.

Table III gives results for the tests where copper sulphate was added before xanthate conditioning and flotation was carried out at 2 L/min. It can be seen that the sulphide recoveries are greater at a copper dosage of 100 g/t CuSO₄ than a dosage of 300 g/t. The overall gold recovery remains largely unchanged at 69 %, but the gangue recovery increases significantly from 3.9 to 5.0 %. This could mean that the higher dosage of copper is causing more solids to be entrained. There is also a slightly higher water recovery obtained when 300 g/t CuSO₄ is used instead of 100 g/t. This is further evidence that a higher proportion of hydrophilic gangue material may be recovered by entrainment under these conditions.

Fig. 3 and Fig. 4 show the results for the flotation tests at the various air flow rates where 100 g/t or 300 g/t CuSO₄ was added prior to P.A.X. conditioning. The data in Fig. 3 show that the true flotation of the refractory gold increases to 44 % when 100 g/t CuSO₄ is added compared with zero when no copper was added. This occurs because the copper-xanthate (Cu-X) hydrophobic species provides greater insolubility and hydrophobicity towards the gold bearing sulphide minerals than the iron-xanthate species that forms in the absence of the copper, as mentioned previously (Fuerstenau and Mishra, 1980). The entrainment factor of the refractory gold decreases from 1.8 to approximately 0.6 which could be a result of the increase in true flotation of this species. Owing to a lack of data in these experimental figures, the shift in slope which represents the change in the entrainment factor has a low level of confidence. The slope of the free gold line increases slightly because there is less room on the bubbles for its attachment since there is a greater true flotation of the sulphides. The true flotation of the free gold increases from 37 to 42 %. This phenomenon can be explained by the action of the water being transported from the pulp phase to the froth. As more copper is added, the froth becomes stabilised (O’Connor et al., 1988) and hence a greater amount of water and solids are entrained, so that the flux of water upwards is higher and it is this washing action which decreases the bubble loading and leaves enough room for the free gold to attach. The effect is even more pronounced when 300 g/t CuSO₄ is added.
Fig. 4 shows the results for the tests where 300 g/t CuSO$_4$ is added prior to conditioning the slurry with P.A.X. From this graph it can be seen that the greater amount of copper addition increases the entrainment factor of the refractory gold from 0.6 to 1.4 and the true flotation decreases from 44 % to 12 %. The high addition of copper could oxidise the xanthate and thus could be the reason why sulphide flotation is depressed instead of being activated. An alternative explanation is that the high copper level causes a greater flux of water up into the froth which washes a significant amount of attached sulphide material off the bubbles so that more refractory gold is entrained and less is recovered by true flotation. The free gold behaves in the opposite way. Its entrainment factor decreases from 1.7 to 0.6 and its true flotation increases from 42 % to 56 % because of the low sulphide bubble loading.

During these tests froth images were taken using a video camera to provide further evidence that the dosage of copper added to the slurry affects the entrainment of material in the froth and the bubble loading, as shown in Fig. 5 and Fig. 6. Fig. 5 shows the froth image from the test where 100 g/t CuSO$_4$ was added prior to conditioning with P.A.X. It shows a very stable froth with evenly sized bubbles that give off a metallic iron colour which indicates that a relatively high loading of the iron-sulphide minerals has been established. Fig. 6 illustrates the type of froth generated during flotation when 300 g/t of CuSO$_4$ and 100 g/t is added during conditioning. This froth is similar to the last one except it has more of a metallic colour, and the bubble size is more uneven. This indicates that a greater proportion of free gold has attached to the bubbles since the increase in copper addition creates a greater flux of water that washed some of the sulphide material off. The difference in bubble size may be due to the physical changes occurring within the froth, that is, the entrainment of water and gangue and the removal of sulphide material by the flux of water.

**Flotation with copper sulphate added after P.A.X.**

Table IV shows the results for the test where 25 g/t P.A.X. was conditioned before 100 g/t CuSO$_4$ was added to the slurry. It can be seen that by adding the copper after the P.A.X. the sulphide recoveries decrease compared with the results for the same test of opposing sequence tabulated in Table III. However, the gangue recovery of 4.5 % obtained from using this sequence of P.A.X. and copper addition is greater than the 3.9 % obtained when adding the 100 g/t CuSO$_4$ before the P.A.X. This indicates that it is likely there is a greater extent of entrainment of solids and water occurring when this sequence is implemented.
Fig. 7 and Fig. 8 show the results from the flotation tests at various air flow rates where 100 g/t and 300 g/t CuSO₄ were added after the P.A.X. conditioning period. Fig. 7 shows that adding 100 g/t CuSO₄ after the P.A.X. gives a similar degree of entrainment of about 1.7 for the free gold as the test which used the same amount of copper but opposite addition sequence. The true flotation of the free gold remains approximately the same at 43%. The recovery of refractory gold proved to be very different with the data giving a negative slope. The true flotation of 51% is some 8% higher than its corresponding test with the same amount and opposite sequence of copper addition, but the entrainment factor is -2.4 compared with +0.8. This suggests that instead of the entrainment having a positive effect on the recovery of refractory gold, none of the refractory sulphides are being entrained, possibly due to their shape and size (Ross, 1990), and also the increase in water recovery is washing those sulphides attached to bubbles back towards the pulp. This phenomenon is possible when copper is added after the xanthate. The exchange reaction which occurs between the copper and iron-sulphide surfaces which promotes stronger sulphide hydrophobicity when xanthate is added to the slurry (Fuerstenau and Mishra, 1980) does not have a chance to proceed when the xanthate has already been added and adsorption has taken place. As a result, the sulphides display a weaker tendency to attach to bubbles and remain attached even after the copper is added. It is likely that a substantial amount of copper still complexes with the xanthate adsorbed onto the minerals so that the amount of copper in solution diminishes, but there would be less elemental exchange of Cu²⁺ and Fe²⁺ ions that typifies copper activation of iron sulphide surfaces.

By comparing Fig. 7 with Fig. 8 we can see that the entrainment factor for free gold increases from 1.7 to 2.2. Also, if one compares the results shown in Fig. 8 to the opposite addition sequence of copper and P.A.X. shown in Fig. 4, it can be observed that the entrainment factor for free gold increases from 0.6 to 2.2. The reason why this occurs when 300 g/t CuSO₄ is added after xanthate conditioning is because there is more copper available to stabilise the froth which could not adsorb onto the sulphide surfaces due to previous adsorption of P.A.X. From Fig. 7 and Fig. 8 it can be seen that because more free gold is entrained it is expected that the true flotation should decrease as it does from 43% to 23%. It could be argued that the higher addition of copper in Fig. 8 oxidises the xanthate, so that the free gold is depressed. However, a similar depression of refractory gold is not observed, unlike the case where copper is added before xanthate as in Fig. 4. The refractory gold shows the same negative slope as when 100 g/t CuSO₄ is added after the P.A.X. except that the magnitude of the negative entrainment factor decreases slightly.

An image of the froth taken during flotation under conditions of 25 g/t P.A.X. and 100 g/t CuSO₄ is shown in Fig. 9. If one compares this picture with that in Fig. 5 where the opposite addition
sequence of CuSO₄ and P.A.X. was used, it can be seen that the bubbles are much darker, smaller and very uneven in size. This indicates that some sulphide material is attached to the bubbles, but as the flotation time elapses it is more likely that the sulphide particles will be removed from the bubbles by the flux of water upwards to the froth and subsequent drainage.

The effect of air flow rate and addition sequence of copper sulphate on gold recoveries

Fig. 10 illustrates how the recovery of free gold and total gold behaves in relation to air flow rate and addition sequence of copper for the tests where 100 g/t CuSO₄ and 25 g/t P.A.X. were used. In most cases it can be seen that the recovery of free gold has a substantial effect on the total gold recovery. At low air flow rates of 0.5 litres per minute the total gold recovery, when copper is added before the collector, is much greater than the opposing sequence since about 30 % more free gold is recovered. It is not until a flow rate of 2.0 L/min is reached that the total gold recovery for copper added after the P.A.X. becomes greater than when it is added prior to P.A.X. conditioning. This is due to a greater amount of free gold being recovered which is mainly a result of the increase in entrainment caused by the copper added after the collector that does not adsorb onto the sulphide minerals. At very high flow rates of 4.0 L/min when copper is added before the P.A.X., the total gold recovery becomes greater again due to the higher true flotation of the free gold, and because of the washing effect of the water on the refractory sulphides.

The results in these experiments done at various air flow rates give an overall picture as to why the gold recovery in the initial flotation tests was greater for copper added after the P.A.X. compared with when it was added before the P.A.X. The extra 6-7 % gold recovery was a result of up to 10 % more free gold floating into the concentrates due to the greater entrainment.

Relationship between water and free gold recovery

An important aspect of the work outlined in this paper is that it proves that under certain conditions of copper dosage, addition sequence and air flow rate, between 10 and 30 % of the free gold available in the pulp could enter the concentrate by entrainment. This can be calculated by taking the difference between the total free gold recovery (at a particular water recovery) and the free gold recovery at zero water recovery. Nearly all the data gathered during this test work confirmed that the free gold recovery increased when the water recovery increased, and because it is known that higher water recovery gives a greater amount of entrained material, this observation means that significant entrainment of the free gold must be taking place.
These results agree with the work done by Teague (1998) which showed that adding oxygen and nitrogen with the xanthate during conditioning had a different effect on water and free gold recoveries. When oxygen was used the water and free gold recoveries would increase and when nitrogen was used the water and free gold recoveries would decrease slightly. In this work it was hypothesised that there may be a relationship between the water recovery and the type of xanthate species present at the mineral surface during flotation where dixanthogen would most likely form in the presence of oxygen and a metal xanthate would most likely form in the presence of nitrogen. The experimental investigations carried out in the current paper suggest that a relationship may exist between recovery of water, free gold and the type of collecting species present at the mineral surface, because it was noticed that greater amounts of copper addition increased the recovery of water and free gold.

The significance of the copper addition with respect to the above discussion is that copper is renowned to be an oxidant for xanthate (Rao and Finch, 1991; Fuerstenau and Mishra, 1980; Jones and Woodcock, 1983) and so when it is added during xanthate conditioning in increasing amounts, it will oxidise greater amounts of xanthate to dixanthogen. It has been noted in past research that dixanthogen is a more powerful collector than metal xanthates but is less selective (Fuerstenau and Mishra, 1980), and if it is formed in significant amounts it can affect the frothing characteristics of the pulp whether it is dissolved or suspended in the pulp (Jones and Woodcock, 1983). Finkelstein and Poling (1977) found that if more dixanthogen is formed the amount of fine particles entrained into the concentrate may increase. When the CuSO₄ was added after the xanthate, it was postulated that any copper that had not adsorbed onto the mineral surfaces would help to stabilise the froth and induce greater entrainment. Based on the current discussion, it may be possible that the species responsible for stabilising the froth is actually the dixanthogen which can be a by-product of copper addition, and because greater copper dosages increase the oxidation of xanthate to dixanthogen it appears that the copper is directly responsible. If this occurs and more particle entrainment takes place, then it is understandable why the recovery of water would also increase, since the entrained material usually exists in the films of water present between the air bubbles.

Even though this work has proved that a significant proportion of the free gold floats by entrainment, it must be realised that under normal flotation conditions, the free gold is hydrophobic and tries to attach to the air bubbles but is usually only successful when the bubble load is low. Hence there may be a critical bubble load at which free gold cannot attach successfully to air bubbles.
**P.A.X. adsorption**

Tests were conducted to investigate the P.A.X. adsorption during conditioning prior to copper sulphate activation. These tests were done to complement the flotation work that was outlined in the previous sections and the results are shown in Fig. 11. Overall, at the end of the five minute conditioning period there seems to be little difference between the four different aeration conditions, but to draw suitable conclusions for these tests it is more important that we focus on the adsorption occurring in the first minute. The reason for doing this can be explained. In all of the tests shown in Fig. 11 over 60 % of the xanthate adsorbs within the first minute of conditioning when the sulphide surfaces are still relatively uncovered. As conditioning continues between 1 and 5 minutes there is an increasing chance that the xanthate still remaining in solution could oxidise to dixanthogen since this has been known to happen in high sulphide ores (Jones and Woodcock, 1983). If this occurs, then it is possible that the amount of P.A.X. removed from solution after 5 minutes may not represent the actual amount of xanthate adsorbed onto the sulphide surfaces. This amount could include dixanthogen which is in solution or which has been precipitated out of solution. Hence, in these tests it is only after one minute of adsorption that the amount of P.A.X. adsorbed onto the mineral surfaces can be compared meaningfully under the different conditions.

In Fig. 11 it can be seen that after the first minute of adsorption the greatest amount is adsorbed when P.A.X. is conditioned by itself. It is about 10 % greater than when nitrogen and oxygen are added during conditioning. At the end of the 5 minute conditioning period the amount of P.A.X. adsorbed in each case is between 80 and 90 % which indicates that significant adsorption takes place even without previous copper activation. This finding has been confirmed by O’Connor et al., (1988) who came to the same conclusion when studying the adsorption characteristics of butyl xanthate onto pyrite. These adsorption results indicate that it is not the amount of P.A.X. that is adsorbed which increases the floatability of the sulphide minerals, but it is the relative insolubility of the metal-xanthate complex that induces greater hydrophobicity. Hence, activation with copper sulphate before P.A.X. conditioning may adsorb the same amount of xanthate as a slurry would without copper activation, but the greater insolubility of the Cu-X complex facilitates greater hydrophobicity for the sulphide minerals than the Fe-X complex does.

**CONCLUSIONS**

The investigations carried out in this chapter have established a number of important findings with regard to the effect of copper activation on the recovery of gold bearing minerals and the
transport characteristics of free gold, refractory gold, water and gangue. It is expected that these results may elucidate the role of copper activation during the flotation of refractory gold ores, which up to this stage have proven difficult to concentrate. The major findings are summarised below:

- Increasing the dosage of copper sulphate increases the entrainment of refractory gold when the copper is added before the P.A.X. because there is a greater flux of water upwards to the froth which provides a decrease in the amount of sulphide material that is attached to the air bubbles.

- When the true flotation of refractory gold decreases, it has a higher degree of entrainment and the true flotation of free gold increases since there is a larger proportion of non-mineralised surface sites on the bubbles where attachment can take place.

- Adding 300 g/t copper sulphate after conditioning with P.A.X. provides an even greater level of entrainment for the free gold than when the copper is added before the P.A.X. This is because not as much copper has the opportunity to adsorb onto the sulphide mineral surfaces prior to P.A.X. adsorption so that there is more copper available to stabilise the froth.

- When the copper is added after the P.A.X. the refractory gold displays a negative slope versus the recovery of water. This shows that because the copper does not have a chance to exchange ions with the iron-sulphide surfaces, the strongly hydrophobic Cu-X compounds do not form. The sulphide minerals can then be removed easily from the bubbles with increasing amounts of water so that the recovery of refractory gold decreases instead of increasing.

- At air flow rates of 2.0 L/min and above the total gold recovery becomes 6-7 % greater when copper is added after the P.A.X. compared with the standard sequence of adding the copper first. This occurs because there is a 10 % increase in the free gold recovery which is a result of the increased levels of entrainment.

- The adsorption of P.A.X. prior to copper activation indicates that a significant proportion of the xanthate still adsorbs onto the sulphide minerals without prior activation which shows that it is not the amount of xanthate which determines particle hydrophobicity, but the strength and insolubility of the collecting species.
• It is proposed that greater additions of copper sulphate may have a stabilising effect on the froth due to the formation of dixanthogen which has been known to change the frothing characteristics of high sulphide ores whether it is dissolved or suspended in the pulp.

ACKNOWLEDGEMENTS

The assistance of Stawell Gold Mines Pty Ltd for funding this research, providing ore samples and gold analysis is gratefully acknowledged. Also, Stafford McKnight at the University of Ballarat is thanked for the Siroquant X.R.D. analysis.
REFERENCES


LIST OF TABLES

I  Flotation results for initial tests

II  Mineral recovery for flotation test with zero copper

III  Mineral recoveries for flotation tests using copper activation before xanthate conditioning at 2 L/min

IV  Mineral recoveries for the flotation test using 25 g/t P.A.X. and 100 g/t CuSO₄
Table I

Flotation results for initial tests

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Pyrrhotite Recovery (%)</th>
<th>Pyrite Recovery (%)</th>
<th>Gold Recovery (%)</th>
<th>Water Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central Mill Feed</td>
<td>78.6</td>
<td>90.7</td>
<td>74.5</td>
<td>18.6</td>
</tr>
<tr>
<td>Central Mill Feed Cu/P.A.X.</td>
<td>45.2</td>
<td>69.0</td>
<td>81.3</td>
<td>19.3</td>
</tr>
<tr>
<td>Cyclone overflow</td>
<td>100.0</td>
<td>88.5</td>
<td>71.1</td>
<td>19.2</td>
</tr>
<tr>
<td>Cyclone overflow Cu/P.A.X.</td>
<td>85.8</td>
<td>56.9</td>
<td>76.8</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Table II

Mineral recovery for flotation test with zero copper

<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>Mass in concentrate (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>14.1</td>
<td>44.7</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>43.7</td>
<td>44.8</td>
</tr>
<tr>
<td>Gangue</td>
<td>42.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table III

Mineral recoveries for flotation tests using copper activation before xanthate conditioning at 2 L/min

<table>
<thead>
<tr>
<th>Test</th>
<th>Pyrite recovery (%)</th>
<th>Pyrrhotite recovery (%)</th>
<th>Gangue recovery (%)</th>
<th>Total gold recovery (%)</th>
<th>Water recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 g/t Cu</td>
<td>87.5</td>
<td>72.7</td>
<td>3.9</td>
<td>68.9</td>
<td>18.1</td>
</tr>
<tr>
<td>25 g/t P.A.X.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 g/t Cu</td>
<td>73.6</td>
<td>66.4</td>
<td>5.0</td>
<td>69.6</td>
<td>18.7</td>
</tr>
<tr>
<td>25 g/t P.A.X.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table IV

Mineral recoveries for the flotation test using 25 g/t P.A.X. and 100 g/t CuSO₄

<table>
<thead>
<tr>
<th>Mineral phase</th>
<th>Mass in concentrate (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>27.8</td>
<td>63.7</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>33.2</td>
<td>39.4</td>
</tr>
<tr>
<td>Gangue</td>
<td>4.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Fig. 1 Correlation between the recovery of free gold and refractory gold with water for zero CuSO₄ and 25 g/t P.A.X.

Fig. 2 Froth image taken at 1 minute of flotation using zero copper and 25 g/t P.A.X.

Fig. 3 Correlation between the recovery of free gold and refractory gold with water for 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 4 Correlation between the recovery of free gold and refractory gold with water for 300 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 5 Froth image taken at 1 minute of flotation using 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 6 Froth image taken at 1 minute of flotation using 300 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 7 Correlation between the recovery of free gold and refractory gold with water for 25 g/t P.A.X. and 100 g/t CuSO₄.

Fig. 8 Correlation between the recovery of free gold and refractory gold with water for 25 g/t P.A.X. and 300 g/t CuSO₄.

Fig. 9 Froth image taken at 1 minute of flotation using 25 g/t P.A.X. and 100 g/t CuSO₄.

Fig. 10 Free gold and total gold recovery versus air flow rate using different sequences of 100 g/t CuSO₄ and 25 g/t P.A.X.

Fig. 11 P.A.X. adsorption before copper activation for different conditions.
Fig. 1  Correlation between the recovery of free gold and refractory gold with water for zero CuSO₄ and 25 g/t P.A.X.
Fig. 2 Froth image taken at 1 minute of flotation using zero copper and 25 g/t P.A.X.
Fig. 3  Correlation between the recovery of free gold and refractory gold with water for 100 g/t CuSO₄ and 25 g/t P.A.X.
Fig. 4 Correlation between the recovery of free gold and refractory gold with water for 300 g/t CuSO₄ and 25 g/t P.A.X.
Fig. 5  Froth image taken at 1 minute of flotation using 100 g/t CuSO$_4$ and 25 g/t P.A.X.
Fig. 6 Froth image taken at 1 minute of flotation using 300 g/t CuSO$_4$ and 25 g/t P.A.X.
Fig. 7 Correlation between the recovery of free gold and refractory gold with water for 25 g/t P.A.X. and 100 g/t CuSO₄.
Fig. 8 Correlation between the recovery of free gold and refractory gold with water for 25 g/t P.A.X. and 300 g/t CuSO₄.
Fig. 9  Froth image taken at 1 minute of flotation using 25 g/t P.A.X. and 100 g/t CuSO₄.
Fig. 10 Free gold and total gold recovery versus air flow rate using different sequences of 100 g/t CuSO₄ and 25 g/t P.A.X.
Fig. 11 P.A.X. adsorption before copper activation for different conditions.
Chapter 11

DEPENDENCE OF FROTH BEHAVIOUR ON GALVANIC INTERACTIONS

J.S.J. VAN DEVENTER

11.1 INTRODUCTION

The occurrence of galvanic interactions between different minerals, and between minerals and grinding media during froth flotation is well known, as mentioned in some introductory textbooks on the subject [1]. In an interesting review of the chemical effect of the type of grinding medium on the flotation of sulphides, Martin et al. [2] stated that this phenomenon is "now reasonably well understood" and even accepted in economic evaluations. They concluded that, in general, stainless steel or autogenous grinding vis-à-vis mild steel grinding leads to improved flotation of unactivated sphalerite, galena, pyrrhotite, chalcopyrite and pentlandite. However, contradictory results have been
obtained on the effect of media type on pyrite flotation. Moreover, the
effect of the type of grinding medium on the flotation of other minerals
becomes less pronounced when ores contain a large proportion of
pyrite [2]. In addition, Van Deventer et al. [3,4] showed that in the
case of a complex sulphide ore galvanic interaction caused by the
presence of metallic iron in a ceramic mill yielded a stable, well-
drained froth and high sulphur grades, while the absence of metallic
iron produced an extremely brittle froth with high recovery of iron
minerals and low sulphur grades.

These contradictory results imply that the interaction between
flotation variables remains largely unclear despite the fact that froth
flotation has been used for many decades to beneficiate complex
sulphide ores. It is hence the aim of this chapter to review the literature
on the effect of galvanic interactions on flotation behaviour, and to
reconcile the opposing views in the literature regarding inhibition
or enhancement of flotation performance. The main focus of this
chapter will be an experimental study of the flotation of a complex
ore containing mainly chalcopyrite, galena, sphalerite, magnetite,
pyrrhotite and pyrite under different milling conditions [3–5]. An
analysis of froth characteristics will show that incorrect conclusions
could be drawn by considering only the pulp phase phenomena, as is
usually the case in the literature.

As demonstrated in an earlier study [6], the electrochemical
behaviour of minerals in a pulp could differ significantly from that in
a solution, even at the same pH and concentrations of active species,
mainly because of the interaction between minerals. Similarly, the
flotation behaviour of pure or single minerals could differ substantially
from that in real ores. This could partially be the reason for the contra-
dictory observations on galvanic interaction mentioned above. Never-
theless, numerous fundamental studies have been undertaken on the
flotation of pure minerals [2,7–10] in order to gain an understanding
of the various mechanisms involved in the flotation of lead, zinc and
copper sulphides, while real ores have received much less attention
[2–6,11,12]. As explained by Wills [1], flotation results for mixtures
of sulphides are not necessarily applicable to real ores, as cations
produced by sulphide oxidation may react in different ways in a given
system. Apart from modifying the surfaces of some minerals by surface
interactions, these cations may precipitate as hydroxides which may
have a profound effect on sulphide floatability. As will be indicated
below, galvanic interactions could affect this phenomenon. Of special
interest in the present study is the depressing effect of the sulphite ion
on the flotation of galena [6]. The level of dissolved oxygen and the
redox potential appear to have a major effect on the differential flotation of chalcopyrite and galena from complex ores [5,6,12,13]. In the next sections the interrelationship between redox potential, galvanic interaction, the formation of surface layers and hence hydrophobicity will be discussed with reference to the pulp phase.

11.2 MINERAL–MINERAL INTERACTIONS

Most studies on galvanic interactions during flotation deal with interactions between grinding media and minerals, with less attention paid to interactions between individual minerals. Subrahmanyam and Forssberg [14] speculated that the higher degree of liberation in the overflow of a hydrocyclone compared with the underflow will result in less galvanic interaction and hence higher pulp potentials. Nakazawa and Iwasaki [15] investigated the interaction between pyrite and pyrrhotite, as these minerals occur together in many important ores. The rest potential and galvanic current were measured for a combination electrode of pyrite and pyrrhotite under aeration conditions of nitrogen, air and oxygen, and these results were correlated with the oxygen consuming characteristics and flotation behaviour of these minerals. The galvanic contact improved the floatability of pyrrhotite, but adversely affected that of pyrite. Auger electron spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) indicated that the formation of hydroxide or oxide and sulphate species of iron on pyrrhotite decreased, whereas that on pyrite increased when these minerals were held in contact. Since pyrrhotite is nobler than nickel arsenide, pyrrhotite would act as a cathode and nickel arsenide as an anode upon contact. Nakazawa and Iwasaki [16] observed that the magnitude of the galvanic current was largest in oxygenated solutions and smallest in deoxygenated solutions, while the galvanic contact accelerated the consumption of oxygen as well as the oxidation of nickel arsenide. When nickel arsenide was contacted with pyrrhotite, nickel arsenide as a whole acted as an anode and hydrogen generated by the anodic dissolution prevented nickel ion from precipitating as nickel hydroxide. Surface analysis with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) showed that galvanic contact inhibited the formation of nickel hydroxide coatings, which were found to decrease the floatability of nickel arsenide. In contrast, galvanic contact caused pyrrhotite as a whole to act as a cathode, so that the generation of hydroxyl ions was accelerated which led to an
increased formation of iron hydroxide layers, and hence a decrease in floatability [15].

Electron spectroscopy for chemical analysis (ESCA) was used by Yelloji Rao and Natarajan [17] to identify reaction products on sulphide minerals after different types of mineral–mineral interactions, involving chalcopyrite, galena and sphalerite. In general, galvanic interaction between a “noble” mineral such as chalcopyrite and “active” minerals such as sphalerite or galena affects the floatability of the noble mineral significantly, while the effect on the active mineral is minimal. However, prolonged interaction of sphalerite with chalcopyrite could lead to sphalerite activation by dissolved copper from the mineral slurry and hence could be beneficial in the flotation of sphalerite. The deleterious effect of ageing of single sulphides such as sphalerite in the presence of oxygen could be minimised if they are present in galvanic combinations. These conclusions are fundamentally sound despite criticism by Ahn and Gebhardt [18] that Yelloji Rao and Natarajan [17,19,20] used 0.5 M of NaCl as electrolyte which is not relevant to conditions in flotation plants.

Rao and Finch [21] observed that the combination potentials of pyrite–galena and pyrite–sphalerite couples were lower than the rest potential of the pyrite on its own. The adsorption of xanthate on pyrite was also lower in pyrite–sphalerite mixtures compared with pyrite on its own. Galena was preferentially floated with air from galena–pyrite mixtures, but with nitrogen pyrite was preferentially floated [21].

In a study of binary mixtures of chalcocite, chalcopyrite and pyrite, Tolley et al. [22] observed that the floatability of fresh chalcocite and pyrite changed little when mixed, as compared to the floatability of the single minerals. Similarly, the mixture of freshly crushed chalcocite and chalcopyrite floated much like the single minerals. However, the mixture of freshly crushed chalcopyrite with pyrite behaved differently. Pyrite was activated, probably by copper ions derived from the chalcopyrite, while the chalcopyrite was oxidised and depressed in the fresh mixture. This was believed to be due to galvanic oxidation of chalcopyrite by pyrite. The net result was a poor separation, as is often observed in plant practice. Tolley et al. [22] observed significant changes for oxidised mixtures, with floatability being completely depressed in oxidised mixtures containing chalcocite. In contrast, the chalcopyrite–pyrite mixture floated much like the fresh mixture. Pyrite floatability was activated and chalcopyrite floatability was depressed as compared to the floatability of the fresh, single minerals. The net result was again poor separation of chalcopyrite from pyrite.
11.3 GRINDING MEDIUM–MINERAL INTERACTIONS

The majority of flotation experiments mentioned above were conducted in Hallimond tubes, so that mainly pulp phase phenomena were observed with unfortunately no attempt made to investigate froth processes. Similarly, the papers reviewed below will show that no attention has been paid to the effect of floatability on froth stability during galvanic interaction.

Rao et al. [23] measured the mixed potentials developed by different mineral electrodes in xanthate solutions both with and without direct contact with a metallic iron electrode. They noted that without a galvanic contact between the sulphide and the iron, the values of mixed potentials were in the vicinity of the xanthate/dixanthogen redox potential. However, when contact with iron was established, the mixed potentials shifted towards a more negative value. This decrease in potential rendered the minerals too reducing for a xanthate collector to be oxidised to dixanthogen. The flotation response of pyrrhotite in a Hallimond tube was shown by Adam et al. [24] to be strongly dependent on the metal with which the pyrrhotite particles were contacted prior to conditioning with a xanthate; the more active the metal, the greater the adverse effect on the floatability of pyrrhotite. When the contact was broken the potential of pyrrhotite remained in the active region indicating the formation of some coating on the pyrrhotite surface. Since pyrrhotite acted as a cathode on which oxygen was reduced to hydroxyl ions, the mild steel or active metal which constitutes the grinding medium acted as the anode. Ferrous ions released by the pyrrhotite reacted with hydroxyl ions and formed a stable layer of iron hydroxide. It was possible that some sulphide ion was oxidised to sulphate at the surface of the iron hydroxide coating to form an iron basic sulphate.

Similarly, the X-ray photoelectron spectroscopic analysis by Yelloji Rao and Natarajan [19] showed that the decrease in the floatability of sphalerite owing to galvanic interactions with steel grinding balls could be ascribed to the formation of iron oxy–hydroxide species caused by the anodic dissolution of the steel. The severity of such a galvanic effect depended upon the duration of contact as well as the presence or absence of oxygen and flotation reagents during the contact. However, the presence of sufficient copper sulphate as the activator minimised the decrease in floatability. It was significant that the presence of any amount of xanthate on its own or in combination with copper sulphate did not minimise the deleterious effect of galvanic interaction. No attempt was made to explain the change in
flotation behaviour during galvanic contact in terms of the electrochemistry of xanthate/dixanthogen adsorption.

Ahn and Gebhardt [18] observed that stainless steel was more easily passivated than high-carbon steel, and the collectorless floatability of chalcopyrite was significantly higher after grinding with stainless-steel. Increased floatability of chalcopyrite was observed with more positive pulp potentials. As expected, flotation with air yielded higher recovery of chalcopyrite than when nitrogen was used. In view of the fact that this investigation was conducted in the absence of xanthate, the conclusions from this study cannot be generalised. Nevertheless, Tolley et al. [22] postulated that the oxidation of chalcopyrite probably caused the formation of a hydrophilic layer of copper and iron hydroxides and oxysulphides, which adsorb significant amounts of xanthate compared with fresh chalcopyrite, but nevertheless impede flotation. Göktepe and Williams [25] observed enhanced selectivity between chalcopyrite and pyrite in a more oxidising atmosphere.

Learmont and Iwasaki [26] attributed the formation of oxidation products of iron on galena surfaces to the use of mild steel. Guy and Trahar [27] observed that for galena ground in non-reducing conditions, xanthate induced flotation was rapid over a wide range of pulp potentials. For galena ground in reducing conditions the range in which flotation is rapid is much narrower. In the absence of xanthate, flotation occurred only in a narrow range of potentials. Again, this implies that no general conclusions can be drawn from flotation studies without collector and in which the main focus is the iron oxyhydroxide formed by the anodic dissolution of the grinding medium. In addition to any effect on the surface properties of the ground mineral, the corrosive wear of the grinding media is also affected by galvanic interactions between the minerals and the grinding media in a mill [26].

As mentioned before, Martin et al. [2] summarised a wide range of studies on the effect of grinding media on sulphide mineral flotation. Whereas contact with mild steel generally leads to inhibited floatability of sphalerite, galena, pyrrhotite, chalcopyrite and pentlandite, ambivalent observations have been made on pyrite. It is generally believed that pyrite floats faster at higher pulp potentials due to the oxidation products of the disulphide ion which promote the formation of dixanthogen on the mineral surface [8,29]. However, Rao et al. [23] suggested that the hydrophobicity of pyrite could also be due to the formation of elemental sulphur on the pyrite surface, resulting from galvanic contact between pyrite and abraded iron, although
Tolley et al. [22] considered this to be a less likely alternative. Furthermore, the effect of the type of grinding medium on the flotation of other minerals becomes less pronounced when ores contain a large proportion of pyrite [2]. Petruk and Hughson [30] observed that mild steel yielded superior flotation of galena compared with stainless steel or autogeneous media. This contradictory result was attributed to the high pyrite content of the ore, which resulted in reducing conditions similar to those which would result from the use of mild steel media [30]. The ore used in the experimental case study in the last part of this chapter contains significant fractions of magnetite, pyrite and pyrrhotite, so that a possible explanation will be offered for these contradictory results in the literature. As stated above, the explanations in the literature have all been based on pulp phase phenomena with no attempt to investigate processes in the froth phase.

11.4 IMPORTANCE OF REST AND PULP POTENTIALS

It is evident from the above two sections that galvanic interactions could change the potential at the surface of minerals and hence affect the nature of adsorbed species and therefore the hydrophobicity and floatability of a mineral. Many of the studies cited above have explained the change in floatability on the basis of iron oxyhydroxide formation due to anodic dissolution of the grinding medium, especially in the case of collectorless flotation. The electrochemistry of xanthate oxidation has been considered only in a few cases, and will be explained below as it could be important in the experimental case study given later. Significant evidence in the literature [2,7,13,31] indicates that sulphide minerals develop hydrophobicity in the presence of xanthate (X⁻) from an anodic process coupled to a cathodic process.

The anodic process is usually charge transfer chemisorption of xanthate:

\[ X^- \rightarrow X_{ads} + e^- \]

and/or oxidation of xanthate (X⁻) to dixanthogen (X₂):

\[ 2X^- \rightarrow X_2 + 2e^- \]

and/or formation of a metal xanthate (MX₂):

\[ MS + 2X^- \rightarrow MX_2 + S + 2e^- \]

The sulphur component of the mineral surface can also be oxidised to form \( S_xO_y \) species as metal xanthates.
Generally the *cathodic process* involves the reduction of oxygen:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

As explained by Martin *et al.* [2], the general effect of galvanic interaction is the enhanced formation of a stable coating of metal hydroxides which inhibits flotation. However, an equally important effect of galvanic interaction between mild steel grinding medium and a mineral surface could be the significant lowering in rest potential of the mineral surface, which will inhibit the formation of dixanthogen [23]. Oxidation of xanthate to its dimer occurs only on those minerals that display a rest potential above the corresponding reversible potential for dimer formation [7,8]. Metal-collector compounds are formed instead for those minerals that give a rest potential below this value. Studies of contact angles have shown that, when dixanthogen is the dominant species formed on a mineral surface, a strongly hydrophobic surface results [8]. The formation of dixanthogen on galena surfaces in copper–lead separation would be seriously detrimental to the depression of galena because of the irreversibility of the xanthate adsorption reaction when the dimer is formed [6].

Ross and Van Deventer [6] measured the rest potentials of chalcopyrite and galena electrodes in a $1.92 \times 10^{-4}$ M solution of sodium ethyl xanthate as well as in an aerated pulp containing 33 mass % of Black Mountain sulphide ore with an initial xanthate concentration of $1.39 \times 10^{-4}$ M, using sulphurous acid, sulphuric acid and hydrochloric acid as pH modifiers. A possible decrease in the concentration of the collector as a result of adsorption or reaction with the other species was taken into account in the calculation of the $\text{X}^-/\text{X}_2$ redox potential using the Nernst equation and the residual xanthate concentration in the pulp after 10 minutes.

Figures 11.1 and 11.2 show that the rest potentials of chalcopyrite and galena in aerated pulp were higher than the maximum $\text{X}^-/\text{X}_2$ redox potential at the pH values investigated. This indicates that dixanthogen was probably formed on both minerals in the pulp. It is possible, however, that rest potentials may differ depending on the origin of the mineral. For this reason, although measurements of rest potentials may yield valuable information regarding the processes on the mineral surfaces, no absolute conclusions can be drawn from these data. The rest potentials in the xanthate solutions suggested that dixanthogen was probably formed on chalcopyrite surfaces at pH values less than 7. However, lead xanthate was probably formed on galena because the rest potentials were lower than the calculated minimum reduction potential. Evidently the different pH modifiers
Figure 11.1. Effect of pH regulators on the rest potential of chalcopyrite (Ross [5]) Xanthate/dixanthogen redox potentials: solution……., pulp ———.

GALVANIC INTERACTIONS
Figure 11.2. Effect of pH regulators on the rest potential of galena (Ross [5]) Xanthate/dixanthogen redox potentials: solution.......pulp .........
GALVANIC INTERACTIONS

gave widely different rest potentials, so that the conditions determining the rest potential and hence the surface composition are highly complex. Most other authors have measured rest potentials in clear solution, so that our knowledge is insufficient to explain the higher rest potentials in pulps. This means that the conclusions drawn from the literature cannot always be extrapolated to industrial flotation pulps. Furthermore, the pulp potential (Eh) and rest potential can differ by a constant amount, depending on the mineral [6]. Ralston [13] concluded that the pulp potential is a controversial but useful parameter, and could be related to the nature of the surface species.

Rao et al. [23] observed that most sulphides had mixed potentials at or above the xanthate/dixanthogen redox potentials at various concentrations of potassium ethyl xanthate, while the mixed potentials of the same minerals in contact with metallic iron were substantially below the xanthate/dixanthogen redox potential. As indicated in the previous paragraph, it is not a simple problem to predict whether the metal xanthate or dixanthogen will form on the mineral surface under specific conditions. However, on the basis of the aforementioned discussion there is a high probability that the metal xanthate with a lower hydrophobicity (than dixanthogen) will form on sulphide minerals when they are in galvanic contact with mild steel. In contrast, if these minerals are on their own such as when they are milled in a ceramic mill, there is a good chance that dixanthogen will form on their surfaces. This will cause low selectivity between the minerals and even an overloading of the froth by hydrophobic particles.

The experimental case study described below will indicate that the high percentage of magnetite in the ore has a significant effect on the recovery of chalcopyrite and galena by flotation. Unfortunately, the behaviour of magnetite in xanthate systems has hardly received any attention in the literature. Nevertheless, magnetite in grinding mill water revealed a rest potential of about 130 mV (SHE) [28,32], which is close to the xanthate/dixanthogen redox potential given by Rao et al. [23]. As explained above it is impossible to draw accurate conclusions on the basis of rest potentials in solutions alone. With the close proximity of magnetite and sulphide particles in a slurry it is not clear to what extent the magnetite could have affected the xanthate/dixanthogen redox potential.

Complex sulphide ores usually contain pyrite and other iron minerals such as magnetite, the effect of which has not been considered in any study on galvanic interactions. Therefore, despite all the meticulous research on the chemical effects of grinding media on individual minerals, the effect of galvanic interaction on the flotation
of real ores is still not understood adequately. Many studies have been conducted on isolated minerals, or in solutions only, and these artificial conditions bear little relevance to the complex interactions in the froth flotation of real ores.

11.5 EFFECT OF PARTICLES ON FROTH STABILITY

In all the publications surveyed above, only factors affecting the floatability of minerals in the *pulp phase* have been considered, and no mention has been made of phenomena in the *froth phase*. Moreover, overall flotation results are usually given without any analysis of the solids/water ratio or the behaviour of the froth. As explained by Ross [11], transport phenomena in the froth phase are complex and depend *inter alia* on the floatability of the flotation species.

As summarised by Harris [10], researchers have long been aware that the stability of froths is affected significantly by the presence of solids. Dippenaar [33,34] and Harris [10] observed that very hydrophobic particles of all sizes can destroy froths and that, unless the frother adsorbs onto the particles, the destabilising effect is independent of the frother used. Furthermore, one particle can rupture many films, so that only a few particles of a sufficiently high hydrophobicity are required to reduce dramatically the froth stability. For example, Dippenaar [33,34] found that if small amounts of galena particles (<37μm) treated with butyl xanthate were added to a solution of frother, then the froth stability could be completely destroyed. Similarly, quartz particles (<37μm) pretreated with dichlorodimethylsilane completely destroyed the froth. However, if the galena particles were treated with ethyl xanthate then no effect was observed on the froth stability even at very high solid additions. Johansson and Pugh [35] showed that particles of high hydrophobicity can rupture films and suppress froth stability, while particles of lower hydrophobicity remain dispersed in the lamellae and appear to have little effect on froth stability.

Stabilisation of a froth film requires more than one particle, and Dippenaar [33,34] showed that stabilisation of a film with particles of low hydrophobicity occurs only when a closely-packed monolayer of particles is formed in the froth films. In this case the particles which are attached to both interfaces cannot be forced out of the film and the two interfaces are physically kept apart. Similarly, if the particles are highly flocculated they will prevent the coalescence of the bubbles in the froth [10].
Therefore, the type, condition and size of the particles in a flotation system can have a dramatic effect on the stability of the froth and, in some systems, changes to the froth stability may be brought about more easily by modifying the nature (such as hydrophobicity) of the particles than by changing the type of frother used [10]. Consequently, galvanic interactions that enhance floatability may not necessarily enhance flotation recovery owing to a destabilisation of the froth. This phenomenon has not been studied before in relation to galvanic interactions, and is the subject of the experimental case study [4,5] presented below. Here, a Black Mountain complex sulphide ore containing chalcopyrite, galena, sphalerite, pyrrhotite, pyrite and magnetite is floated with the purpose to selectively recover the chalcopyrite. The effect of galvanic interactions between grinding media and ore particles is simulated by adding metallic iron powder to a ceramic mill in some tests. It will be shown that the high magnetite content of the ore results in a serious destabilisation of the froth in the absence of iron powder.

11.6 CASE STUDY: EXPERIMENTAL TECHNIQUES

Copper, lead and zinc sulphides are recovered by sequential flotation at the Black Mountain mine, which is located in the Northern Cape Province of South Africa. It was decided to emulate plant conditions in the copper circuit for most of the runs in this experimental case study. However, for experimental purposes some conditions and reagent additions differed from those on the plant [3-5]. Rod mill feed obtained from the Black Mountain concentrator was stored in air-tight containers and used as experimental material.

XRF analyses showed that the ore contained 6.3 wt% Pb as galena (7.3 wt%), 2.4 wt% Zn as sphalerite (3.6 wt%) and 0.32 wt% Cu as chalcopyrite (0.93 wt%). Quantitative XRD and image analysis showed that the ore contained 42 wt% magnetite, 9.1 wt% pyrrhotite, 3.9 wt% pyrite, 28.5 wt% quartz, and 4.7 wt% other non-sulphide gangue minerals such as rutile, muscovite, biotite, chlorite and pyroxene. With the total sulphur (S) content being 7.9 wt% and the total iron (Fe) content being 38.3 wt%, the total iron sulphide composition was taken as 13.0 wt% FeS$_{1.24}$. The concentrate samples and the tailings were analysed for Cu, Pb, Zn, Fe and S using XRF spectroscopy. After calculating the stoichiometric amount of sulphur associated with the base metal sulphides, the amount of sulphur associated with the iron sulphides
was calculated from the total sulphur in the concentrate. It was impossible to distinguish between pyrite and pyrrhotite, so that for estimation purposes it was assumed that FeS$_{1.24}$ was recovered. The error introduced by this assumption was negligible as only about 3 wt% of the total iron in the concentrate was associated with the iron sulphides. The non-sulphidic gangue minerals including quartz but excluding magnetite contained less than 1 wt% of the iron, so that the iron associated with magnetite was taken as the difference between the total iron in the concentrate and the iron associated with the FeS$_{1.24}$ and chalcopyrite. “Gangue” is defined here as mainly quartz, but also includes rutile, muscovite, biotite, chlorite and pyroxene. The recovery of “gangue” was calculated from the recovery of total solids by subtracting the recoveries of base metal sulphides, iron sulphides and magnetite. These calculations show that the recovery of FeS$_{1.24}$ was less than 2.5%, so that only the recoveries of magnetite and “gangue” will be considered in the next section as being indicative of the behaviour of non-valuable minerals.

In order to emulate plant conditions, the ore was ground to 70%-75 μm immediately before being floated. An atmosphere of nitrogen or oxygen in a ceramic mill was used, so that the oxidation of the ore and galvanic interaction with the grinding medium could be controlled. The mill load consisted of 1.00 kg of ore, ceramic balls, 500 ml of deoxygenated tap water and different amounts of powdered metallic iron with 70%-212 μm. After milling, the ore was transferred to the 3-litre Wemco flotation cell (with induced aeration), and deoxygenated tap water was added at 22°C to bring the pulp density to 35 wt% solids. Ore that had been milled in the absence of metallic iron was pre-aerated in the flotation cell for a period of 12 min at an air flowrate of 2.51/min. In these cases, the dissolved oxygen concentration of the pulp remained constant at 8.5 ppm throughout the 8 min of flotation. When the ore was milled in the presence of the iron powder, it was conditioned and floated directly after milling so as to avoid excessive oxidation of the iron. The level of dissolved oxygen varied between 0.3 ppm and 2 ppm initially at iron additions of 10 and 2 kg/t ore respectively, but increased gradually during flotation to 8.5 ppm. An oxygen electrode was used to measure the level of dissolved oxygen in the pulp.

In order to emulate plant practice, sulphurous acid (H$_2$SO$_3$) was used as a pH regulator. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0.2 in extreme cases. In some experiments sodium sulphite (Na$_2$SO$_3$) was added as a modulator and the pulp was then
conditioned for 3 min. The pulp was subsequently conditioned with sodium ethyl xanthate (NaEtX) and/or Dow Z-200 (isopropyl ethyl-thionocarbamate) as collector for another minute, which was followed by the addition of tri-ethoxybutane (TEB) as frother, and conditioning of the pulp for a further minute. Table 11.1 summarises the experimental conditions governing the eleven runs discussed in this chapter.

Table 11.1. Experimental milling and flotation conditions.

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Milling Gas</th>
<th>Pre-Aeration Iron (kg/t)</th>
<th>Milling Time (min)</th>
<th>Aeration (with air) (l/min)</th>
<th>Reagents</th>
<th>pH*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>3.0</td>
<td>TEB 10</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>9.8</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>TEB 10</td>
</tr>
<tr>
<td>3</td>
<td>N₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
<td>TEB 80</td>
</tr>
<tr>
<td>4</td>
<td>N₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
<td>NaEtX 20</td>
</tr>
<tr>
<td>5</td>
<td>O₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
<td>NaEtX 20</td>
</tr>
<tr>
<td>6</td>
<td>O₂</td>
<td>6.0</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>NaEtX 20</td>
</tr>
<tr>
<td>7</td>
<td>N₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
<td>NaEtX 20</td>
</tr>
<tr>
<td>8</td>
<td>N₂</td>
<td>6.0</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>Na₂SO₃ 50</td>
</tr>
<tr>
<td>9</td>
<td>N₂</td>
<td>–</td>
<td>12</td>
<td>2.5</td>
<td>2.5</td>
<td>NaEtX 20</td>
</tr>
<tr>
<td>10</td>
<td>N₂</td>
<td>6.0</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>Na₂SO₃ 90</td>
</tr>
<tr>
<td>11</td>
<td>N₂</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>Z-200 20</td>
</tr>
</tbody>
</table>

*Sulphurous acid was used as pH regulator.
lip in an uncontrolled fashion. When iron was added before milling, an aeration rate of up to 10 l/min. could be used without producing an uncontrolled froth, although only low aeration rates are shown in Table 11.1. The initial froth height in the flotation cell was 4 cm, and this increased during a run as the pulp became depleted. The conditioned pulp was floated for 8 min, and the concentrate was collected by manual scraping at intervals of one minute. The froth surfaces were photographed and the bubble size distributions in the froth were estimated by measuring the bubble sizes visually from the enlarged photographic image at the intersections of an evenly spaced 20 × 20 grid.

11.7 CASE STUDY: DISCUSSION OF FLOTATION RESULTS

Table 11.1 gives the index numbers of experiments which are being referenced in Figures 11.3–11.15. In experiments 2, 6, 8, 10 and 11 different amounts of metallic iron powder were added to the ore before milling. The solid lines on Figures 11.6–11.15 merely indicate an approximate trend in the experimental data in terms of the effect of iron addition. It should be noted that different experimental conditions were used for each data point, so that a one-dimensional interpretation of results in terms of iron addition is an over simplification of reality. For example, experiment 6 is the only one in which both sodium ethyl xanthate and iron were used.

This case study showed that different milling conditions could cause significant differences in the behaviour of the froth phase. When no metallic iron was added before milling, the froth was very brittle and bubbles collapsed almost as soon as they were formed, as illustrated in Figure 11.3. Initially, the froth was very mobile and had a dark colour due to the high recovery of magnetite, but it later changed to a greyish, foamy texture as most of the magnetite had been removed. When iron was added to the ceramic mill, or when the ore was milled in a steel mill, the froth had plenty of “body” and revealed a dark-green colour due to the high recovery of chalcopyrite, as illustrated in Figure 11.4. The bubble size distributions at the surface of the froth phase in Figure 11.5 show that, when iron was added before milling, the bubbles were significantly larger than when no iron was added. With increasing bubble size the laminar thickness of a bubble often increases, which could explain why Figure 11.6 reveals higher recoveries of water in those experiments where iron was added and larger bubble sizes were observed.
Figure 11.3. Photograph of froth surface in experiment 9 with no addition of iron.

Figure 11.4. Photograph of froth surface in experiment 11 with the addition of 2 kg of iron per tonne of ore.
Figure 11.5. Cumulative number distribution of bubble sizes in flotation experiments 5 (no Fe) and 6 (Fe added). The mean bubble size on a number basis for no iron added=1.6 mm, and that for iron added=5.3 mm.

Figure 11.6. Recovery of water in the froth for different amounts of iron added during milling.
Figure 11.7. Ratio of solids to water recovery in the froth for different amounts of iron added during milling.

Figure 11.8. Calculated recovery of non-sulphidic “gangue” excluding magnetite for different amounts of iron added during milling.
Figure 11.9. Calculated recovery of magnetite in the concentrate for different amounts of iron added during milling.

Figure 11.10. Grade of iron in the flotation concentrate for different amounts of iron added during milling.
Figure 11.11. Recovery of chalcopyrite by flotation for different amounts of iron added during milling.

Figure 11.12. Recovery of galena by flotation for different amounts of iron added during milling.
Figure 11.13. Selectivity of chalcopyrite/galena recovery by flotation for different amounts of iron added during milling.

Figure 11.14. Total recovery of sulphides by flotation for different amounts of iron added during milling.
Figure 11.15. Grade of sulphur in the flotation concentrate for different amounts of iron added during milling.

Figure 11.7 reveals very high ratios of cumulative solids/cumulative water recovered in the concentrate when no metallic iron was present during milling. This indicates either poor drainage of gangue particles from the froth back to the pulp phase, or an activation of some unwanted minerals in the absence of metallic iron. In general, the recovery of non-sulphidic “gangue”, including quartz but excluding magnetite, was reasonably low (<8%), as shown in Figure 11.8. In fact, the recovery of “gangue” increased slightly with increased addition of iron. When no iron was added an unstable froth structure was obtained in which entrainment of hydrophilic gangue was inhibited. In contrast, Figure 11.9 shows that the recovery of magnetite decreased significantly as the iron addition was increased. Similarly, Figure 11.10 indicates that the grade of iron (Fe) in the concentrate was significantly higher in the absence of iron (despite the additional contribution of metallic iron) than when galvanic interactions were prevalent when metallic iron was added to the mill.

The recovery of magnetite (Figure 11.9) and the grade of iron (Figure 11.10) for experiments without iron addition were not significantly different when xanthate was added (experiments 4, 5, 7 and 9) compared with the absence of xanthate (experiments 1 and 3). This indicates that galvanic interaction between magnetite and iron is likely...
to cause the formation of iron oxyhydroxides rather than a change in the formation of dixanthogen as in the case of sulphides. It appeared as if the iron minerals and especially magnetite were activated in the absence of iron in a ceramic mill, but the nature of this activation is still unknown. Conversely, if iron is added to the mill, most mineral surfaces shift to more cathodic values as a result of galvanic interaction. This usually inhibits the formation of dixanthogen on sulphide surfaces and enhances the formation of iron oxyhydroxides, which results in decreased hydrophobicity and floatability. In the literature this phenomenon is usually proposed to explain why galvanic interaction is detrimental to flotation recovery, as demonstrated by the behaviour of the magnetite in this case. However, Figures 11.3 and 11.4 illustrate that the enhanced magnetite recovery in the absence of iron destabilises the froth structure. As explained above, an overload of hydrophobic particles could rupture films and cause watery and brittle froths, which are expected to yield low recoveries of valuable sulphide minerals. The difference in solid/liquid ratios between the experiments with and without iron addition indicates that galvanic contact between metallic iron and the various minerals affected not only the hydrophobicity of minerals, but also the mass transport phenomena in the froth phase. This ambivalent effect of galvanic interaction could be the reason why Martin et al. [2] reported contradictory results on the effect of grinding media on the flotation of pyrite.

Figures 11.11 to 11.15 depict this anomalous behaviour where galvanic interaction enhances the selective recovery of valuable sulphides due to improved froth stability. Significant recoveries of chalcopyrite were obtained only during those flotation tests where metallic iron was present during milling, with the final copper recoveries for experiments 1, 3, 4, 5, 7 and 9 (no iron addition) being less than 2.5% (Figure 11.11). The recoveries of galena illustrated in Figure 11.12 were also higher when iron was added before milling, although this effect was less prominent than in the case of chalcopyrite. It is noteworthy that a high recovery of lead was obtained only in experiment 6 where iron was added during milling and xanthate was used. It is important to note that acceptable copper-lead selectivity could only be obtained when iron was added before milling, as depicted in Figure 11.13. Although not shown here, the grades of copper were also substantially higher when iron was added before milling. The rest potentials in Figures 11.1 and 11.2 suggested that dixanthogen could be formed on both chalcopyrite and galena surfaces in the pulp after the ore had been milled in the absence of iron, which probably accounted for the poor copper-lead selectivity attained under these conditions.
However, no dixanthogen could be formed on either chalcopyrite or galena when these minerals were in galvanic contact with iron [5], which yielded an enhanced copper-lead selectivity.

Except in the case of experiment 6, Figure 11.14 reveals that the recovery of total sulphur was not actually dependent on the addition of iron before milling. This could possibly be explained by the substitution of chalcopyrite and galena by sphalerite, pyrite and pyrrhotite in the flotation froth as iron was added prior to milling. Figure 11.15 shows that the sulphur grades for experiments in which iron was added before milling were significantly higher than the sulphur grades obtained in the absence of iron. In general, an increase in the grade of sulphur was accompanied by a significant decrease in the recovery of magnetite and the grade of iron, which indicates that the magnetite was depressed significantly after the ore was milled in the presence of iron. It appears as if the flotation of magnetite prevented the recovery of valuable minerals after the ore had been milled in a ceramic mill, even at low aeration rates.

By comparing experiments 10 and 11 in Table 11.1 and Figure 11.7, it can be seen that the ratio of cumulative solids/cumulative water recovered in the concentrate increases as the iron addition before milling is decreased. The froth obtained in experiment 11 had much less “body” than the froth in experiment 10. Furthermore, the recovery and grade of magnetite in experiment 11 were significantly higher than those in experiment 10, and as could be expected, the opposite was true for the grade of sulphur (Figures 11.9, 11.10, 11.15). A dosage of 20 g Dow Z-200/t ore was necessary to increase the recovery of chalcopyrite in experiment 11, which was still lower than in experiment 10 (Figure 11.11).

Except for experiment 6, the recoveries of sulphur (Figure 11.14) did not change as much as the grades (Figure 11.15) when iron was added, due to the much higher recovery of solids in the absence of iron. In experiment 6, the ore was milled in an oxygen-flushed mill with an iron addition of 6 kg/t ore. This increased exposure of the ore to oxygen in the presence of iron increased significantly the recovery and grade of sulphur, as well as the recoveries of chalcopyrite and galena, in spite of the increase in the recovery of both the total solids and water (Figures 11.6 and 11.7). These results imply that a high percentage of sulphide minerals, especially sphalerite, was floatable under these conditions; the sphalerite recovery was 70% after 8 min of flotation.

Moreover, the dissolved oxygen content of the pulp with no metallic iron being present was much higher than in experiments with
iron. Earlier work [6,12] showed that an increased level of dissolved oxygen enhanced the selective flotation of chalcopyrite. As can be seen from the experiments conducted without the addition of iron, very low recoveries of galena were obtained after the pulp was subjected to extensive pre-aeration (Figure 11.12). Presumably, oxidised species on the surface of the galena rendered this mineral less hydrophobic.

11.8 CONCLUSIONS

Although numerous papers have appeared on the effect of galvanic interaction on flotation, most of these have considered only the floatability of minerals in the pulp phase. The effect of iron-bearing minerals such as pyrite and magnetite on the stability of the froth phase in flotation has not been studied with respect to galvanic interaction. In the case study presented above it was found that milling in a ceramic mill without the addition of metallic iron yielded extremely brittle froths with very fine bubbles and high solids/water ratios. This was caused by the high floatability of magnetite which destabilised the froth phase owing to bubble-overloading, and resulted in poor grades of copper and sulphur, and poor copper–lead selectivity. Moreover, previous work suggested that dixanthogen formed on both chalcopyrite and galena in the pulp after the ore had been milled in the absence of iron, which probably also contributed to the poor copper–lead selectivity.

When milling occurred in the presence of metallic iron, galvanic interaction caused by the rubbing-off of iron onto both valuable and gangue minerals reduced the rest potential of such minerals. This inhibited the floatabilities of all minerals, especially the iron-bearing gangue minerals, which yielded more stable and well-drained froths with larger average bubble sizes and lower solid/liquid ratios. Consequently, greatly improved copper grades, copper recoveries and copper–lead selectivities were obtained, even without pre-aeration. An oxygen-saturated pulp milled in the presence of iron yielded the best recovery of chalcopyrite and copper–lead selectivity.

This study has shown that the flotation recovery of a valuable mineral is not merely a function of galvanic interaction with that mineral, but also strongly dependent on the effect of galvanic interactions with associated minerals and their effect on the stability of the froth phase. For example, contradictory results have been reported in the literature on the effect of galvanic interaction on the flotation efficiency of ores containing pyrite. It is suggested that such
conflicting results could be reconciled by considering both the two mechanisms proposed in this chapter, i.e. (a) the general decrease in floatability due to galvanic interaction, and (b) the destabilisation of the froth phase by undesirable activation in the absence of galvanic interaction.

REFERENCES

364  J.S.J. VAN DEVENTER

HYDROCYCLONES

3rd International Conference on

30 September - 2 October 1987

Paper H2

FLOTATION OF PYRITIC ORE IN AN AIR-SPARGED HYDROCYCLONE

F.L.D. CLOSTE
A.J. BURGER
J.S.J. VAN DEVENTER

Department of Metallurgical Engineering
University of Stellenbosch
7600 South Africa

SYNOPSIS

A potential new application of the hydrocyclone is in flotation. Air is fed through the porous cylindrical wall of the hydrocyclone into the slurry stream. Non-wettable particles are selectively attached to small bubbles and are floated out of the feed slurry into the overflow. Wetted particles do not attach to bubbles and thus pass out in the underflow.

A South African gold ore containing 3.26% iron pyrites was treated in such a hydrocyclone to produce a flotation concentrate recovering 85-93% of the iron pyrites in the feed. Comparative tests using a batch laboratory flotation cell recovered up to 95% of the pyrites.

INTRODUCTION

Froth flotation is a well-established technique for concentrating minerals on the basis of selective wetting since the early years of this century and is used on a very large scale. Large numbers of flotation cells are required for handling economic throughputs of coal and the low-grade sulphidic ores of copper, zinc, lead and pyrites.

Several phenomena play a rôle in the process of flotation. Particles above 150 µm at the upper end of the flotation range have sufficient inertia to break the liquid film on collision with a bubble and attach to it. At the lower end of the flotation range particles below about 20 µm tend to follow the streamlines round a bubble and thus contact is avoided. On the other hand the highly turbulent flow occurring in flotation cells generates shear forces which tend to disengage the larger particles from bubbles to which they have attached.

The chemical nature of the surface of the particles is of critical importance in flotation since the separation depends on a difference in properties between the product and the waste. Some minerals are naturally hydrophobic but in most cases it is necessary for a "collector" to be added. Such reagents are often organic substances containing an amine group which adsorbs onto or reacts with the mineral surface.

One method of reducing the large numbers of flotation cells and the size of the buildings required is to intensify the operation. This allows the separation to take place more rapidly and smaller equipment can be used.

Various unconventional techniques have been suggested in order to enhance the rate of flotation. Examples include Iona (1), Miller and Van Camp (2), Chernykh et al. (3), Kosaka and Uchio (4), Bahr, Lüdke and Mehrhoff (5).

The approach followed by Miller and Van Camp (2) was to develop a new type of hydrocyclone in which air is fed through the porous wall and finally emerges in the overflow. Miller and co-workers have successfully demonstrated their concept in the beneficiation of fine coal (2), copper sulphide ore (6) and the de-oiling of water (7). The results of flotation tests on one type of ore are not necessarily applicable to a different ore. It is therefore essential to study the effects of operating variables in each case.

Therefore the work by Burger (8) reported here was undertaken to study the applicability of Miller's technique to the flotation of iron pyrites from a coarse Witwatersrand quartzitic gold ore.

The flotation of pyrites is an important process in South Africa in which many tens of millions of tons of ore are treated annually. The 1 - 5 % pyrite component of these ores acts as a carrier for much of the trace levels of gold and uranium present as well as constituting a valuable feedstock for the manufacture of sulphuric acid.

THE AIR-SPARGED HYDROCYCLONE

The basic features of Miller's design (2) are the use of a porous cylindrical wall for a hydrocyclone, a conventional tangential feed and a central vortex finder. Air is sparged through the porous wall, is broken up into small bubbles by the high velocity of slurry and floats hydrophobic particles out through the vortex finder.

Alternative locations for the discharge of the waste slurry have been tested as reported by Miller and Van Camp (2). The design used here is shown in Fig. 1, which follows the version recommended by Miller (2). The cylinder is arranged vertically with feed at the top and overflow through the vortex finder at the top of the unit.

The underflow slurry of non-floated particles flows downwards through the annular opening between the wall and a plug supported on the base. The rate of flow is controlled by an orifice plate held in position below the plug by the epigot. Some of the results reported here were obtained using a conical plug mounted on a screw thread to vary the annular outlet opening. However this proved difficult to control due to blockages in the narrow gap.

Stellenbosch University  https://scholar.sun.ac.za
EXPERIMENTAL

The ore used was an easily-floatable coarse pyritic ore from the large ERO Ltd. plant near Brakpan on the East Witwatersrand. The average pyrite (as FeS$_2$) content was 3.26% and the absolute density 2747 kg/m$^3$. The particle size distribution is given in Table 1 as well as the distribution of sulphur grade with size fraction. These figures show that about 68% of the sulphur in the ore was present in the fraction between 53 $\mu$m and 150 $\mu$m.

The hydrocyclone illustrated in Fig. 1 was incorporated in a simple rig. Feed slurry was prepared in an agitated conditioning tank with a volume of 470 L and fed by a centrifugal slurry pump through a magnetic flowmeter to the hydrocyclone. The flow rate of air was also measured. Samples of overflow and underflow products were taken and weighed. Discrepancies in mass balance were below 5%.

The solids were filtered out, dried and analysed for sulphur. The particle size distribution was determined by dry sieving down to 38 $\mu$m and wet sieving below this size.

The chemical treatment of an ore fed to flotation must be controlled carefully and ore, once treated, cannot be re-cycled in experiments since reaction will have further modified the surface.

The charge of slurry was made up with fresh ore from sealed drums and tap water. It was conditioned for 10 minutes before each series of experiments by adjusting the pH in the range 4 - 4.5 and adding potassium amyl xanthate and a proprietary frothing agent (Bowlthrot 250 : polypropylene glycol methyl ether). Most of the work used feed slurries of 10% solids by mass although some experiments were done using 30% and 45% solids.

A set of experiments was also done using the same ore and reagents in a 3 L Leeds batch laboratory flotation cell. The object of these experiments was to provide a comparative set of flotation results using a conventional technique.

RESULTS

RECOVERY OF WATER WITH NO SOLIDS PRESENT

Experiments on the hydrocyclone were conducted using clear water as feed and measuring the recovery of water in the overflow at various feed and air flow rates. The object was to characterise its flow behaviour with the simplest possible system. One set of readings is shown in Fig.2.

The curve for the lowest air flow rate of 50 L/min shows the constraining effect of the base. As the water flow rate increases, more water is simply forced out of the overflow. Here the hydrocyclone is merely acting as if it were an unequal T-piece.

With increasing air flow, more water is entrained by the air at low water flow rates. As the feed rate of water increases, its centrifugal force overcomes the entraining effect of air to reduce the recovery to a minimum at about 35 L/min. At higher water feed rates the restricting effect of the base again forces water into the overflow to increase recovery.

Burger (8) also showed that the addition of frothing agent to water feed stabilised the foam causing minimum recovery to occur at a feed rate of 40 L/min.

CLASSIFICATION OF ORE WITHOUT REAGENTS

Experiments were next done using 10% ore slurry as feed but with neither collector nor frother added. A typical set of results is shown in Fig.3 for a relatively high air flow rate of 205 L/min.

It is clear that little separation of particles occurs in the hydrocyclone below a feed rate of 30 L/min. An increase in feed rate to 30 L/min forces 99% of the solids in the feed out in the underflow. The remaining 1% solids recovered in the overflow consist mainly of -45 $\mu$m particles and the cut point for the hydrocyclone is below 25 $\mu$m, as given by Burger (8).

The presence of solids increases the viscosity of the underflow. This effect causes an increased recovery of water compared to the data in Fig.2. The point of minimum recovery of water also occurs at a lower feed rate.

RECOVERY OF PYRITES USING REAGENTS

A set of results from Burger (8) is given in Fig.4 where both collector and frother were used as in a normal flotation process. Values of the recoveries of water and solids are shown for slurry feeds of 10, 30 and 45% solids by mass. When Figs.3 and 4 are compared, it is clear that the flotation reagents increase the recoveries of solids in the effective operating range between 30 and 50 L/min feed rate.

Analyses of the concentrates provided the results on the recoveries of sulphide and the grade of the concentrates shown in Fig.5. Feed flow rates between 30 and 40 L/min produce over 80% recovery of sulphide and a grade of 40% sulphide (i.e. 75% FeS$_2$). These results compare favourably with those normally obtained for rougher flotation in plants operating on this ore.

The selectivity of various size ranges to flotation is summarised in Figs.6 and 7 where the recovery and grade are given in terms of particle size with dosage of frother as parameter. The shape of the recovery curves for size fractions below 100 $\mu$m is generally similar to that for the batch flotation cell. However the hydrocyclone showed a sharper drop in recovery for larger size fractions in Fig.6 which was not obtained in the batch cell. This drop is attributed to higher turbulence in the hydrocyclone compared to the batch cell.

The most noticeable effect of increased dosage of frother is shown in Fig.7 as a decrease in sulphide grade of the concentrate recovered. This represents additional gangue recovered due to the non-selective entrainment caused by a more stable froth. Results from the batch cell are little different from the hydrocyclone.

The level of collector is most important as shown in Fig.8. The dosage of 40 g/tone ore used in conventional operations is shown to be quite inadequate at high flow rates and 240 g/tone ore was used to obtain good recoveries. Further experiments by Burger (8) showed that 120 g/tone ore was sufficient for this ore.
An interesting change in operational behaviour of the hydrocyclone occurs at the point of minimum water recovery. This is illustrated by considering the sharp increase in grade of concentrate in Fig. 5 just above the point of minimum water recovery shown in Fig. 3 (although for slightly different conditions). This was noted in all cases studied by Burger [8].

**THE EFFECT OF AIR FLOW RATE**

Air flow rate has been shown in Fig. 2 to have had a pronounced effect on the recovery of water. The effect of air flow on the recovery of sulphide is shown in Fig. 9. Below a slurry feed rate of 40 L/min there is almost no effect at all.

**THE EFFECT OF SLURRY SOLIDS CONTENT**

The various effects of the solids content on the performance of the hydrocyclone are demonstrated in Figs. 4 and 5, which include curves for feed slurries of 10%, 30% and 45% solids by mass.

The recovery of water in the overflow in Fig. 4 is increased quite significantly by a change in feed from 30% to 45%. A similar, though less extensive increase is also shown in the recovery of solids, even at high feed rates. The throttling effect of the spigot with increasing slurry viscosity is the likely cause.

The curves in Fig. 5 confirm what Kinneberg and Miller [6] observed for copper sulphide ores, namely that the recovery of sulphide increased with solids content but that the grade decreased significantly.

**RESULTS USING A LABORATORY FLOTATION CELL**

Batch tests on the same ore were done in a 3 L Leeds laboratory cell with an air supply of 6 L/min as reported by Burger [8]. Various dosages of collector from 20 to 110 g/tonne were used.

Total recoveries of sulphide up to 96% were obtained after 300 seconds but with a relatively low grade of 32.5%. Particles ranging from 20 µm to 300 µm were recovered at over 90% efficiency. These data are plotted in Figs. 6 and 7 for comparison with the hydrocyclone.

The flotation time of 300 seconds used here for comparison with the hydrocyclone was longer than that of 240 seconds used in practice in large conventional cells operating on this type of ore. Nevertheless the results serve as a basis for comparing the performance of the hydrocyclone with a conventional operation under controlled conditions.

The comparison of the residence times of slurry in the hydrocyclone of about 1 second to 200 - 300 seconds in a conventional operation highlights the significant potential saving in plant volume of the hydrocyclone.

**CONCLUSIONS**

(1) Pre-treatment of the ore containing 3.26 % FeS₂ with flotation reagents enabled the hydrocyclone to recover 85-93% of the sulphides as overflow concentrates with grades up to 65-75 % FeS₂. The best recoveries were obtained for particles between 38 and 75 µm. Feed slurry passed through the hydrocyclone in about 1 second.

(2) Tests with the same ore in a laboratory batch flotation cell gave recoveries of sulphides up to 95%. Good recoveries of pyrites were obtained over a wider range of particle size than in the hydrocyclone. Flotation times of 300 seconds were used.

(3) The hydrocyclone has a potential advantage over conventional flotation cells in its very high throughput per unit volume, 300:1 in this case.

(4) The main disadvantage of the hydrocyclone for this application is that it requires three times more collector reagent.

**ACKNOWLEDGEMENTS**

The authors wish to acknowledge with thanks financial and technical assistance from the Council for Mineral Technology.

**REFERENCES**


(in Afrikaans)
TABLE 1
Distribution of particle size and grade of sulphide in ore

<table>
<thead>
<tr>
<th>Size fraction (μm)</th>
<th>Mass %</th>
<th>Mass % S in size range</th>
<th>Mass % of total S in ore in size range</th>
</tr>
</thead>
<tbody>
<tr>
<td>+212</td>
<td>11.5</td>
<td>0.322</td>
<td>2.13</td>
</tr>
<tr>
<td>+150</td>
<td>30.0</td>
<td>0.748</td>
<td>13.0</td>
</tr>
<tr>
<td>+106</td>
<td>22.4</td>
<td>2.08</td>
<td>26.9</td>
</tr>
<tr>
<td>+75</td>
<td>15.5</td>
<td>2.70</td>
<td>24.2</td>
</tr>
<tr>
<td>+53</td>
<td>9.3</td>
<td>3.14</td>
<td>16.8</td>
</tr>
<tr>
<td>+38</td>
<td>2.8</td>
<td>3.61</td>
<td>8.2</td>
</tr>
<tr>
<td>-38</td>
<td>8.5</td>
<td>5.39</td>
<td>11.2</td>
</tr>
<tr>
<td>all fractions</td>
<td>100</td>
<td>1.74</td>
<td>100</td>
</tr>
</tbody>
</table>

Open to atmosphere to prevent siphoning

Concentrate

Vortex Finder

Slurry feed (tangential) 15.8 x 5.4 mm

Porous cylinder (ceramic)

Outer PVC - cylinder

Froth phase

Air flow

Polyethylene spigot

Tailings

1 Sectional sketch of air-sparged hydrocyclone
2. Recovery of water in overflow with no solids.

3. Recovery of water and solids in overflow using no flotation reagents: Air flow 205 L/min; 10% solids.

4. Recovery of water and solids with reagents: Air flow 200 L/min; Collector 160 g/ton; Frother 35 mg/L.

5. Recovery of sulphide and grade of concentrate: Air flow 200 L/min; Collector 160 g/ton; Frother 35 mg/L.
6 Recovery of sulphide in various size fractions
Cyclone: Slurry feed 35 L/min; Air flow 200 L/min; Collector 160 g/ton; 10% solids
Batch cell: Air flow 7 L/min; Collector 160 g/ton; float time 300 s; 30% solids

7 Grade of concentrate in various size fractions
Cyclone and batch cell conditions as for Fig. 6

8 Recovery of sulphide at high and low collector dosages: Air flow 205 L/min; Frother 50 mg/L; 10% solids

9 Recovery of sulphide at various air flow rates
Collector 160 g/ton; Frother 35 g/ton; 10% solids
A Computer Model to Predict Froth Behaviour in the Scale-up of Flotation Cells

V.E. ROSS* and J.S.J. VAN DEVENTER**

*Ore-Dressing Division, Mintek, Randburg and **Department of Metallurgy, University of Stellenbosch, Stellenbosch, South Africa

A computer program was developed that incorporates a novel analysis of the behaviour of the froth in full-scale cells to predict the performance of the froth over a wide range of operating conditions. The program has the distinct advantage that it can be easily implemented on a microcomputer, which allows rapid computation and processing of the results.

The program utilizes experimental data obtained in flotation-plant and laboratory testwork to provide parameters for the froth model under an initial set of operating conditions. These parameters can then be used in conjunction with a model describing the transfer of material from the pulp to the froth to predict the performance of the cell when its dimensions and operating variables are changed during scale-up.

Introduction

The scale-up of flotation cells from the laboratory to an industrial scale is complicated by several factors, particularly those relating to the effects of the structure and the residence time of the froth.1-4 These complications are due to significant differences in the dimensions of the cells, in the operating conditions, such as the depth of the froth and the aeration rate, and in the methods of froth removal.

The flotation rate constants are closely related to the rate of aeration,2 the extent to which the surfaces of the bubbles are covered by floating particles,5 and the height of the froth column.6 On a laboratory scale, the residence time of mineral particles in the froth is extremely short, owing to the rapid removal of the froth. On a plant scale, however, the longer residence times have a significant effect on the recovery of and selectivity for any particular species.

Hitherto, the prediction of the performance of large-scale flotation cells from batch data was accomplished by the implementation of a scale-up factor of between 1,5 and 3,5, i.e. the ratio of the residence time in a full-scale cell to that in a laboratory-scale cell, while the contribution of froth effects was totally neglected.7,8 However, the method has limited application, since the laboratory and plant flotation rate constants are based on a specific set of operating conditions.

A computer program, which utilizes
a mathematical model of the froth phase as well as experimental flotation data to predict the performance of an industrial-scale froth, is described. It takes the characteristics of the froth into account during scale-up since they can cause significant deviations from predicted performance when only the residence time of the pulp has been considered.

The model

In the model developed in the present work, the froth phase is subdivided into four stages, which are indicated by the circled numbers in Figure 1. Stage 1 represents the inefficient part of the total froth volume, i.e. the part that does not contribute towards the transfer of particles from the pulp into the concentrate stream. The relative size of this stagnant region is determined by tests in which small polystyrene beads are sprinkled onto the surface of the froth to indicate its velocity. Plug flow is assumed here, since no froth is transferred from this stage to any other stage.

A fraction $\epsilon$ of the total volume of air, $G_t$, flowing into the cell is transferred into stages 2 and 3 via the pulp-froth interface. Of this
air, a fraction \( \beta \) is transferred into stage 2. The distribution of the air over the pulp-froth interface can be described by an equation of the form

\[
(G_0)_x = g_0 \sin \pi x / L
\]  

where \((G_0)_x\) is the superficial air flux at a distance \(x\) from the cell backplate, \(g_0\) is the air flux at the centre of the cell, and \(L\) is the length of the cell.

This form of equation was verified by measurement of the air distribution in plant-scale cells with apparatus specifically designed for this purpose. A model of the froth phase by Moys, which can predict concentrate flowrates only if the air distribution is independent of the distance from the cell backplate, can therefore not be applied in this case.

In stage 2, froth flow patterns can be observed in the direction of the froth discharge launder, i.e. the bubble velocity has both vertical \((z)\) and horizontal \((x)\) components. These bubble streamlines can be described by modification of the equation for an incompressible fluid flowing round a rectangular bend, to give:

\[
x^* (F_1 + z_\nu - z) = c_2
= x^* (C_1 - z)
\]  

where \(x^*\) is the distance from the right-hand boundary of stage 1 \((X = X_0\) in Figure 1), \(F_1\) is a characteristic constant \((m)\) that is calculated from the surface velocity of the froth (measured on the plant in tests using small polystyrene beads) and the volume of air and slurry transferred across the pulp-froth interface into the froth, and \(c_2\) is a characteristic constant \((m^2)\) for every bubble streamline. As the surface velocity of the froth in stage 2 is largely determined by the rate of concentrate removal, \(F_1\) is a function of the rotational speed of the froth paddles.

The bubble velocity \((m/s)\) at any coordinate \((x^*, z)\) is

\[
V(x^*, z) = V(x^*_s, 0).
\]

\[
\left[ \frac{x^*^2 + (C_1 - z)^2}{x^*_s^2 + C_1^2} \right]^{1/2}
\]

where \(V(x^*_s, 0)\) is the bubble velocity \((m/s)\) at the pulp-froth interface at a distance \(x^*_s\) into stage 2, i.e.

\[
V(x^*_s, 0) = (G_0)x^*_s (1 + \text{SLAR})
\]

where SLAR is the ratio of the volumetric flowrate of the solids and water to that of the air as they enter the froth, as determined in laboratory testwork.

A fraction \(\alpha\) of the air entering stage 2 at the interface between \(X_0\) and \(L'\) is transferred into stage 3 at \(X = L'\) between the boundaries \(z = 0\) and \(z = H\). The value of \(L'\) is determined by an iterative procedure from the calculated residence time of the froth in stage 3 (see the Addendum, Section 2).

The froth is transferred into stage 3 via stage 2 and via the pulp-froth interface. As a result, the vertical upward velocity of the
ft of height above the interface:

\[ V_2(z) = a_3 + \frac{g_0 L}{z} \left( \frac{\cos \pi \frac{L'}{L} - \frac{z(L' - x_a)}{z_x L}}{L'} / L \right) \]  \[ (5) \]

where

\[ a_3 = (1-\beta) (1+SLAR) \epsilon G_1 / A_3, \ (m/s) \]

\[ L_3 = L - L' \ (m) \]

\[ A_3 = L_3 W \ (m^2) \]

\[ g_0 = G_1 \epsilon / 2A_z, \] the air flux at the centre of the cell,

\[ x_a = \text{the origin of the bubble streamline corresponding to} \ (L', z_v), \text{distance from the cell backplate,} \]

\[ A_z = \text{cross-sectional cell area,} \]

\[ z_v = \text{height (m) of the concentrate weir above the pulp-froth interface.} \]

The froth is transferred into stage 4 from stage 2 as well as from stage 3. The horizontal velocity of the froth increases linearly towards the froth discharge (the magnitude of which increases with an increase in the rate of concentrate removal) and can be described by the relationship:

\[ V_4(x) = a_4 + b_4 (x - L') \]  \[ (6) \]

where

\[ a = \bar{V}(L', H - \Delta z/2) \]

\[ b = \left[ V_3(z_v) A_3 \right. \]

\[- \left. W \int (g_{b_0} + 2g_{b_1} x) dx \right] / \Delta z A_3 \]

\[ (\text{in s}^{-1}), \]

\[ \Delta z \] is the height (m) at which the concentrate overflows the weir, and

\[ g_{b_0} \ (m/s) \] and \[ g_{b_1} \ (s^{-1}) \] are parameters describing bubble breakage at the froth surface.

The volumetric flowrate of the concentrate is then

\[ Q_c = \bar{V}(L, H - \Delta z/2) \Delta z W, \ (m^3/s), \]  \[ (7) \]

where \[ \bar{V}(L, H - \Delta z/2) \] is the average velocity of the concentrate overflowing the concentrate weir.

The equations describing the concentrations of floated or entrained mineral particles, or both, and water in stage 2 are based on the assumption of first-order kinetics (see the Addendum, Section 1). The same assumption applies to all the other stages. The equations for stages 3 and 4 can be derived by incorporation of the velocity profiles given in Equations [5] and [6], but they are too complex to be described within the confines of this paper.

The drainage velocity (m/s) of any species at the left-hand boundary of stage 2 is

\[ U_i(x_0, z) = \Delta V_i - V(x_0, z), \]  \[ (8) \]

where \[ \Delta V_i \] is the velocity increment between the bubble and the drainage velocity (unique to species i), and \[ V(x_0, z) \] is the magnitude of the bubble velocity at \( (x_0, z) \).

The velocity increment is calculated from the total concentration of species i in the froth at \( (x_0, 0) \), and is used in the calculation of the total concentration of the various species in the froth.
Computer requirements

A distinct advantage of the computer program is that it can be implemented with ease on a microcomputer. This is particularly important when access to a mainframe is not readily available. The program itself occupies less than 40 kilobytes of disc storage space, the computation time being typically about 5 minutes for the complete analysis of the behaviour of one species.
mineral species in the froth.

The computer program was developed on an Olivetti M24 microcomputer with 640 kilobytes of RAM storage capacity, using an MS-DOS operating system. GWBASIC was used as the programming language. A considerable degree of user-friendliness, which improves the versatility of the program and simplifies its application, was also incorporated.

Computational procedures

A simplified flowsheet of the computational procedure labelled SIMULATE is presented in Figure 2. This part of the package involves the analysis of the performance of the froth in the plant-scale flotation cell for calculation of the model parameters. The variables are estimated by iterative procedure. However, for the second part of the package (PREDICT), which calculates the performance of a flotation froth under a new set of conditions, the variables are specified as input. The objective functions (OF) that were minimized by a Nelder-Mead (NELM) optimization routine during SIMULATE are briefly summarized in Section 2 of the Addendum.

Application of the program

This section illustrates the application of the computer program to the analysis of the froth in the flotation of fluorspar. The solids in the froth were divided into six size fractions, as indicated in Table 1. Also shown are the mass flowrates of the respective fractions entering the froth and in the concentrate in the plant-scale cell. The former was calculated from the

| TABLE 1. |
| Analysis of the cleaner flotation froth in the first phase of the calculations. |
| Size, μm | +300 | -300 | -150 | -106 | -75 | -45 |
| +150 | +106 | +75 | +45 |
| Mass flowrate into concrt., g/s | 22 | 99 | 96 | 104 | 207 | 582 |
| Mass flowrate into froth, g/s | 602 | 2118 | 1471 | 1214 | 1535 | 2192 |
| Ratio concrt./froth | 0,04 | 0,05 | 0,07 | 0,09 | 0,14 | 0,27 |
| Ratio to water in tails, kg/kg | 0,05 | 0,19 | 0,03 | 0,12 | 0,10 | 0,09 |
| Total concentration | 12,2 | 42,9 | 29,8 | 24,6 | 31,1 | 44,4 |
| - Entrained | 6,2 | 22,7 | 3,3 | 14,2 | 12,0 | 11,4 |
| = Floated | 6,0 | 20,2 | 26,5 | 10,4 | 19,1 | 33,0 |
| Volumetric ratio of slurry-to-air flow (SLAR) | 0,234 |
| Mass flowrate of water entering froth (g/s) | 6064 |
mass flowrate of solids per unit volume of air that enter the froth, as measured on laboratory scale. It was assumed that this parameter stays constant for both the laboratory and the plant cell under similar conditions. The latter was measured on the plant.

Every size class was further divided into two subclasses, viz a floated and an entrained fraction. The fraction that was entrained into the froth was calculated from the ratio of the concentration of each size fraction to the concentration of water in the tailings (assuming that the pulp is perfectly mixed), and the transfer rate of water into the froth (see Table 1). It was assumed that this ratio stays constant, i.e. there is negligible differential classification of the entrained solids and water as they enter the froth.

Material collected from the pulp in a cleaner cell was first floated in a 5-litre Denver laboratory cell, and the aeration rate and the volumetric transfer of slurry into the froth were measured. Analysis of the slurry thus recovered yielded the mass-transfer rates of the various species as well as the ratio of the volumetric flowrate of the slurry to that of the air (SLAR) as they enter the froth. During these tests, the froth was rapidly removed from the surface of the pulp in a simulation of the rate of transfer of material into the froth, i.e. before drainage can occur.

Subsequently, the performance of the cleaner froth was analyzed by experimental measurement of the parameters listed in Table 2. The experimental and predicted velocities at the surface of the froth are presented in Figure 3.

Froth samples of a fixed volume were also taken at different depths in the froth at the point corresponding to \( x_0 \) in Figure 1. Analysis of these samples, together with the parameters in Table 2, served as the input to SIMULATE. This algorithm calculated the drainage constant of each subclass from a least-squares regression of the curve of the concentration of the mineral in the plant-scale froth at different

<table>
<thead>
<tr>
<th>TABLE 2. Parameters for the cleaner flotation cell.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length ( (L) )</td>
</tr>
<tr>
<td>m</td>
</tr>
<tr>
<td>1.35</td>
</tr>
</tbody>
</table>

Froth breakage parameters: \( g_{b0} \) \( (\text{m/s}) \) \( 2.78 \times 10^{-2} \)
\( g_{b1} \) \( (\text{s}^{-1}) \) \( -3.00 \times 10^{-5} \)

A COMPUTER MODEL TO PREDICT FROTH BEHAVIOUR
FIGURE 3. Experimental and simulated velocities at the surface of the froth

FIGURE 4. Experimental and simulated concentration-height profiles for the froth in the cleaner cell
TABLE 3.
Analysis of the recleaner flotation froth\(^a\) in the first phase of the calculations.

<table>
<thead>
<tr>
<th>Size, (\mu m)</th>
<th>+300</th>
<th>-300</th>
<th>-150</th>
<th>-106</th>
<th>-75</th>
<th>-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flowrate into conc., (g/s)</td>
<td>54</td>
<td>170</td>
<td>120</td>
<td>101</td>
<td>180</td>
<td>426</td>
</tr>
<tr>
<td>Mass flowrate into froth, (g/s)</td>
<td>1328</td>
<td>1443</td>
<td>1073</td>
<td>1014</td>
<td>1597</td>
<td>3281</td>
</tr>
<tr>
<td>Ratio conc./froth (\text{kg/kg})</td>
<td>0.04</td>
<td>0.19</td>
<td>0.11</td>
<td>0.10</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Ratio to water in tails, (\text{kg/kg})</td>
<td>0.17</td>
<td>0.23</td>
<td>0.17</td>
<td>0.14</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>Total concentration(^b)</td>
<td>27.6</td>
<td>30.0</td>
<td>22.3</td>
<td>21.3</td>
<td>33.2</td>
<td>68.2</td>
</tr>
<tr>
<td>- Entrained(^b,c)</td>
<td>22.2</td>
<td>29.6</td>
<td>21.5</td>
<td>18.1</td>
<td>26.7</td>
<td>16.7</td>
</tr>
<tr>
<td>= Floated(^b)</td>
<td>5.4</td>
<td>0.4</td>
<td>0.8</td>
<td>3.2</td>
<td>6.5</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Mass flowrate of water entering froth (g/s) 6152
Cell data the same as in Table 2, except that \(\epsilon = 0.55, F_1 = 0.607 \text{ m and SLAR} = 0.203\)
Froth breakage parameters: \(g_{b0} (\text{m/s}) 2.99 \times 10^{-2}\)
\(g_{b1} (\text{s}^{-1}) -1.33 \times 10^{-4}\)

FIGURE 5. Experimental and simulated concentration-height profiles for the froth in the recleaner cell

A COMPUTER MODEL TO PREDICT FROTH BEHAVIOUR 81
TABLE 4.
Drainage rate constants (s\(^{-1}\)) estimated in SIMULATE from tests on the cleaner and recleaner froths.

<table>
<thead>
<tr>
<th>Size, µm</th>
<th>Cleaner froth</th>
<th>Recleaner froth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Floated</td>
<td>Entrained</td>
</tr>
<tr>
<td>+300</td>
<td>0.21</td>
<td>3.82</td>
</tr>
<tr>
<td>-300+150</td>
<td>0.24</td>
<td>9.52</td>
</tr>
<tr>
<td>-150+106</td>
<td>0.26</td>
<td>9.51</td>
</tr>
<tr>
<td>-106+75</td>
<td>0.27</td>
<td>5.08</td>
</tr>
<tr>
<td>-75+45</td>
<td>0.22</td>
<td>7.18</td>
</tr>
<tr>
<td>-45</td>
<td>0.25</td>
<td>9.40</td>
</tr>
</tbody>
</table>

a Denver no.24 D-R cell
b Concentration (kg/m\(^3\)) in the total volume of slurry and air entering the froth.
c Calculated from the ratio of solids to water in the tailings and the flowrate of water into the froth.

heights. This procedure was repeated for a recleaner cell in the fluorspar circuit. The results of this testwork are summarized in Table 3 and the drainage rate constants in both instances are presented in Table 4. The ability of the model to simulate the concentration-height curves at \(x_0\) is shown in Figures 4 and 5. The maximum error between any of the experimental and predicted values is 12% and 7.5% of the measured concentration in the cleaner and recleaner froths respectively.

Sensitivity analysis
The practical implications of the computer program PREDICT in the scale-up of the performance of the froth can best be illustrated by a sensitivity analysis. This is justified because SIMULATE satisfactorily fitted the experimentally measured concentration-height profiles for the industrial froth. Although, in practice, no flotation variable can be altered without simultaneously affecting a host of other variables, the parametric sensitivity of the model can best be illustrated by changing \(\phi\) of each variable independently, as was done here. The ability of the model to predict the performance of the cleaner froth when the dimensions of the cell and the operating condi-
tions are changed during scale-up, as shown in Figures 6 to 10. Recoveries are presented as fractions of the recovery obtained (i.e. 30% of the total recovery in the cleaner bank) for the parameters in Table 2. The drainage rate constants given in Table 4 were used in the predictions.

As expected, recovery increases with an increase in the rate of aeration and in the ratio of slurry to air as they enter the froth, as shown in Figure 6. Under these conditions, the velocity of the froth increases on the surface of the froth towards the concentrate weir and vertically upwards in stage...
3 if the value of $F_1$ is constant. A change in the distribution of air in the pulp may affect the inefficient fraction of the froth, denoted by $X_0$. As indicated in Figure 7, recovery decreases with an increase in the inefficient fraction of the froth. Furthermore, if $F_1$ increases (i.e. if there is less transfer of froth from stage 2 into stage 3), the recovery decreases if the rate of removal of the concentrate remains constant.

As shown in Figure 8, an increase in the height of the concentrate weir (and the froth column) would result in an overall decrease in the rate of flotation and in the
recovery. (The concentration of the particles in the froth decreases with increasing height owing to the drainage of particles.) Furthermore, recovery increases if $F_1$ decreases (i.e. if there is a greater increase in the velocity in stage 3) and the height of the concentrate weir remains constant.

An increase in the rate of removal of the concentrate with paddles improves the recovery because there is a higher mass flowrate (Figure 9). An increase in the velocity in stage 3 (i.e. a decrease in $F_1$) also results in an increase in the concentration of material in the froth, and consequently also in the recovery for any given rate of removal of the concentrate. If the length of the cell is increased during scale-up, slower transfer of material into the froth (due to a greater cross-sectional cell area) results in a decrease in recovery, as indicated in Figure 10. However, this may be overcome by an increase in the rate of aeration, because the residence time of particles in the froth is reduced.

This example illustrates the complexity of the interactions between the operating variables, the characteristics of the froth, and the dimensions of the cell, and shows that froth effects should be taken into account during scale-up. Significant deviations from predicted performance can occur if the only relationship considered is that between the pulp residence time in the laboratory and industrial scale cells.

Conclusions

An efficient method has been developed for use in the scale-up of industrial flotation cells from laboratory batch tests. The froth model developed for this purpose incorporates control variables as well as easily measurable froth
characteristics, and permits the froth to be analyzed in terms of its mobility and the drainage constants for the various species in the froth. These parameters are determined experimentally as well as through iterative techniques in the computer program. An advantage of the program is that it can be implemented with ease on a microcomputer.

For both the cleaner and recleaner flotation cells, the programme was found to give an adequate description of the variation in the concentration of the various species in the froth with height above the pulp-froth interface. A sensitivity analysis showed that the model yielded realistic descriptions of changes in operating and design variables due to scale-up. Therefore, when used in conjunction with a model describing the transfer of material from the pulp to the froth, the program could be a powerful tool in the design of industrial cells and in efforts to improve the performance of such cells.

Acknowledgements

This paper is published by permission of the Council for Mineral Technology (Mintek).

References


7. KALAPUDAS, R. A study on scaling-up of laboratory batch flotation data to industrial size flotation. XVth INTERNATIONAL METALLURGY: FLOTATION MODELLING


Addendum

I. Equations describing the concentration of mineral species and water in stage 2

Floated mineral species i:

\[ M_{2f1}(l) = \frac{M_{2f1}(0)}{1 + k_v \int_0^l dV(l)} \]  

where

- \( M_{2f1}(l) \) = Concentration of species i at distance \( l \) along bubble streamline,
- \( M_{2f1}(0) \) = Concentration of species floated into froth at origin of the streamline,
- \( k_v \) = Drainage rate constant for floated species i,
- \( l_d_i \) = Distance along streamline where detachment of floated species from bubble surfaces starts occurring. \( l_d_i = 0 \) in this study.

Entrained mineral species i:

\[ M_{2e1}(l) = M_{2e1}(0) \exp[-(k_{2e1} + k_v) \int_0^l dV(l)] \]  

where the parameters are as described above, but for entrained material. \( k_{2e1} \) is the drainage rate constant for entrained species i in stage 2. The same form of equation applies to water.
2. Objective functions for the determination of the model parameters

SIMULATE

(a) $F_1$: characteristic constant describing bubble streamlines in stage 2:

\[
OX_2 = \sum_{j=1}^{\text{NX}_2} (v_{x_j}^m(x^*,H) - v_{x_j}^p(x^*,H))^2
\]

where $\text{NX}_2$ = Number of velocity measurement points on the froth surface. $v_{x_j}^m(x^*,H)$ and $v_{x_j}^p(x^*,H)$ are the measured and predicted surface velocities of the froth respectively.

(b) $L'$: the boundary of stage 2 nearest to the concentrate overflow weir:

\[
OF = (t_{3x} - t_{3z})^2
\]

where $t_{3x}$ and $t_{3z}$ are the calculated residence time of froth volumes in stage 3 in a horizontal and vertical direction respectively.

(c) $k_{2f_1}$ and $k_{2e_1}$: drainage rate constants for floated and entrained species $i$:

\[
OF = \sum_{j=1}^{\text{NX}_2} [M_{2t_1}(x_0,z)_j - (M_{2f_1}(x_0,z)_j + M_{2e_1}(x_0,z)_j + M_{2d_1}(x_0,z)_j)]^2
\]

where $M_{2f_1}(x_0,z)_j + M_{2e_1}(x_0,z)_j + M_{2d_1}(x_0,z)_j$ is the calculated concentration of species $i$ (due to flotation, entrainment, and drainage) in the froth.

$d_{2t_1}(x_0,z)_j$ is the total measured concentration of species $i$.

(d) $k_{3f_1}$ and $k_{3e_1}$: drainage rate constants in stage 3, incorporating the effects of the action of the froth paddle, turbulence, shear stresses, and bubble coalescence:

\[
OF = (M_{c_1}^m - M_{c_1}^p)^2
\]

where $M_{c_1}^m$ and $M_{c_1}^p$ are the measured and predicted mass flow-rates of species 1 in the concentrate stream respectively.
MASS TRANSPORT IN FLOTATION COLUMN FROTHS

V.E. Ross* and J.S.J. van Deventer*

* Ore Dressing Division, Council for Mineral Technology, Private Bag X3015, Randburg 2125, SOUTH AFRICA
* Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7600, SOUTH AFRICA

ABSTRACT

A model has been developed that describes the behaviour of mineral particles and water in the cleaning zone of flotation columns. The possible detachment of particles from their sites of attachment at the bubble surfaces is related to the distance from the interface between the collection and cleaning zones and the rate at which floated particles are transported into the cleaning zone. The drainage velocities of floated and entrained particles are calculated from the drainage velocity of water and the properties of the particles. The effects of wash water and inhibited drainage in the froth are also explicitly accounted for.

Laboratory testwork on a sulphide ore has shown that, for both solids and water, the rate of transfer into the froth and the holdup in the froth increase with an increase in the aeration rate and a decrease in particle size. The model gave an adequate description of the concentration-height profiles of solids and water in the froth. Model parameters estimated from experimental results are discussed in terms of their practical implications in column flotation.

INTRODUCTION

The interactions, during flotation, between mineral particles and bubbles and the consequent collection of hydrophobic material in the pulp phase have been studied and modelled extensively (Reay and Ratcliffe, 1971; Anfruns and Kitchener, 1976; Trahar, 1981; Laplante, Toguri, and Smith, 1983; Ahmed and Jameson, 1985). However, the mechanisms that determine the behaviour of particles in the froth phase are still incompletely understood and, only during the past few years, have attempts been made to model the subprocesses that operate here in more detail (Moys, 1978; Cuttng, Barber, and Watson, 1982).

Flotation columns have been used increasingly in recent years in various applications, especially in cleaning stages. Bobby and Finch (1986) developed a model for the scale-up of column cells from laboratory to industrial size, and implemented mixing parameters to describe the effect of mixing upon the recovery, R_f, from the collection (pulp) zone. However, because the flow conditions and mass transport in the cleaning zone (i.e. the combined washing zone and froth layer) are not well understood, the recovery in this region had to be expressed in terms of only a single parameter, R_C. Although Yianatos, Finch and Laplante (1987) were able to describe the concentration profiles of solids in the cleaning zone by using a modified version of Moys’s model, a detailed study of the interactions between the gas rate, bubble size, wash water etc. and the behaviour of particles has, as far as can be ascertained, not been done before.

A model for the behaviour of mineral particles in the cleaning zone of flotation columns would undoubtedly have numerous applications, both in the scale-up of column cells and in the optimization of existing operations. The present study was undertaken in an effort to provide descriptions of the interactive nature of the processes that operate in the cleaning zone, particularly the detachment of floated particles from the bubble surfaces and the drainage of particles back to the collection zone. This was accomplished by the derivation of new equations and the modification of existing ones that describe the drainage of liquid from two-phase froths.

THE MODEL

In the approach used for modelling the cleaning zone is regarded as consisting of two separate regions: a washing zone and a froth layer (Bobby and Finch, 1986). The same model is used for the successive simulation of both regions, parameters for the washing zone providing the initial conditions for the simulation of the froth layer.
Detachment of floated particles from bubble surfaces

It is assumed that bubbles arriving at the base of the cleaning zone are perfect spheres of average diameter \(2n_b(0)\) (normally between 1 and 2 mm). Every bubble carries with it an enveloping slurry layer of thickness \(\delta\) and consisting of floated and entrained material, into the cleaning zone. The mass flowrate of entrained species entering the cleaning zone can be expressed as

\[
m_{\varepsilon 1}(0) = X_1 \, m_q(0) C_{t1}/C_{tq}
\]

\[
= X_1 \, C_{t1} \left( \frac{3}{2} \pi n_b(0) \delta^2 \right) + \frac{2}{3} \pi n_b(0) \delta^3
- 0.239 \frac{F}{\pi} \frac{V_{f1}(0)}{P_{ln}C_{tq}/P_0 r_b(0)^2}
\]

(1)

where \(X_1\) is the transfer factor for entrained species \(i\), describing the classification of such particles upon their entry into the cleaning zone. This parameter is split into \(X_{1s}\), relating the mass flowrate of solids to that of the water as they enter the froth, and \(X_{1w}\), which describes the contribution of entrainment to the total mass flowrate of solids entering the froth. \(m_q(0)\) is the mass flowrate (g/min) of feed water entering the cleaning zone, \(C_{t1}\) and \(C_{tq}\) respectively are the concentration (g/cm\(^3\) of slurry) of species \(i\) and water in the pulp at the top of the collection zone, \(V_{f1}(0)\) is the volume (cm\(^3\)) of floated species contained in the enveloping slurry layer, \(G\) the aeration rate (cm\(^3\)/min), measured with a rotameter, and \(F\) is the number of floated species in the froth. \(P_{ln}\) and \(P_0\) respectively are the absolute pressures (kPa) at which air is introduced to the cell, and at the collection-cleaning zone interface. Particles can be grouped into different species depending on their size, mineralogical composition, or flotation rate constants. The values of \(C_{t1}\) and \(C_{tq}\) are obtained from analysis of a pulp sample which is extracted just below the collection-cleaning zone interface, while \(X_{1s}\) and \(X_{1w}\) are calculated from results of a batch flotation test, as described under "Experimental methods". The mass flowrate of a species \(i\) entering the cleaning zone due to flotation is

\[
m_{f1}(0) = m_{t1}(0) - m_{\varepsilon 1}(0)
\]

(2)

where \(m_{t1}(0)\) is the total measured flowrate (g/min) of solid species \(i\) entering the cleaning zone, and can be determined, together with \(m_q(0)\), by laboratory testwork and scale-up (e.g. Dobby and Finch, 1986).

The thickness, \(\delta\), of the slurry layer at the interface is iteratively calculated from the volumetric flowrate of the particles and water entering the froth, the volume (cm\(^3\)) of floated species \(i\) per bubble being

\[
\frac{F}{\pi} \frac{V_{f1}(0)}{P_{ln}C_{tq}/P_0 r_b(0)^2} = m_{f1}(0) \rho_i
\]

(3a)

where \(\rho_i\) is the relative density (g/cm\(^3\)) of species \(i\) and the bubble frequency

\[
f_b(0) = \frac{3 G P_{ln}}{4 \pi P_0 r_b(0)^2}
\]

(3b)

The mass (g) of species \(i\) that is floated per bubble at the interface between the cleaning and collection zones can therefore be expressed as

\[
m_{f1}(0) = V_{f1}(0) \rho_i
\]

(4)

If a floated particle of diameter \(d_{pi}(radius r_{pi})\) occupies an effective area of \(\pi r_{pi}^2/\theta\), where \(\theta\) is the maximum particle packing factor on the surface of the bubble (\(\theta < 1.0\)), the fractional coverage of the bubble surface at the collection-cleaning zone interface will be

\[
SC_i(0) = \frac{0.0597 \, V_{f1}(0)}{\theta \, r_{pi} \, r_b(0)^2}
\]

(5)

\(\theta\) is assumed to be independent of the height in the cleaning zone.

It is proposed that detachment of the least hydrophobic floated species (the species that is most easily displaced by other species) will occur at a height \(z\) above the interface if the total fractional bubble surface coverage by all floated species exceeds 1.0, i.e. if

\[
\sum^n_{i=1} SC_i(z) > 1.0
\]

(6)

Although the detachment of floated particles due to the shear forces imposed on them by the draining slurry is not explicitly accounted for in the model, it is implicitly incorporated in the value of \(\theta\).

Before the fractional coverage of the bubble surfaces by floated mineral species at different heights in the washing zone or froth layer can be calculated, the relationship between the equivalent spherical bubble size and the height in the zone must be determined. If a bubble of radius \(r_b(z_{i-1})\) coalesces or expands between two levels \(z_{i-1}\) and \(z_i\) to \(z_i\) times its radius at level \(z_{i-1}\), and a bubble of radius \(r_b(0)\) coalesces or expands over the total height \(0\) to \(q_b\) times its radius at the pulp/froth interface,
\[ C_b = C_1 \cdot C_2 \cdot C_3 \cdots \cdot C_k \]  

where \( k \) is the number of intervals of equal height into which the zone is subdivided. In the washing zone, where little coalescence occurs because of the action of the washing water, \( C_b \) would be relatively small, since the reduction in the hydrostatic pressure is dominant. However, for an equivalent height in the froth layer, \( C_b \) is very large (bubble coalescence, like that in a conventional froth, is dominant). If

\[ \frac{C_j}{C_{j-1}} = \left( \frac{r_b(z_j)}{r_b(z_{j-1})} \right)^{1/2} j \geq 2 \]  

then

\[ C_b = C_1 \left( 1 \cdot 0.75 + 0.75^2 + \ldots + 0.75^{k-1} \right) \]  

The bubble radius at any level \( z_j \) can consequently be calculated as

\[ r_b(z_j) = r_b(0) c_1 \left( 1 \cdot 0.75 + 0.75^2 + \ldots + 0.75^{j-1} \right)^{0.33} \]  

from measurement of the bubble size at the bottom and the top of the zone, and the height of the zone. This expression provided an adequate description of the experimentally measured size of bubbles in conventional froths.

Secondly, the bubble frequency at any height in the froth is calculated in order to determine the total flux of bubble surface area that is ascending in the froth. The profile in the cleaning zone is described in the model by the following relationship

\[ P(z_j) = P_0 \exp(-k_p z) \]  

where \( k_p \) is a constant \((\text{cm}^{-1})\) which ensures that, at the surface of the froth, the pressure is atmospheric. The bubble frequency at any level \( z_j \) is therefore given by

\[ f_b(z_j) = \frac{3 \cdot P(z_j) G}{4 \cdot \pi \cdot P(z_j) \cdot r_b(z_j)^2} \]  

The washing zone and froth layer are assumed to be composed of dodecahedral bubbles, only the bubbles in the first layer above the collection-cleaning zone interface being spherical. The total surface area of a such a bubble is \( A_b(z_j) = 13.824 \cdot r_b(z_j)^2 \) (Hartland and Barber, 1974), which is similar to that of a spherical bubble of the same volume, viz. 12.57 \( r_b(z_j)^2 \). The fractional coverage of the bubble surface by species \( i \) at a height \( z_j \) above the interface between the collection and cleaning zones is calculated as

\[ SC_i(z_j) = \frac{0.0597 \cdot m'_f(z_j)}{r_b(z_j)^2 \cdot r_f \cdot f_i \cdot \theta} \]  

which is similar to Eq. (5).

The mass \((g)\) of species \( i \) that is floated per bubble at any height \( z_j \) is therefore

\[ m'_f(z_j) = m'_f(z_{j-1}) f_b(z_{j-1}) \cdot f_b(z_j) \]  

if the conditions are such that the floated particles do not detach from the bubble surfaces.

Drainage of water and particles

The drainage velocities of the different mineral species are calculated in the model from the drainage velocity of water and the relation of the total area that is available for drainage to the thickness of the bubble wall, i.e. the distance between the bubbles. The drainage velocity of water is calculated in the present work from its measured concentration in the froth, but it can also be determined from experiments using liquid tracers in the cleaning zone. The distance between the bubbles is estimated from the calculated flowrates of water and solids in the froth, as described below. Assuming that the rate of drainage of any entrained species in the froth is proportional to its concentration at that level in the cleaning zone (Mays, 1978), the mass and volumetric flowrates of feed water at a height \( z \) in the cleaning zone are

\[ m_q(z) = m_q(0) \exp[-k_p z/V] \quad (g/\text{min}) \]

\[ = Q_q(z) \quad (\text{cm}^3/\text{min}) \]  

respectively, where \( m_q(0) \) is the flowrate of feed water entering the washing zone or the froth layer, \( k_p \) \((\text{min}^{-1})\) is the drainage rate constant for water, and \( V \) is the average bubble velocity.

At this stage, the exact mechanism of washing and the height of cleaning zone needed for the elimination of any specific amount of entrained gangue are not known. It may be postulated that a certain fraction of the wash water is instrumental in washing hydrophilic particles from the bubble walls at or near the interface, thus significantly reducing their recovery in the concentrate. If, say, 5% of the draining wash water is distributed over the walls of the bubbles, and the remaining water drains along the intersections between the bubbles, the part of the total distance between bubbles that is contributed by water in the washing zone will be given by
\[ \delta_q(z) = \frac{2(0.05(m_{vq} - m_{eq}) + m_q(z))}{f_b(z) 3.456 d_b(z)^2} \]  

(16)

where \( m_{eq} \) and \( m_{vq} \) are the measured flowrate of washing water and the flowrate of the water recovered in the concentrate respectively. In the froth layer,

\[ \delta_q(z) = 0.579 \frac{Q_q(z)}{f_b(z)} d_b(z)^2 \]  

(17)

since there is no downward-flowing wash water. From Eq. (15), the flowrate of water that is draining at any height \( z \) in the washing zone is

\[ m_{dq}(z) = m_q(0) \exp[-k_q z/V] + m_{vq} - m_{eq} = Q_{dq}(z) \]  

(18)

and, in the froth layer,

\[ m_{dq}(z) = m_q(0) \exp[-k_q z/V] - m_{cq} \]  

(19)

For floated mineral species \( i \), the decrease in the mass flowrate due to possible overloading of the bubbles is calculated from the rate of bubble growth (Eq. 7 to 12), assuming complete maximum coverage of bubbles above the detachment height, i.e. the void area fraction is (1-\( \theta \)). Analogous to Eq. (15), for entrained species

\[ m_{e_i}(z) = m_{e_i}(0) \exp[-k_{e_i} z/V] \]  

(20)

The total distance between bubbles at any height \( z \) above the interface can be calculated as

\[ \delta_t(z) = \delta_q(z) + \delta_b(z) \]

\[ \frac{n}{2} \int \rho \left[ \sum_{i=1}^{n} \frac{(m'_{f_i}(z) + m'_{e_i}(z))/\rho_i)}{\rho_i} \right] \]

\[ = \delta_q(z) + \frac{13.824 \ r_b(z)^2}{\rho_b(z)^2} \]  

(21)

where \( \delta_q(z) \) is the part of the bubble wall thickness that is contributed by floated and entrained particles and \( f_p(z) \) is the average volume fraction of particles immersed in bubble walls, its value being a complex function of the ratio of the floated to the entrained solids and water at different levels in the froth. As no method is currently available by which the value of this parameter can be estimated with any accuracy, it was assumed to stay constant at 0.9 in the washing zone, and to decrease from 0.9 to 0.8 between the base and the top of the froth layer because of the virtual absence of entrained particles in this zone. \( m'_{e_i}(z) \) is the mass of species \( i \) that is entrained per bubble and \( n \) is the total number of mineral species in the froth.

The equation that describes the radius of curvature of a Plateau border, \( r_{PB}(z) \), for a two-phase froth (Hartland and Barber, 1974) is now modified for a mineralized froth as follows:

\[ r_{PB}(z) = 7.02 \left[ \frac{2 \delta_t(z) Q_{e}(z) \ r_b(z) V^{0.15}}{ \rho_e(z) g r(z)^2} \right] \]  

(22)

where \( \mu_e(z) \) is the viscosity (g/cm.min) and \( \rho_e(z) \) the relative density of the slurry in the bubble walls, and \( g \) is the gravitational acceleration. The air holdup fraction, \( \epsilon(z) \), is approximated from the volumetric flowrates of the different mineral species being floated and entrained, and water, i.e.

\[ \epsilon(z) = \frac{[\Lambda_c - \frac{Q_e(z)}{V} - \frac{Q_{q}(z)}{U_q(z)}]}{\Lambda_c} \]  

(23)

where \( \Lambda_c \) is the cross-sectional area (cm\(^2\)) of the cell, \( U_c(z) \) is the calculated drainage velocity (cm/min) of water, and \( Q_{q}(z) \) is the volumetric flowrate of particles that are floated and entrained. (Normally, \( Q_q(z) << Q_e(z) \).) The viscosity of the slurry at any height \( z \) is (Kunitz, 1926 in: Perry and Chilton, 1973, p.3-247)

\[ \mu_e(z) = \mu_w \left[ 1 + 0.5 \phi_e(z) \right] \]  

(24)

where \( \mu_w \) is the viscosity of the water and \( \phi_e(z) \) the volume fraction of solids in the entrained slurry that is entrapped between the bubbles, calculated from Eq. (15) to (20), the mass flowrate of draining water, and the relative densities of the minerals. In other words, it is assumed that the floated particles form part of a rigid, ascending bubble surface. The hydraulic diameter of a border is (Hartland and Barber, 1974)

\[ d_h(z) = 0.205 \ r_{PB}(z) \]  

(25)

if \( \delta_t(z) \ll r_{PB}(z) \)  

Two criteria regarding the size and the properties of the Plateau borders must always be met, viz a) The thickness of the bubble walls decreases with increasing height above the interface owing to drainage of the entrained particles and water, i.e.

\[ \delta_t(z_j) \leq \delta_t(z_{j-1}) \]  

(26)
b) The radius of curvature of the Plateau border at any height is always smaller than or equal to the radius of the bubble at that specific height (Figure 1), i.e.

\[ r_{pB}(z) = r_b(0) \quad z = 0 < r_b(z) \quad z > 0 \]  

(27)

\[ \delta(z) < \frac{r_b(z)^2 \rho_b(z) g \epsilon(z)^2}{2 (7.02)^4 \mu_s(z) V} \quad z > 0 \]  

(28)

Therefore, from Eq. (22),

\[ U_1(z) = CF_I \left(1 + \frac{1 - \beta_1^2}{(1 + \beta_1^4)^{0.5}}\right) \]  

(30)

where

\[ CF_I = \frac{1 - \beta_1^2}{(1 + \beta_1^4)^{0.5}} \]

(31)

\[ \beta_1 = \frac{d_p}{d_b(z)}. \]

The correction factor CF\( I \) incorporates the wall effects in the terminal settling velocity of the different solid species, while the effect of the concentration of solids in the slurry that is draining on their terminal settling velocity is incorporated by the relationship (Madsen and Whittmore, 1958, in: Perry and Chilton, 1973; p. 5-64)

\[ U_{is}(z) = U_1(z)\left[1 - \phi_d(z)\right]^{1.22} \]  

(32)

\[ U_{is}(z) \] is the terminal settling velocity (cm/min) of species \( i \) in the suspension, and \( \phi_d(z) \) is the volume fraction of solids in the draining slurry. The value of \( \phi_d(z) \) is calculated from the mass flowrate of the floated particles, Eq. (18) and (20), the mass flowrate of solids recovered in the concentrate stream, and their relative densities.

The correction factor CF\( I \) incorporates the wall effects in the terminal settling velocity of the different solid species, while the effect of the concentration of solids in the slurry that is draining on their terminal settling velocity is incorporated by the relationship (Madsen and Whittmore, 1958, in: Perry and Chilton, 1973; p. 5-64)

\[ T_1 = \frac{m_{t1}(0) - m_{c1}}{\mu_c U_{is}(0)[M_{t1}(0) - (m_{f1}(0) + m_{e1}(0))]/\mu_c V} \]  

(33)

where \( m_{t1} \) is the mass flowrate (g/min) of species \( i \) in the concentrate. The factor \( T_1 \) ensures that the measured and calculated concentration of solids in the froth are equal at the interface.

Finally, analogous to Eq. (29), the concentration of species \( i \) ([g/cm\(^3\) of froth]) at any height in the froth can be written as

\[ C_i(z) = \frac{[m_{f1}(z) + m_{e1}(z)]}{\mu_c V} \left[1 + \frac{m_{f1}(z) + m_{e1}(z) - m_{c1}}{\mu_c T_1[U_{is}(z) + U_q(z)]}\right] \]  

(34)
EXPERIMENTAL METHODS

At the time of writing, the testwork was still in the initial stage. To verify the applicability of the model to the simulation of conventional froths, with a view to its application in flotation columns, tests were conducted on a laboratory scale in a modified Leeds open-top flotation cell. A deep froth was simulated by building up the sides of the cell so that the removal of concentrate was not possible.

Three size fractions of a sulphide ore, -212 +150 μm, -75+38 μm, and -38 μm, were obtained by milling and screening, and were used in tests to show the effect of particle size on the model parameters. The effects of aeration rate and collector (sodium ethyl xanthate) addition were also studied. Frother (Dowfroth 250) was added in standard amounts of 50 g/t. The results of some tests are summarized in Table 1. The -212+150 μm fraction formed a very shallow froth, even at high aeration rates, and therefore, for this fraction, no meaningful concentration-height profiles could be obtained from which simulations could be carried out.

During the tests, samples of froth were collected in trays at different heights above the pulp. A slide simultaneously separated the pulp and froth phases, permitting the ratio of the mass of solids and water in the froth to that in the pulp to be calculated. The built-up section of the cell was then replaced with a section that allowed the surface of the pulp to be scraped. Using the same aeration rate as before, the mass of solids and water that enters the froth per unit volume of air was determined by manual removal of the froth in a batch flotation experiment. The parameter \( X_{i2} \) is calculated from the mass flowrate of water and solids entering the froth and their concentrations in the pulp, i.e.

\[
X_{i2} = \frac{m_{i1}(0)C_{i2}q}{m_{q}(0)C_{i1}}
\]  

(34)

while \( X_{i2} \) is determined from the rate at which water and solids are recovered at the start and at the end of the batch flotation test. The value of \( X_{i2} \) and hence the mass flowrates of the floated and entrained fractions as they enter the froth, could therefore be calculated (see Table 1).

A sampling methodology for assessment of the continuous operational performance of the cleaning zone in a flotation column, is being developed.

DISCUSSION

Estimation of model parameters

Model parameters were estimated by fitting of the experimentally measured profiles of the concentration of water and of the respective size fractions in the froth at different heights above the pulp-froth interface. A simplified flowsheet of the computer program that was developed for this purpose is given in Figure 2.

If no detachment is to occur, the bubble surface area must be greater than that occupied by floated particles. A routine has therefore been incorporated in the program to ensure that this requirement is met at all levels in the froth during every iteration step in the estimation of \( k_q \) and \( k_ei \).

As shown in Figure 3, the model satisfactorily fitted the concentration-height profiles for the solid species in the froth. The corresponding calculated drainage velocity, bubble size and viscosity of the slurry that is entrapped in the bubble films are presented in Figures 4 to 6. The experimental conditions and the estimated model parameters are listed in Table 1.

Rate of aeration. Comparison of tests 1 and 2 shows that, at an increased rate of aeration, the equilibrium height of the froth increases, but the coalescence of bubbles is retarded (also see Figure 5). These findings are in accordance with the results of Vianatos, Finch, and Iaplanle (1986), and can be ascribed to the increased thickness of the bubble walls (due to a greater rate of transfer (RT) of solids and water into the froth), which reduces the probability of film rupture and consequent bubble breakdown. On the other hand, a simultaneous increase in the particle size increases the rate of coalescence, and bubble breakdown is enhanced (test 5). However, the thickness, \( \delta \), of the enveloping slurry layer at the pulp-froth interface is decreased. The transfer factor \( X_{i2} \) decreases with increasing particle size, and the empirical relationship

\[
X_{i2} = 1 - 0.429[\log(d_{p1})-1]([\rho - 1]
\]

where \( d_{p1} \) is expressed in microns, was found to fit the calculated data very well.

The drainage rate constants of water and entrained solids increase, possibly because of a reduced probability of entrapment, due to the increased bubble film thickness. The relatively high value of \( T \) and the increased (calculated) drainage velocity of solids from the froth (Figure 4) substantiate these results.

Particle size. Tests 1, 3 and 5 illustrate the effect of particle size on the model parameters. It should be noted that test 5 was performed at an aeration rate of 8 l/min (as in test 2), since only about 5 mm of froth was formed at an aeration rate of 4 l/min. The height of the froth increases with decreasing particle size, which has an effect similar to that of an increased rate of aeration, in that the rate of bubble coalescence decreases (Figure 5). Again, this can be ascribed to an increased RT of solids and water into the froth and an increased holdup of solids and water in the froth.
As expected, the drainage rate constants of entrained solids and water decrease significantly when the particle size is decreased, since the smaller particles drain less easily. As would be expected from the reduced size of the particles and the increased bubble film thickness, the relatively high value of \( T_4 \) suggests that entrapment of the ~38 μm fraction does not play a significant role in the drainage of these particles.
FIGURE 5. The variation in bubble size with distance above the pulp-froth interface.

FIGURE 6. Calculated viscosity of the slurry that is entrapped in the bubble films.

TABLE 1

Model parameters estimated from experimental testwork and the simulation of the concentration profiles of solids and water in the froth

<table>
<thead>
<tr>
<th>Test no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured and calculated parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aeration rate, l/min*</td>
<td>4.0</td>
<td>8.0</td>
<td>4.0</td>
<td>4.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Particle size, µm</td>
<td>-75+38</td>
<td>-75+38</td>
<td>-38</td>
<td>-75+38</td>
<td>-212+150</td>
</tr>
<tr>
<td>Particle radius, µm</td>
<td>27</td>
<td>27</td>
<td>12</td>
<td>27</td>
<td>90</td>
</tr>
<tr>
<td>Collector, g/t</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Froth height, cm</td>
<td>30</td>
<td>40</td>
<td>44</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>No.of bubbles at froth surface</td>
<td>36</td>
<td>40</td>
<td>225</td>
<td>36</td>
<td>900</td>
</tr>
<tr>
<td>Holdup in froth, g</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids</td>
<td>70.9</td>
<td>87.5</td>
<td>182.7</td>
<td>59.5</td>
<td>32.1</td>
</tr>
<tr>
<td>Water</td>
<td>357</td>
<td>769</td>
<td>635</td>
<td>349</td>
<td>204</td>
</tr>
<tr>
<td>C_{tq}', g/cm²</td>
<td>0.864</td>
<td>0.839</td>
<td>0.863</td>
<td>0.863</td>
<td>0.867</td>
</tr>
<tr>
<td>X_{is}</td>
<td>0.407</td>
<td>0.372</td>
<td>0.768</td>
<td>0.437</td>
<td>0.306</td>
</tr>
<tr>
<td>X_{i}</td>
<td>0.45</td>
<td>0.42</td>
<td>0.75</td>
<td>0.47</td>
<td>0.04</td>
</tr>
<tr>
<td>X_{i}X_{i}X_{i} g</td>
<td>0.183</td>
<td>0.156</td>
<td>0.576</td>
<td>0.205</td>
<td>-</td>
</tr>
<tr>
<td>m_{f}(0), g/min</td>
<td>39.93</td>
<td>66.60</td>
<td>30.43</td>
<td>33.49</td>
<td>41.86</td>
</tr>
<tr>
<td>m_{f}(0), g/min</td>
<td>32.67</td>
<td>48.23</td>
<td>91.31</td>
<td>29.69</td>
<td>1.75</td>
</tr>
<tr>
<td>m_{f}(0), g/min</td>
<td>396</td>
<td>586</td>
<td>362</td>
<td>321</td>
<td>318</td>
</tr>
<tr>
<td>Simulated parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v, 10⁻² cm</td>
<td>1.36</td>
<td>1.02</td>
<td>1.31</td>
<td>1.11</td>
<td>0.548</td>
</tr>
<tr>
<td>z, cm</td>
<td>4.0</td>
<td>8.0</td>
<td>44.0</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>θ</td>
<td>0.33</td>
<td>0.31</td>
<td>-</td>
<td>0.32</td>
<td>-</td>
</tr>
<tr>
<td>K_{x}, min⁻¹</td>
<td>1.84</td>
<td>3.81</td>
<td>0.33</td>
<td>1.97</td>
<td>-</td>
</tr>
<tr>
<td>K_{x}', min⁻¹</td>
<td>3.82</td>
<td>5.32</td>
<td>2.67</td>
<td>4.00</td>
<td>-</td>
</tr>
<tr>
<td>T_{i}</td>
<td>0.04</td>
<td>0.07</td>
<td>0.08</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

* Superficial gas velocity is 3.28 mm/s (0.129 ips) and 6.57 mm/s (0.258 ips) at aeration rates of 4 and 8 l/min respectively

* Estimated bubble size at the pulp-froth interface = 0.8 mm (3.5x10⁻² in)
Collector concentration. A comparison of tests 1 and 4 illustrates the effect of the collector dosage on the model parameters. Although an increase in the collector concentration from 50 to 100 grams per ton has no significant effect on the rate of bubble coalescence and the height of the froth, the rate of flotation is slightly improved, as is evident from Table 1. As shown in Figures 4 and 6, the drainage velocities and the viscosity of the slurry entrapped in the bubble films do not change significantly with collector concentration in the range studied. The drainage rate constants and the value of $T_1$ are similar to those in test 1, as expected. As was the case with the 212-150 micrometer fraction, no meaningful results could be obtained for a simulation when no collector was added, since only a very shallow froth was formed.

Model predictions

Operating conditions and model parameters. From the results of the testwork and simulations, it is possible to predict some trends that can be expected when the operating conditions in a flotation column are changed.

Firstly, an increased aeration rate would increase the RF of solids and water into the cleaning zone, and the drainage rate constants of entrained solids and water can therefore be expected to increase accordingly. Since an increased flowrate of wash water would increase the thickness of the bubble walls and also possibly wash entrained material from these walls, the drainage rate constants can be expected to increase even further. Secondly, the flotation of fine material (in contrast to the flotation of coarse material) would also increase the rate of transfer of solids and water into the cleaning zone, but increased amounts of wash water would probably be necessary to reduce the recovery of hydrophilic fines in the concentrate. As is evident from the results presented above, a larger dosage of collector, while increasing the rate of flotation, is not expected to significantly affect the operational performance of the cleaning zone. However, where the overloading of bubbles is a problem, the height of the cleaning zone should be reduced and the flowrate of wash water possibly increased to maintain a reasonable grade while optimizing recovery.

Performance of the cleaning zone. The ability of the model to predict the performance of the cleaning zone in a flotation column under different operating conditions is illustrated in Figures 7 to 9. While the values of the model parameters were assumed in this example (as summarized in Table 2), they are believed to be representative of the values that would typically be estimated in the simulation of the cleaning zone. However, a higher than normal flowrate of entrained particles was assumed to highlight the predictive ability of the model.

Figure 7 shows the variation in the concentration of solids at increasing heights above the collection-cleaning zone interface. The concentration decreases rapidly in the lower levels due to the drainage of entrained material - slightly faster for simulation 1 than for simulation 2 because of the higher drainage rate constant. As can be seen from Figure 8 (simulation 1), overloading of bubble surfaces occurs 1.2 m above the interface, because of the high flowrate of floated species entering the cleaning zone and the relatively high rate of bubble growth (also see Table 2). An increase in the size of the bubbles generated in the collection zone accelerates this process.

The variation in the thickness of the bubble walls and the parameter incorporating the wall effects in the drainage velocity of solids along
the Plateau borders, $d_p/d_h(z)$, are shown in Figure 9. As previously mentioned, it was assumed that 5% of the draining wash water drains along the bubble walls. A comparison of the results from simulations 1 and 2, with a $d_b(0)$ of 2 mm, shows that the increased thickness of the bubble walls can be ascribed mainly to the decreased drainage rate of water and entrained material. The ratio $d_p/d_h(z)$ is also increased, contrary to what would be expected from an increased wall thickness, but computed results have shown that the size of the bubbles ($r_b(z)$ in Eq. 22) is the dominant factor.

The pronounced effect of the size of the bubbles generated in the collection zone on the performance and properties of the cleaning zone is underlined further when the curves for simulation 1 at an initial bubble size of 2 and 3 mm are compared. The increased thickness of the bubble walls is the result of the decreased bubble surface area, and the decreased ratio $d_p/d_h(z)$ indicates that this also increases the cross-sectional Plateau border area.

![Graph showing the variation of the bubble wall thickness and the ratio $d_p/d_h(z)$ with height in the cleaning zone.](image)

**FIGURE 9.** The variation of the bubble wall thickness and the ratio $d_p/d_h(z)$ with height in the cleaning zone.

**TABLE 2**

Model parameters for the prediction of the properties of the cleaning zone

<table>
<thead>
<tr>
<th></th>
<th>Washing zone Simulation no.</th>
<th>Froth layer Simulation no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Height, m</td>
<td>1.80</td>
<td>1.80</td>
</tr>
<tr>
<td>$r_b(0), \text{mm}$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$C_b$</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>$m_{f1}(0), \text{kg/min}$</td>
<td>5.00</td>
<td>3.75</td>
</tr>
<tr>
<td>$m_{b}(0), \text{kg/min}$</td>
<td>1.75</td>
<td>3.00</td>
</tr>
<tr>
<td>$m_{q}(0), \text{kg/min}$</td>
<td>20.25</td>
<td>20.25</td>
</tr>
<tr>
<td>$k_{s1}, \text{min}^{-1}$</td>
<td>6.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$k_{q}, \text{min}^{-1}$</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Wash water, kg/min</td>
<td>10.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Water in conc., kg/min</td>
<td>0.50</td>
<td>0.60</td>
</tr>
<tr>
<td>Solids in conc., kg/min</td>
<td>4.5</td>
<td>3.75</td>
</tr>
</tbody>
</table>

**Conditions**
- Aeration rate 150 l/min (5.3 cfm)
- Superficial gas velocity 1.2 m/min (3.94 fpm)
- Packing factor 0.5
- Particle diameter 50 μm (2x10^-2 in)
- Relative density of particles 3.0 g/cm³ (187 lb per cu ft)
CONCLUSIONS

A model has been developed that describes the behaviour of mineral particles in the cleaning zone of flotation columns. The possible detachment of floated particles from bubble surfaces is related to the flux of bubble surface area with increasing distance from the collection-cleaning zone interface, while the drainage velocities of the particles are calculated from their properties, the drainage velocity of the water, and the cross-sectional area available for drainage.

Laboratory testwork on a sulphide ore has shown that an increased rate of aeration would increase the rate of transfer of particles and water into the cleaning zone, and their respective drainage rate constants would increase accordingly. A finer grind increases the holdup of solids and water in the froth, and the drainage rate constants of mineral particles and water are significantly decreased.

The model can successfully simulate the concentration-height profiles of solids and water in a conventional froth. Also, because of its predictive ability, the model may be utilized as a powerful and flexible tool to provide additional insight into the operational performance of flotation-column froths.

Much work needs to be done on the simulation of flotation columns, particularly the cleaning zone. Also, the relationships between the model parameters under different operating conditions should be investigated further so that the model can be used as an aid in the scale-up and design of flotation columns.

ACKNOWLEDGEMENT

This paper is published by permission of the Council for Mineral Technology (Mintek).

REFERENCES


Evaluation of the Performance of the Froth Phase in Flotation

V E ROSS* and J S J VAN DEVENTER†

*De Beers Diamond Research Laboratory, P.O. Box 916, Johannesburg 2000. Formerly at: Minerals Engineering Division, Mintek, Private Bag X3015, Randburg 2125. †Dept of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7600

Techniques were developed to evaluate the behaviour of mineral particles and water in the froth phase of flotation cells. This paper describes a simple method, requiring only a single kinetic batch flotation test, to separate the contributions made by the true flotation and entrainment of mineral particles during laboratory-scale test work. It also details methods for analysing the behaviour of the various mineral species in the froth phase of large-scale cells, requiring the rates of transfer from the pulp into the froth and from the froth into the concentrate to be measured. The possible detachment of floating species in the froth, causing reduced recoveries, may be inferred from the grade and concentration profiles of the various particle size fractions that are measured in the froth. This allows the optimum froth depth in terms of grade, recovery and froth mobility to be established.

The practical application of the various techniques to interpret flotation results is illustrated by examples from laboratory-scale and on-site plant testwork.

Introduction

The efficiency of the flotation process and the characteristics of the froth are dependent upon a large number of factors, such as the type and concentration of the collector and frother, particle size and degree of liberation, the degree of hydrophobicity, and the presence of slimes. In order to optimize the operation of a flotation circuit, it is necessary that the best suite of conditions for the particular orebody/mineral is found.

Batch flotation tests play a very important part in the optimization of flotation circuits. Such tests are often used in investigations of the effect of flotation reagents on the efficiency of the flotation process before these reagents are tested on an industrial scale. It is therefore very important that the results that are obtained from such a test are interpreted correctly (i.e. that an estimation of true flotation and entrainment is made) so that it can be of use in the development and improvement/optimization of flotation operations.

Often the performance of flotation circuits or banks is evaluated by calculating the overall recoveries and grades obtained in any section of the circuit. This is normally accomplished by measuring feed, concentrate and/or tailings flowrates and grades. While such a procedure is essential to ensure that production objectives are met, it normally provides little, if any, information on the performance of individual flotation cells, or that of the pulp and the froth phases in any particular cell. Improvements can only be accomplished if the factors responsible for poor performance are identified and rectified.

Although the behaviour of the froth phase influences both the grade and the recovery of valuable mineral in the concentrate, little work has been done on assessing its performance in an industrial environment, i.e. to tell whether it is operating satisfactorily or not. Since rich orebodies are being depleted rapidly, it has become increasingly important to fine-tune flotation cells, and especially the froth phase. This paper describes some simple methods and apparatus that have been developed to (1) evaluate laboratory batch flotation results by distinguishing between the contributions made by the true flotation and entrainment of mineral...
particles, and (2) assessing the performance of the froth phase in large-scale flotation cells by interpreting the concentration and the grade profiles of the various species in the froth. The practical application of these methods is illustrated by examples from laboratory and on-site plant testwork.

**Methods, apparatus and application**

**Contributions of true flotation and entrainment:**

**Batch flotation tests**

**Method**

The method for distinguishing between the contributions of true flotation and entrainment during batch flotation tests, proposed by Ross, involves only one kinetic batch flotation test, in which the recoveries of solids and water, and the consequent changes in the composition of the pulp and the characteristics of the froth with time, are used in the calculation of a transfer factor, \( X_i(t) \), for entrained particles that belong to species i. The transfer factor describes the differential classification of entrained solids and water during flotation, and is defined as

\[
X_i(t) = \frac{m_{ei}(t)C_{\text{eq}}(t)}{m_{eq}(t)C_{\text{ei}}(t)} \tag{1}
\]

where \( m_{ei}(t) \) and \( m_{eq}(t) \) are, respectively, the masses of entrained solids and water that are recovered in a specific time interval \( t \), and \( C_{\text{eq}}(t) \) and \( C_{\text{ei}}(t) \) are the corresponding concentrations (g/L of pulp) of water and solid species i in the pulp. It is important that the time-dependence of the transfer factor is considered and interpreted correctly, since factors such as the entrapment of particles in the bubble films, for example, can cause errors in the calculated amount of entrained material.\(^7\) The concentrations of solids and water in the pulp at any time \( t \) can be calculated if the level of the pulp is kept constant by the addition of make-up water.

The value of \( X_i(t) \) is determined from the relationship \( Y_i(t) \) between the total masses of solids and water that are recovered during flotation, viz.

\[
Y_i(t) = \frac{m_{ei}(t)C_{\text{eq}}(t)}{m_{eq}(t)C_{\text{ei}}(t)} \tag{2}
\]

where \( m_{ei}(t) \) (in grams) is the total mass of solids recovered in any specific time interval \( t \). It is assumed that only entrained solids are recovered at the end \( (t \rightarrow t_a) \) of the batch flotation test, i.e. after flotation has ceased. Therefore,

\[
X_i(t) = Y_i(t)
\]

when \( t \rightarrow t_a \) \tag{3}

The mass \( m_{ei}(t) \) of particles that were recovered by true flotation can then be calculated from the total mass \( m_{ti}(t) \) and the mass \( m_{ei}(t) \) that was recovered by entrainment.

**Apparatus**

Laboratory-batch flotation tests may be carried out in any suitable cell, although one that facilitates the unobstructed removal of concentrate (such as the Leeds open-top or Autofloat cells) is preferable. The cell should be equipped with a pulp level controller (or a transparent cell wall if make-up water is to be added manually), and care should be taken that the froth is removed at a constant depth and a constant rate throughout the flotation test. Figure 1 gives examples of froth scrapers that are suitable for removing concen-
Particle size distribution and composition of the feed material of the batch flotation test

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Mass percentage</th>
<th>Mass % of feed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>+212</td>
<td>85.05</td>
<td>93.40</td>
</tr>
<tr>
<td>-212 to +150</td>
<td>10.60</td>
<td>5.50</td>
</tr>
<tr>
<td>-150 to +106</td>
<td>2.19</td>
<td>1.10</td>
</tr>
<tr>
<td>-106 to +75</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>-75 to +53</td>
<td>0.71</td>
<td>-</td>
</tr>
<tr>
<td>-53 to +38</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>-38</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>+38</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Feed mass = 910 g solids

Other particles

- 7,5 mg/L of liquid for a further 2 minutes. After this, the air was turned on. The impeller speed and aeration rate were kept constant at 1 200 r/min and 6 L/min respectively for the duration of the test. Time $t = 0$ was taken as the instant the froth overflowed into the first froth-collecting tray. The froth was removed at a constant, controlled rate of 10 scrapes per minute, the entire surface of the froth being covered with each scrape. Make-up water was added throughout the test to maintain the pulp level. Timed samples were obtained at cumulative flotation times of 0.25, 0.5, 1, 2, 4, and 8 minutes.

**FIGURE 2.** Recoveries of solids and water and the variation in the parameter $Y(t)$ during the batch flotation test
Figure 2 gives the recoveries of solids and water, as well as the changes that occurred in the values of the parameter \( Y_i(t) \). It must be noted that, although in this example the total amount of solids is considered to belong to the same single species for simplicity, the same method of analysis can be applied to both individual size fractions and the various minerals such as pyrite and silica. The values of \( Y_i(t) \) decreased sharply with time during the initial stages of flotation, suggesting a corresponding drop in the rate of true flotation. (A high value of \( Y_i(t) \) in relation to \( Y_i(\infty) \) means that the ratio of floating material to entrained material is high, as shown by Equations [1] and [2].) Figure 2 also shows the calculated amounts of material recovered by true flotation and entrainment. From the total 33 g of solids that reported to the concentrate after 8 minutes, a calculated 22 g was recovered due to true flotation. These figures correlate well with the final concentrate grade of 11.9% sulphur.

This method involves only one kinetic flotation test, and is therefore suitable for use in the investigation of the effect of froth depth on the amount of material that is recovered by true flotation. (Variations in the possible detachment of floating particles from the bubbles in the froth with variation in the froth depth are considered.) Since the changes in the characteristics of the froth and the composition of the pulp with flotation time are also taken into account, it can be applied over any flotation time interval. For example, if a large amount of solids is recovered by true flotation and/or entrainment, the corresponding drop in the solids content of the pulp will result in a decreased possibility for the entrainment of particles. The method has been found to be of acceptable accuracy.6,8

The assumption that the pulp is perfectly mixed may not be true for very coarse feeds and for low pulp densities, and under conditions of poor suspension the ratio \( C_T(t)/C_T(\infty) \) near the pulp-froth interface maybe higher than was calculated from the assumption. If this ratio has a marked effect on the entrainment of particles in the upper regions of the pulp, i.e. if the composition of the pulp at the pulp-froth interface determines the amount and nature of species that is entrained, the values of \( X(t) \), and hence \( m_e(t) \), may be underestimated. Therefore, under these conditions, the mass of particles recovered through true flotation may be over-estimated.

**Rate of pulp-froth transfer: Large cells**

**Method**

The rates at which solids and water enter the froth in large-scale cells may be determined by assuming that, at the same superficial air flux, the ratio of the volume of slurry to the volume of air that enters the froth is the same in the case of both large-scale and laboratory-scale cells. This procedure is necessary since, as far as can be ascertained, no procedure is currently available whereby these mass flowrates can be measured directly, or more accurately.

A pulp sample that is extracted just below the pulp-froth interface in the plant cell may be batch-floated in a laboratory cell at the same superficial air flux as used on the plant. The recovery of solids and water at the start of the batch test will therefore allow the mass flowrates of solids and water entering the froth in large cells to be calculated from a knowledge of the aeration rate.

**Apparatus**

A representative pulp sample can be extracted from the pulp phase in the large-scale cell by vacuum. Since the ratio of solids to water (i.e. the effective pulp density) can change at various positions within a large flotation cell, it is advisable to carry out testwork on a number of such samples.

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Ratio to water in pulp</th>
<th>Transfer factor</th>
<th>Flowrate into conc. (A)</th>
<th>Flowrate into froth (B)</th>
<th>Ratio A/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( +300 )</td>
<td>0.17</td>
<td>0.1</td>
<td>54</td>
<td>1328</td>
<td>0.04</td>
</tr>
<tr>
<td>(-300 +150 )</td>
<td>0.23</td>
<td>0.24</td>
<td>170</td>
<td>1443</td>
<td>0.19</td>
</tr>
<tr>
<td>(-150 +106 )</td>
<td>0.17</td>
<td>0.30</td>
<td>120</td>
<td>1073</td>
<td>0.11</td>
</tr>
<tr>
<td>(-106 +75 )</td>
<td>0.14</td>
<td>0.49</td>
<td>101</td>
<td>1014</td>
<td>0.10</td>
</tr>
<tr>
<td>(-75 +45 )</td>
<td>0.21</td>
<td>0.59</td>
<td>180</td>
<td>1597</td>
<td>0.11</td>
</tr>
<tr>
<td>(-45 )</td>
<td>0.13</td>
<td>0.71</td>
<td>426</td>
<td>3281</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**TABLE 2. Analysis of the fluor spar recleaner froth**

---

Stellenbosch University https://scholar.sun.ac.za
and correlate the results. The rates at which the various species enter the froth from the pulp can be determined by flotation of the pulp sample in a laboratory-scale flotation cell, such as described above. During this test, which should be done directly after extraction of the pulp sample, no additional flotation reagents should be added. The rates at which the various solid species and water enter the concentrate may be determined by taking timed samples at the overflow weir of each flotation cell. These data also allow a recovery curve for the cells in a flotation bank to be determined, which is essential if the possible poor performance of a particular cell is to be identified and improved.

Application
Batch flotation tests were carried out on a pulp sample that was extracted from a recleaner cell on a fluorspar flotation plant. The solids in the pulp were divided into six size fractions, as shown in Table 2. The results show that the transfer factors increased with decreasing particle size, which is in accordance with previous work. The ratio of the flowrates in the concentrate to that entering the froth showed that approximately 11% of the -150 μm fractions survived the cleaning action of the froth, while only 4% of the particles in the +300 μm fraction that entered the froth, reported to the concentrate.

This method could be useful to identify and rectify unacceptable losses or high entrainment of particles in the froth phase. For example, the high entrainment of low-grade fines (indicated by a large transfer factor X; and a high ratio of the transfer rates into the concentrate and into the froth, i.e. A/B in Table 2) could be overcome by spraying the froth with wash water, similar to the technique used in flotation columns. Conversely, the suspension and flotation of the coarser size fractions in a pulp could be improved by increased impeller speeds/aeration rates if the transfer factors and the ratios of froth-concentrate transfer are low.

This method should be used essentially as an instrument for the fine-tuning of flotation cells by optimizing the rates at which the size fractions that are rich in valuable mineral are transported into the froth and into the concentrate.

Froth concentration and grade profiles: Large cells
In addition to determining the rates at which the various species in a flotation cell are transferred from the pulp into the froth and the concentrate (which gives only a global picture of froth behaviour), the concentration and grade profiles in the froth may be studied to obtain information on their respective drainage rates, detachment, etc. The detachment, and consequent loss, of floating particles from the bubble surface can occur due to two major mechanisms. Firstly, weakly hydrophobic particles can be displaced by other, more hydrophobic particles if the froth is overloaded (e.g. in cleaner cells), or they can become dislodged if the bubble films are not stable enough to support them (e.g. in the upper regions of the froth). They can also be 'washed' from the bubbles in the lower regions of the froth owing to the friction between the bubbles and the slurry draining back to the pulp. It is important that this type of data is interpreted correctly if recovery and the grade of the concentrate product are to be optimized.

Method
The concentration (expressed in mass of solids per unit volume of froth) and grade (expressed in %)
profiles of the various species in the froth phase of large flotation cells may be calculated from froth samples of a known volume that are extracted at various heights above the pulp-froth interface.

**Apparatus**

A froth sampling lance, such as the one shown in Figure 3, may be used to extract froth samples of a known volume from large-scale cells. The sample flows into the collecting chamber under the hydrostatic pressure in the froth, i.e. no vacuum is used to extract the sample. (Corrections must be made for the variation in the hydrostatic pressure in the froth, i.e. the flowrate of froth into the sampling lance.) The volume of froth that is collected is given by the product of the area of the opening and the distance that the lance traverses in the froth, sliding on rails positioned above the froth surface.

Cutting et al.\(^{10}\) described a stationary, multi-point sampling lance in which froth samples for grade and pulp density analysis are extracted by vacuum. The concentration profiles are determined by differentiating the hydrostatic pressure profile that is measured in the froth via a dip tube assembly. The pressure data can contain considerable noise, an effect which can be overcome largely by fitting an exponential function to the data.

**Application**

Froth samples of a fixed volume were extracted at
different heights above the pulp-froth interface in a rougher cell in a pyrite flotation plant and a cleaner cell in a fluorspar flotation plant, using the 'mobile' froth sampling lance described above.

The grade (i.e. mass percentage) profiles for the various size fractions in the pyrite rougher froth are shown in Figure 4. The +212 μm fraction started to detach at a height of approximately 8 cm above the pulp-froth interface, as can be inferred from the rapid decrease in the grade of this species above this height. This particular froth was well-drained, and it is believed that this effect was caused by the bubble films which became too fragile to support such large particles. In a similar way, the -212 +150 μm fraction started to detach at a height of 12 cm above the pulp-froth interface. The calculated concentration of the floating particles in all the size fractions at the pulp-froth interface was significantly higher than the total concentration of the particular size fraction at the surface of the froth, from which it can be concluded that, in all the size fractions, floating particles actually detached from the bubbles in the froth. In the grade profiles (Figure 4), the detachment of the -75 +53 μm fraction, for example, was obscured by the behaviour of the +150 μm fractions in the froth.

The grade profiles for sulphur within the various size fractions are shown in Figure 5. From these profiles, it would also not have been possible to infer the detachment of floating species, since, in all size fractions, the sulphur grade increased consistently with increasing height in the froth. This happened presumably because the rate at which the floating particles (high sulphur content) detached from the bubbles was slower than that at which the gangue (low sulphur content) drained from the froth. This example shows that the behaviour or particles of a different size can obscure that of the species under observation, and it is therefore important that the concentration of floating species entering the froth, as well as the grade profiles in the froth, be determined.

Figure 6 shows that the ratio of solids to water decreased with increasing height above the pulp-froth interface in the pyrite rougher froth, but increased in the froth of a cleaner cell on the same plant. These trends were simulated accurately by a computer package that was developed to study the behaviour of mineral particles and water in the froth phase of large-scale flotation cells (more details of this package are given elsewhere11). Previous work6 has shown that, when a dilute pulp containing a high percentage of hydrophobic particles is floated, the fluidity (i.e. mobility) of the froth will be low. This is because unhindered drainage of water occurs in the lower regions of the froth, while the presence of floating particles rapidly increases the viscosity of the slurry in the upper regions of the froth. Under such conditions, it may be useful to use water sprays to enhance both the grade and the mobility of the froth.

In froths that are heavily loaded with floating material, particles of different sizes can behave similarly. The results for the fluorspar cleaner froth in Figure 7 show that the total concentration of all the size fractions decreased smoothly and to the same degree with increasing height in the froth. Therefore, no significant changes occurred in the grade (i.e. mass percentage) profiles of the respective size fractions in the froth (Figure 8). The grade within the various size fractions
(expressed in percent CaF$_2$) also increased consistently with increasing height above the interface.

Contrary to the example given in Figure 4, no detachment of floating species in any size fraction could be detected by observation of the grade profiles, since there was no decrease in the grade of any species with increasing height in the froth. Table 3 shows that, for all the size fractions, the concentration of the floating species at the pulp-froth interface was larger than the total measured concentration of the species at the froth surface. Detachment of floating particles from the bubbles due to the friction between the bubbles and the slurry draining back to the pulp was therefore taking place. (Because the bubbles were heavily loaded, it is possible that a certain degree of displacement also occurred. However, as yet it is not possible to distinguish between the two mechanisms if both are operating in the froth.)

It can be assumed that floating particles are lost from the bubble surfaces in the froth at a height $z$ above the pulp-froth interface if their total concentration in the froth at all heights above $z$ is lower than at $z$. This will normally be accompanied by a decrease in the grade of the particular species of valuable mineral with further height in the froth. However, the concentration of the floating species in the froth at the pulp-froth interface must also be determined to ascertain
whether this concentration is greater than the total concentration of the species at any height in the froth. If it is, and if no sharp changes in the grade profiles are observed, especially in the middle or upper regions of the froth (Figure 4), it can be reasonably assumed that detachment of floating particles occurs in the lower regions of the froth. This process will be caused mainly by the shear forces and interaction between the bubbles as they crowd at the base of the froth, and the draining of the slurry back to the pulp. In flotation columns, where wash water is used to clean the froth, this process will occur in a narrow region at the pulp-froth interface.\textsuperscript{12}

These results have highlighted the following points:

(1) In addition to the measuring of the grade profiles of species in the froth (determined from samples of froth extracted at different heights above the pulp-froth interface), their concentration in the froth should be measured, i.e. it must be known what volume of froth was extracted;

(2) Only size-by-size concentration data of the solids should be compared when froth data is interpreted. This is necessary since the behaviour of particles of a different size and composition can obscure the behaviour of the species under observation;

(3) The possible detachment of floating particles from the bubbles due to their displacement or dislodgement, which could occur in overloaded or well-drained froths, must be inferred from the grade profiles in conjunction with the concentration profiles in the froth.

Conclusions

Simple methods and equipment have been developed to distinguish between the contributions by true flotation and entrainment of mineral particles during batch flotation tests, and to evaluate the performance of the froth phase in large-scale flotation cells.

A 'transfer factor' may be used to describe the differential classification of entrained mineral particles and water during batch flotation tests. This factor is calculated from the recoveries of solids and water, and from the changes in the composition of the pulp and the characteristics of the froth with time during a single batch flotation test. The amount of material that is recovered through true flotation (i.e. solids that are attached physically to the bubble surfaces) is obtained from the calculated amount of entrained material and the total measured mass of solids recovered in any specific time interval.

The determination of both the rates of pulp-froth and froth-concentrate transfer for the various particle size fractions in large-scale cells allows possible problem areas with regard to pulp-froth transfer and froth removal methods to be identified. The following parameters should be estimated to assess the metallurgical performance of such cells:

(1) \textit{The rate of pulp-froth transfer.} The respective rates at which the different species in the pulp enter the froth may be estimated by the laboratory-scale flotation of a representative sample of pulp that is extracted from the plant-scale cell. This flotation test should be carried out at the same superficial air flux in both cells;

(2) \textit{The concentration of the various species in the froth.} Interpretation of concentration profiles of solids and water can yield important information on the drainage rates of the various species in the froth. These profiles can be determined by extracting froth samples of a known volume at different heights above the pulp-froth interface;

(3) \textit{The grade of the various species in the froth.} The grades of valuable mineral and pulp density profiles can be determined from froth samples extracted at various heights above the pulp-froth interface. This will allow the optimum froth depth in terms of grade, recovery and froth mobility to be established.

\begin{table}
\centering
\caption{Concentration data for the fluor spar cleaner froth}
\label{tab:fluorspar_froth}
\begin{tabular}{llll}
\hline
Size & Concentration of floating species at interface & Total concentration at froth surface	\\
\mu m & g/l & g/l \\
\hline
+300 & 11.1 & 8.0 \\
-300 + 150 & 36.8 & 21.5 \\
-150 + 106 & 22.9 & 12.5 \\
-106 + 75 & 18.6 & 9.0 \\
-75 + 45 & 24.3 & 24.0 \\
-45 & 37.0 & 17.5 \\
\hline
\end{tabular}
\end{table}
Acknowledgements
This paper is published with permission of Mintek, and is based on doctoral research carried out at the University of Stellenbosch.

References
FOURTH WORLD CONGRESS
OF CHEMICAL ENGINEERING

Karlsruhe/Germany
16–21 June 1991

STRATEGIES 2000

PROCEEDINGS
Session 6.3: Metallurgical Industries

Selected Paper

The Evaluation of Flotation Froth Behaviour on the Basis of Mass Transport Phenomena

V. E. Ross, J. S. J. Van Deventer, Stellenbosch/ZA

ABSTRACT

A mathematical model has been developed to evaluate the behaviour of the flotation froth phase on the basis of mass transport phenomena, by simulation of the flotation, entrainment and drainage of solid particles and water. An example is given of how the model may be applied to simulate the froth surface velocity and the concentration profiles in the froth phase of a large-scale flotation cell. These profiles were described satisfactorily by the model, the simulation results showing that the drainage rate constants of both the floating and the entrained fractions increased with increasing particle size. This indicates that the recovery of coarse particles in large cells could be improved by maximising the lip length of the cell, e.g. by providing additional concentrate launderers in the froth phase.

INTRODUCTION

The importance of the froth phase of the flotation process, and the role it plays in cleaning the concentrate product, have long been realized. Although most of the early attempts to model the froth phase were based on the model of Arbiter and Harris (Ref. 1) who assumed that both the pulp and the froth phases are perfectly mixed, many studies carried out in recent years have shown that, especially in large cells, the assumption of a perfectly mixed froth phase is over-simplified. The principal uncertainties that have limited the application of such models resulted from an inability to quantify the behaviour of the froth phase. For instance, Cutting et al. (Ref. 2) used a cell efficiency factor to account for the limited probability of pulp-to-concentrate transfer during scale-up, while Woodburn et al. (Ref. 3) and King (Ref. 4) used a froth transfer coefficient in network simulation. However, the flotation behaviour, residence time and drainage of the froth in cleaner banks differ widely from that in roughers (Ref. 5), and the use of rate constants that have been obtained in one flotation stage or under a particular set of operating conditions can thus give incorrect estimates of the performance of a complete flotation plant. Clearly, it is important that the influence of operating conditions on the behaviour of solids and water in the froth, and the interactions between the sub-mechanisms operating in the froth, be understood fundamentally before flotation cells and networks can be modelled more accurately.

This paper describes the methodology of evaluating the behaviour of the froth phase on the basis of mass transport phenomena, viz the flotation, entrainment and drainage of solids and water. The application of the model to investigate the behaviour of solid species in the froth phase of large-scale flotation cells is illustrated.
MODEL DEVELOPMENT

For brevity, only the most important features of the model are presented here. (A more detailed description is presented elsewhere (Refs. 6, 7). Although the model is applied to the more complex case where the kinetics of the froth are approximated by two-dimensional flow patterns, the same principles can be applied in simulating froth behaviour under plug-flow conditions, such as in flotation columns where the length-to-diameter ratio of the froth is high (Ref. 8).

A schematic representation of a typical froth phase in a so-called conventional, or mechanically-agitated, flotation cell is given in Figure 1. The dimensions of the froth phase are characterized by the length of the flotation cell, $L$, its width $W$, the total froth depth $H$, and the height of the concentrate discharge weir above the pulp-froth interface, $z_w$. The froth overflows the concentrate weir at a height $z_w$. The total volume of the froth is divided into 4 different stages, denoted by the circled numbers in Figure 1, that are identified on the basis of froth flow characteristics that are dominant in each stage under observation.

It is assumed that the flux of air entering stages 1 to 3 at the pulp-froth interface is independent of the distance from the cell backplate, i.e. the distance from the centre of the cell in the case of dual concentrate weirs, in each stage. (A model to evaluate froth performance when the air is distributed unequally over the pulp-froth interface, is described elsewhere (Ref. 7). All the air that enters stage 1, $G_1$, leaves the surface of the froth within its boundaries and is thus inefficient for the purpose of flotation.

The shape of bubble streamlines at any coordinate $(x, z)$ in stage 2 is given by (Ref. 7)

$$ x (c_h - z) = c_0 $$

$$ c_h = F_h + z_w $$

where $c_0$ is a characteristic constant for a particular streamline, and $F_h$ a parameter describing the surface velocity of the froth. The bubble velocity at the border between stages 1 and 2, i.e. at $x = 0$ and at a height $z$ above the pulp-froth interface, is (Ref. 7)

$$ V(0, z) = V(0, 0) (c_h - z)/c_h $$

where $V(0, 0)$ is the velocity of the bubbles as they enter the froth. The volumetric flowrate ($L/min$) of air from stage 2 (i.e. to a depth of $z_c$) into stage 4 is

$$ G_{2 \rightarrow 4} = G_2 \frac{x_a}{L_2} \int_0^{L_2} B(x) \, dx $$

where $G_2$ ($L/min$) is the volumetric flowrate of air entering stage 2, $x_a$ is the origin of the bubble streamline that intersects the coordinate $(L_2, z_c)$, and $B(x)$ ($m/min$) is the flux of air through the surface due to bubble breakage. A fraction $\alpha$ of the air that enters stage 2 is transferred laterally over the $x = L_2$ boundary into stage 3. The bubble velocity in stage 3 therefore increases linearly with increasing height above the pulp-froth interface, i.e.

$$ V_3(z) = a_3 + b_3 z $$

where

$$ a_3 = G_3/A_3 \phi \quad b_3 = \alpha G_2/A_3 z_w \quad A_3 = L_3 W $$
In these equations, \( G_3 \) is the volumetric flowrate of air entering stage 3, and \( \phi \) is the fractional air hold-up at the pulp-froth interface. For computational simplicity, it is assumed that froth is distributed homogeneously in a horizontal direction over the interval \( L_3 \) once it is transferred from stage 2 into stage 3. The total volumetric flowrate of air into stage 4 is therefore

\[
Q_4 = G_{2\rightarrow 4} + \alpha G_2 + G_3
\]

(5)

the magnitude of the froth velocity (horizontally) being

\[
V_d(x) = a_d + b_d(x - L_2)
\]

(6)

where

\[
\alpha_4 = \frac{G_{2\rightarrow 4}}{W z_c}
\]

and

\[
\alpha G_2 + G_3 - \frac{1}{L_2} \int B(x) dx
\]

\[
b_4 = \frac{1}{A_3 z_c}
\]

Kinetics of solids and water

The kinetics of the solids may be described in terms of the kinetics of the carrier medium, i.e. the bubbles, by classification in terms of size, grade and/or floatability. If it is assumed that the rate of detachment of mineral particles or water from the bubble films is proportional to the concentration of the specific component in the froth, the concentration \( C(l) \) of any particular species in the froth at a distance \( l \) along a bubble streamline is

\[
\begin{align*}
C(l) &= C(0), & \text{if } l < l_d \\
C(l) &= C(0) \exp\left[-k(l - l_d)/V(l)\right], & \text{if } l \geq l_d
\end{align*}
\]

(7)

where \( C(0) \) (g/l) is the concentration of the species as it enters the froth, \( k \) (min\(^{-1}\)) is the drainage rate constant (DRC), describing the rate at which the species detaches from the upward-flowing stream of slurry, and \( l_d \) (cm) is the distance along a bubble streamline at which this process commences. Both entrained solids and water are assumed to start draining back to the pulp as soon as they enter the froth, since they are not physically attached to the surfaces of the bubbles (i.e. \( l_d = 0 \)). The concentration as a result of entrainment is calculated by using a transfer factor \( X \) to describe the differential classification of entrained solids and water upon their entry into the froth (Refs. 9, 10).

Since the characteristics of the froth in the region next to the concentrate weir (i.e. stages 3 and 4 in the model) may be different to those in the main body of the froth (stages 1 and 2) where the conditions are generally more quiescent, the DRCs of the floating and the entrained species will also differ. For simplicity, it is consequently assumed that the DRCs of corresponding species in stages 3 and 4 are equal; similarly, those in stages 1 and 2 are equal.

**CALCULATIONS**

The DRCs of the various species in stages 1 and 2 of the froth are estimated from simulation of the concentration profiles at the border of these two stages, i.e. at \( x = 0 \). The DRCs in stages 3 and 4 of the froth are calculated from the constants in stages 1 and 2, and the experimentally measured rate at which the respective species report to the concentrate.
RESULTS AND DISCUSSION

Figure 2 gives a typical example of the ability of the model to simulate the surface velocity and the concentration profiles of the various species in the froth phase of an industrial-scale flotation cell. Table 1 gives the values of some of the model parameters that describe the dimensions of the froth and the kinetics of the bubbles, while Table 2 gives the drainage rate constants (DRCs) that were estimated from simulation of the concentration profiles in the froth.

The DRCs of both the floating and the entrained solid species in stages 1 and 2 of the froth decreased with decreasing particle size. This indicates that the finer particles were less severely influenced by the conditions in the main body of the froth than the coarser particles, since they were draining at a slower rate. In the region next to the concentrate weir, denoted by stages 3 and 4, the DRCs of especially the floating particles in the coarser size fractions increased relative to those in stages 1 and 2. This suggests that the turbulence prevailing in the froth in this region affected the recovery of the coarser particles more severely than that of the fines. Furthermore, the calculated residence time of particles in stage 3 was considerably less than the average residence time of particles in the main body of the froth, where the gangue had sufficient time to drain back to the pulp. This implies that the contamination of the concentrate was largely due to the short-circuiting of fine gangue material from the pulp-froth interface in stage 3 into the concentrate.

Analysis of the results indicated that the recovery of the coarser particles, and also the concentrate grade, could be improved by providing additional concentrate launders in the froth, or using smaller cells. This would decrease the effective residence time of the coarse particles in the froth, especially those entering stage 2, and thus result in an increased recovery. Furthermore, it would reduce the adverse effects of froth turbulence in stages 3 and 4 on the recovery of coarse floating particles and would also decrease the effect of fine gangue short-circuiting into the concentrate.

CONCLUSIONS

A mathematical model has been developed to evaluate the behaviour of flotation froths on the basis of mass transport phenomena, by simulation of the flotation, entrainment and drainage of solid species and water. The fundamental principles of the model were described together with an example of how the model may be applied to investigate the behaviour of solids and water in the froth phase of large-scale mechanical flotation cells. The results of the simulation showed that the drainage rate constants of both the floating and the entrained fractions increased with increasing particle size. This indicates that, if the recovery of coarse particles is to be maximised, smaller cells should be used or additional concentrate launders should be provided in the froth phase.

REFERENCES


Table 1: Parameters describing the dimensions of the froth and the bubble kinetics.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of cell = L₁+L₂+L₃</td>
<td>L</td>
<td>3.0</td>
<td>m</td>
</tr>
<tr>
<td>Length of stage 1</td>
<td>L₁</td>
<td>0.95</td>
<td>m</td>
</tr>
<tr>
<td>Length of stage 3</td>
<td>L₃</td>
<td>0.72</td>
<td>m</td>
</tr>
<tr>
<td>Width of cell</td>
<td>W</td>
<td>2.5</td>
<td>m</td>
</tr>
<tr>
<td>Aeration rate = G₁+G₂+G₃</td>
<td>Gᵣ</td>
<td>6500</td>
<td>L/min</td>
</tr>
<tr>
<td>Froth depth</td>
<td>H</td>
<td>24</td>
<td>cm</td>
</tr>
<tr>
<td>Bubble streamline parameter</td>
<td>Fₜ</td>
<td>0.56</td>
<td>m</td>
</tr>
</tbody>
</table>

Table 2: Drainage rate constants (min⁻¹) of the floating (F) and the entrained (E) species in the froth, estimated from simulation of the concentration profiles.

<table>
<thead>
<tr>
<th>Particle size, μm</th>
<th>Stages 1 and 2 F</th>
<th>Stages 1 and 2 E</th>
<th>Stages 3 and 4 F</th>
<th>Stages 3 and 4 E</th>
</tr>
</thead>
<tbody>
<tr>
<td>+212</td>
<td>12.4</td>
<td>34.5</td>
<td>30.7</td>
<td>42.4</td>
</tr>
<tr>
<td>-212+150</td>
<td>10.2</td>
<td>34.4</td>
<td>28.5</td>
<td>40.6</td>
</tr>
<tr>
<td>-150+106</td>
<td>10.0</td>
<td>33.1</td>
<td>27.6</td>
<td>40.2</td>
</tr>
<tr>
<td>-106+75</td>
<td>9.4</td>
<td>32.4</td>
<td>15.7</td>
<td>39.6</td>
</tr>
<tr>
<td>-75+53</td>
<td>8.9</td>
<td>30.9</td>
<td>12.2</td>
<td>38.7</td>
</tr>
<tr>
<td>-53+38*</td>
<td>-</td>
<td>25.7</td>
<td>-</td>
<td>26.8</td>
</tr>
<tr>
<td>-38*</td>
<td>-</td>
<td>23.9</td>
<td>-</td>
<td>26.6</td>
</tr>
</tbody>
</table>

* No detachment of the floating particles in these size fractions was observed.
Figure 1: Schematic representation of the froth phase.

Figure 2: Simulation of the surface velocity and total concentration profiles of solids in the froth.
XVIIth International Mineral Processing Congress
Dresden/FRG, September 23 - 28, 1991

PREPRINTS
Volume II
Fine Particles Processing
Flotation
(Fundamentals, Hydrodynamics, Modelling)
THE EFFECT OF MILLING ENVIRONMENT ON THE SELECTIVE FLOTATION OF CHALCOPYRITE FROM A COMPLEX SULPHIDE ORE

J.S.J. van Deventer*, V.E. Ross*+ and R.C. Dunne#

* Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch, 7600, South Africa
# Newmont Australia Ltd, 179 Great Eastern Highway, Belmont, WA 6104, Perth, Australia

SUMMARY

Ore from the Black Mountain mine in the North Western Cape Province of South Africa was milled to 70% -75 μm and then subjected to batch flotation tests in a 3-litre Wemco cell. The complex sulphide ore contained about 0.35% Cu, 6.5% Pb and 2.2% Zn, with the main gangue components being pyrrhotite, pyrite, magnetite and quartz. Metallic iron powder was added in different quantities to a ceramic mill operated under a nitrogen atmosphere in order to investigate the effect of the milling environment on flotation.

The best recovery of chalcopyrite, copper grade and copper-lead selectivity were obtained in the case of an oxygen-saturated pulp milled in the presence of iron. Poor copper grades and copper-lead selectivity were obtained when the ore was milled in a ceramic mill under a nitrogen atmosphere in the absence of metallic iron. Whereas an extremely brittle froth was formed under these conditions, milling in the presence of iron resulted in a stable, well-drained froth with plenty of "body." In contrast with the improvement in the copper recovery and copper-lead selectivity obtained when the pulp was pre-aerated after milling in the presence of iron, no significant increase in the copper grade was observed after extensive pre-aeration when milling occurred in the absence of iron.

INTRODUCTION

The Black Mountain complex sulphide ore body is located in the north western Cape Province of South Africa. At the time of the research project, sequential flotation was practised to recover copper, lead and zinc sulphides [1,2]. The crushed ore was ground to a
particle size of 70% - 75 μm in a rod-mill/ball-mill circuit, and zinc sulphate and Dow Z-200 (isopropyl ethylthionocarbamate) were added at that stage. The cyclone overflow was conditioned with more collector, while sulphurous acid (H₂SO₃) was added to bring the pH down to a value of 6.5. Methyl isobutylcarbinol (MIBC) frother was added, and a copper rougher concentrate was recovered. The tailings from the copper circuit were conditioned with lime to a pH of 8.5, with both zinc sulphate and sodium cyanide being added. Sodium ethyl xanthate and R242 (salts of aryl dithiophosphoric acid) were added as collectors, and the lead rougher concentrate obtained, was cleaned further. The lead rougher tailings were conditioned with CuSO₄ and lime to a pH value of 10.5. Dow Z-200 was added as collector and a zinc rougher concentrate was recovered, which proceeded to cleaning.

Although the flotation of sulphide has been practised for many years, the interaction between the flotation variables remains largely unclear. Many investigators have undertaken basic work on pure minerals [3-6], and to a much lesser extent on ores [4,7,8], in order to gain an understanding of the various mechanisms involved in the flotation of lead, zinc and copper sulphides. Of special interest are investigations into the depressing influence of the sulphite ion in the flotation of galena [9], and the influence of the level of dissolved oxygen and the redox potential on the differential flotation of chalcopyrite and galena from complex ores [8].

Pulp potentials and the subsequent flotation of galena were studied by investigators who correlated these results at Mount Isa, Australia [10]. The measurement of rest potentials was used to characterise the reactions occurring at the surface of various sulphide minerals in xanthate solutions [3]. The same technique was used to show that isopropyl ethylthionocarbamate (Z-200) reacts with chalcopyrite but not with galena, although the mechanism remains unclear [11].

Guy and Trahar [12] observed that the floatability of galena was dependent on the oxidation-reduction conditions in the pulp in both grinding and flotation. Grinding in steel mills adversely affects the flotation of pyrrhotite, and galvanic coupling of pyrrhotite with active metals resulted in the formation of hydroxide or oxide and sulphate species of iron on the pyrrhotite surface [13]. Galvanic interactions between grinding media and minerals in a mill influence the corrosive wear of the media as well as the surface properties of the ground mineral [14]. Nakazawa and Iwasaki [15] found that galvanic contact between pyrrhotite and pyrite enhanced the floatability of pyrrhotite, but adversely affected that of pyrite. Galvanic contact between nickel arsenide and pyrrhotite improved the flotation of nickel arsenide, but adversely affected the floatability of pyrrhotite [16]. Rao and Finch [17] observed that the combination potentials of pyrite-galena and pyrite-sphalerite couples were lower than the rest potential of the pyrite on its own. The adsorption of xanthate on pyrite was also lower in pyrite-sphalerite mixtures compared with pyrite on its own. Galena
was preferentially floated with air from galena-pyrite mixtures, but with nitrogen, pyrite was preferentially floated [17].

Despite all these studies on the effects of galvanic interactions, little is understood about the effect of milling environment on the flotation of real ores. Many studies have been conducted on isolated minerals, or in solutions only, and these artificial conditions bear little relevance to the complex interactions in real ores. Moreover, overall flotation results are usually given without any analysis of the solids/water ratio or the behaviour of the froth. As explained by Ross [7], transport phenomena in the froth phase are complex and depend inter alia on the surface chemistry of the flotation species.

The purpose of this paper is therefore to investigate the effect of galvanic interaction between metallic iron powder and minerals, during grinding in a ceramic mill, on the subsequent flotation behaviour of the Black Mountain ore. Different aeration conditions will also be used. The results will be related to the electrochemical study of Ross and Van Deventer [4] on the same ore, in which rest potential measurements were used to characterise the reagent species on the surfaces of chalcopyrite and galena.

EXPERIMENTAL

In view of the fact that the experimental procedures have been described in detail by Ross [18], only selected aspects thereof will be outlined in this paper. The ore samples used were rod mill feed obtained from the Black Mountain concentrator, and contained about 6.5 % Pb, 2.2 % Zn and 0.35 % Cu. A mineralogical analysis by Mintek showed that the ore contained about 65 % magnetite, 24 % other non-sulphide minerals such as quartz, rutile, muscovite, biotite, chlorite and pyroxene, and pyrrhotite and pyrite as gangue sulphide minerals.

Before being floated, the ore was ground to 70 % -75 μm under an atmosphere of nitrogen in a ceramic mill. The mill load was as follows: 1 000 g of ore, ceramic balls, and 500 ml of deoxygenated tap water. Different amounts of powdered metallic iron (purity 2N+) were added to the ore before milling in the ceramic mill. After being milled, the ore was transferred to the flotation cell, and deoxygenated tap water was added to bring the pulp density to 33 % solids.

Pre-aeration of pulp in the 3-litre Wemco flotation cell (with induced aeration) was done only on the ore that had been milled in the absence of metallic iron, i.e. for a period of 15 minute at an air flowrate of 3 L/min. In these cases, the dissolved oxygen concentration of the pulp remained constant at 8.2 p.p.m. throughout the 8 minutes of flotation. Ore that had been milled in the presence of iron was floated directly after
milling. The initial level of dissolved oxygen varied between 0.3 p.p.m. and 2 p.p.m. at iron additions of 10 and 2 kg/ton ore respectively. The concentration of dissolved oxygen in the pulp was measured with a Schott CG 867 dissolved-oxygen electrode.

After aeration, the pulp was conditioned for 3 minutes with sodium sulphite as a pH regulator in some experiments. Subsequently, the pulp was conditioned with a collector such as sodium ethyl xanthate (NaEtX) and/or Dow Z-200 (isopropyl ethylthionocarbamate) for another minute, which was followed by the addition of a tri-ethoxybutane (TEB) as frother, and conditioning of the pulp for a further minute. Table 1 summarises the experimental conditions relevant to these tests.

After conditioning and pre-aeration, the pulp pH was measured with a Beckman pH70 pH meter. The ore was then floated for 8 minutes. Samples of the concentrate were collected at intervals of 1 minute by manual scraping, and analysed for Cu, Pb, Zn, Fe and S. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0.2 in extreme cases. An aeration rate of between 1.5 and 3.0 L/min. (Table 1) was used in order to prevent the froth from overflowing the cell lip in an uncontrolled fashion. If iron was added before milling, an aeration rate of 10 L/min. could be used without producing an uncontrolled froth. The initial froth height in the flotation cell was 4 cm, and this increased during a run.

Rest potential measurements were conducted as described earlier [4]. Both the chalcopyrite and galena electrodes were rubbed in a fine iron powder (purity 2N+) before immersion in a xanthate solution or pulp. These experiments were done in order to simulate milling conditions in a steel mill.

RESULTS AND DISCUSSION

Tables 2(a) & 2(b) summarise the % recovery of chalcopyrite, galena, solids, water, total sulphur and iron, as well as the grades of sulphur and iron after 8 minutes of batch flotation. The index numbers of experiments correspond to those used in Table 1. In experiments 2, 6, 8, 10 and 11, different amounts of metallic iron were added to the ore before milling. The kinetics of recovery of chalcopyrite and galena for these experiments are depicted in Figures 1 and 2 respectively.

As can be seen from Tables 2(a) & 2(b), significant recoveries of chalcopyrite were obtained only during those flotation tests where metallic iron was present during milling. Copper recoveries are not given for experiments 1, 3, 4, 5, 7 and 9 as the Cu assays of these concentrates were less than 0.2 %. This phenomenon can be ascribed only to the great difference in the froth characteristics caused by the different milling environments. Moreover, the dissolved oxygen content of the pulp with no metallic iron being present was
much higher than in experiments with iron. Earlier work [4,8] showed that an increased level of dissolved oxygen enhanced the flotation of chalcopyrite. As can be seen from the experiments conducted without the addition of iron, very low recoveries of galena were obtained after the pulp was subjected to extensive pre-aeration. Presumably, oxidised species on the surface of the galena rendered this mineral less hydrophobic.

The presence or absence of iron during milling had a drastic effect on the characteristics of the froth phase. When iron was added to the ceramic mill, or when the ore was milled in a steel mill, the froth had plenty of "body" and revealed a dark-green colour due to the high recovery of chalcopyrite. If no iron was added, the froth was very brittle and bubbles collapsed almost as soon as they were formed. Initially, the froth was very mobile and had a dark colour owing to the high recovery of iron-bearing minerals, but it later changed to a greyish, foamy texture as most of the iron minerals had been removed. When iron was added before milling, the average bubble diameter was 1.9 mm, while the corresponding value was 0.4 mm when no iron was added.

Tables 2(a) & 2(b) reveal very high ratios of cumulative solids/cumulative H₂O recovered in the concentrate when no metallic iron was present during milling. This indicates poor drainage of gangue particles from the froth back to the pulp phase. It is well-known that high concentrations of hydrophobic particles in the froth could destabilize the froth structure [7], which is manifested in the brittle froths observed in experiments 1, 3, 4, 5, 7 and 9. As expected, low ratios of cumulative solids/cumulative H₂O were observed when iron was added before milling. These low ratios correspond to the relatively low recovery of iron minerals such as magnetite, pyrite and pyrrhotite in experiments 2, 6, 8, 10 and 11. The high recoveries of water in the latter experiments where larger bubble sizes were observed, correspond to the fact that the laminar thickness of a bubble increases with increasing bubble size. The drainage of the froth was also greatly improved, as indicated by the lower recoveries of solids in comparison with experiments with no iron added.

It is clear from Tables 2(a) and 2(b) that the sulphur grades for experiments in which iron was added before milling were significantly higher than the sulphur grades obtained in the absence of iron. Except for experiment 6, the recoveries of sulphur did not change as much as the grades. In experiment 6, the ore was milled in an oxygen-flushed mill with an iron addition of 6 kg/ton ore. This increased exposure of the ore to oxygen in the presence of iron increased significantly the recovery and grade of sulphur, as well as the recoveries of chalcopyrite and galena, in spite of the increase in the recovery of both the total solids and water. These results imply that a high percentage of sulphide minerals, especially sphalerite, was floatable under these circumstances; the sphalerite recovery was 69 % after 8 minutes of flotation.
In general, an increase in the recovery and grade of sulphur was accompanied by a significant decrease in the recovery and grade of iron, which indicates that the drainage of gangue particles such as magnetite was greatly improved after the ore was milled in the presence of iron. It appears as if the flotation of iron-bearing minerals prevents the recovery of valuable minerals after the ore had been milled in a ceramic mill, even at low aeration rates.

By comparing experiments 10 and 11 in Table 2(b), it can be seen that the ratio of cumulative solids/cumulative H₂O recovered in the concentrate increases as the iron addition before milling is decreased. The froth obtained in experiment 11 had much less 'body' than the froth in experiment 10. Furthermore, the recovery and grade of iron in experiment 11 were significantly higher than those in experiment 10, but the opposite was true for sulphur recoveries and grades. A dosage of 20g Z-200/ton ore was necessary to increase the recovery of chalcopyrite in experiment 11, which was still lower than that in experiment 10.

Rest potential measurements [4] suggested that dixanthogen could be formed on both chalcopyrite and galena surfaces in the pulp after the ore had been milled in the absence of iron, which probably accounted for the poor copper-lead selectivity which was obtained by flotation under these conditions. However, no dixanthogen could be formed on either chalcopyrite or galena when these minerals were in galvanic contact with pure iron. Galvanic contact between steel and gangue minerals such as magnetite, pyrite and pyrrhotite reduced the rest potential of these minerals [13,14], with a concomitant inhibition of their floatabilities. This inhibiting effect of the addition of iron before milling was more severe in the case of non-valuable minerals, which yielded a net increase in the recovery of chalcopyrite. The difference in solid/liquid ratios between the experiments described in Table 1 indicate that galvanic contact between metallic iron and the various minerals influenced not only the hydrophobicity of minerals, but also the mass transport phenomena in the froth phase.

A comparison of experiments 8, 10 and 11 with experiment 2 indicates that copper-lead selectivity was increased when less oxygen-consuming iron was present during milling. These results are in accordance with findings by Graham and Heathcote [8]. The results for experiments 8 and 10 in Table 2(b) indicate that an increased addition of sodium sulphite increased not only the recovery of chalcopyrite, but also enhanced the copper-lead selectivity and reduced both the recovery and grade of iron. According to Ross [18], this effect was attained only when iron was present during milling. Milling without the addition of iron resulted in an increased recovery of both copper and lead when the addition of sodium sulphite was increased [18]. Pre-aeration would have enhanced the copper-lead selectivity even further.
CONCLUSIONS

Under the aeration conditions studied, poor copper grades and copper-lead selectivity were obtained when the ore was milled in a ceramic mill under an atmosphere of nitrogen. Milling in the presence of metallic iron, followed by pre-aeration, greatly improved copper grades and copper-lead selectivity when sulphurous acid was used as pH regulator. Even without pre-aeration, the copper grades obtained after milling with an iron addition of 6 kg/ton ore were significantly higher than those obtained when the ore was milled in the absence of iron and subjected to extensive pre-aeration. Whereas milling in a ceramic mill without the addition of iron resulted in a flat and brittle froth with small bubbles, a stable and well-drained froth with larger bubbles was formed when iron was added before milling.

ACKNOWLEDGEMENTS

The financial sponsorship and technical support received from the Council for Mineral Technology (Mintek) in South Africa, as well as the supply of ore samples by the Black Mountain Mineral Development Co. are greatly appreciated. Thanks are also extended to Mr W.P. van Reenen for constructing the experimental equipment.

REFERENCES


Table 1. Details of flotation experiments with and without the addition of metallic iron before milling

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Milling</th>
<th>Pre-aeration</th>
<th>Aeration</th>
<th>Reagents</th>
<th>pH⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas</td>
<td>Fe (kg/t)</td>
<td>Time (min)</td>
<td>(L/min)</td>
<td>Type</td>
</tr>
<tr>
<td>1</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>O₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>O₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>8</td>
<td>N₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>10</td>
<td>N₂</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>11</td>
<td>N₂</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
</tr>
</tbody>
</table>

+ Sulphurous acid was used as pH regulator in all the flotation tests conducted at a value of 6.1
Table 2(a). Cumulative % recovery $R$ and grade ($G$) of different species after 8 minutes of batch flotation for the various milling and flotation conditions given in Table 1

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe added</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$R(\text{CuFeS}_2)$</td>
<td>17.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>43.20</td>
</tr>
<tr>
<td>$R(\text{PbS})$</td>
<td>0.59</td>
<td>11.22</td>
<td>1.21</td>
<td>7.25</td>
<td>2.41</td>
<td>34.52</td>
</tr>
<tr>
<td>$R(\text{Solids})$</td>
<td>9.68</td>
<td>4.79</td>
<td>10.18</td>
<td>9.27</td>
<td>8.37</td>
<td>12.08</td>
</tr>
<tr>
<td>$R(\text{H}_2\text{O})$</td>
<td>53.4</td>
<td>150.0</td>
<td>53.5</td>
<td>52.6</td>
<td>55.5</td>
<td>237.9</td>
</tr>
<tr>
<td>$R(\text{Solids})$</td>
<td>1.81</td>
<td>0.32</td>
<td>1.90</td>
<td>1.76</td>
<td>1.51</td>
<td>0.51</td>
</tr>
<tr>
<td>$R(\text{Water})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R(\text{Fe})$</td>
<td>17.33</td>
<td>3.09</td>
<td>19.39</td>
<td>19.08</td>
<td>16.15</td>
<td>8.57</td>
</tr>
<tr>
<td>$G(% \text{Fe})$</td>
<td>62.78</td>
<td>24.02</td>
<td>61.55</td>
<td>58.15</td>
<td>61.78</td>
<td>26.81</td>
</tr>
</tbody>
</table>

Table 2(b). Cumulative % recovery $R$ and grade ($G$) of different species after 8 minutes of batch flotation for the various milling and flotation conditions given in Table 1

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe added</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>$R(\text{CuFeS}_2)$</td>
<td>22.10</td>
<td></td>
<td></td>
<td>33.49</td>
<td>24.82</td>
</tr>
<tr>
<td>$R(\text{PbS})$</td>
<td>3.03</td>
<td>10.07</td>
<td>3.37</td>
<td>8.00</td>
<td>6.01</td>
</tr>
<tr>
<td>$R(\text{Solids})$</td>
<td>9.08</td>
<td>5.68</td>
<td>9.27</td>
<td>4.40</td>
<td>6.16</td>
</tr>
<tr>
<td>$R(\text{H}_2\text{O})$</td>
<td>52.8</td>
<td>139.6</td>
<td>71.4</td>
<td>141.2</td>
<td>109.4</td>
</tr>
<tr>
<td>$R(\text{Solids})$</td>
<td>1.72</td>
<td>0.41</td>
<td>1.40</td>
<td>0.31</td>
<td>0.56</td>
</tr>
<tr>
<td>$R(\text{Water})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R(\text{Fe})$</td>
<td>17.20</td>
<td>4.47</td>
<td>17.38</td>
<td>3.10</td>
<td>6.66</td>
</tr>
<tr>
<td>$G(% \text{Fe})$</td>
<td>61.57</td>
<td>30.15</td>
<td>59.71</td>
<td>25.72</td>
<td>40.55</td>
</tr>
</tbody>
</table>
Figure 1. Recovery % (R) of chalcopyrite during batch flotation after milling in the presence of iron for the experiments described in Table 1

Figure 2. Recovery % (R) of galena during batch flotation after milling in the presence of iron for the experiments described in Table 1
The Behaviour of Individual Uranium Bearing Minerals During Froth Flotation

L. Lorenzen\(^1\), J S J van Deventer\(^1\) and G P Muller\(^1\)

**ABSTRACT**

A mineralogical analysis has shown that in the Hartbeesfontein ore studied, uranium is associated mainly with uraninite, sulphides such as pyrite and to a lesser degree carbonaceous material such as thulcotic. Little could be learned from the literature regarding the mechanism of flotation of these uranium-bearing minerals. A wide variety of reagents were used so that conditions enhancing the flotation of either the sulphides or uraninite, or combinations thereof, were created. As could be expected, the xanthate based floats gave better selective recovery of sulphides than oleic acid. A substantial fraction of the uraninite is associated with pyrite, so that addition of oleic acid to a xanthate float did not enhance the recovery or grade of uraninite.

After a pre-Float with sulphuric acid in which the pH and Eh were controlled so as to destroy the uraninite, higher uranium recoveries were obtained for the combined float (xanthate, DTP and oleic) and the DTP float. This was most evident when iron was added before flotation. Roasting, which destroyed the sulphides and thulcotic, caused a significant decrease in uranium recoveries. The uraninite liberated in this way was obviously not floatable in the same way as the uraninite liberated from uraninite. A small amount of iron (2 kg/t) added before milling resulted in slightly higher grades and recoveries of sulphur for xanthate based floats. Higher iron additions had a detrimental effect on sulphur recoveries. Even in the case of oleic acid the addition of small quantities of iron had a positive effect on the recovery of sulphur and uraninite.

**INTRODUCTION**

In South Africa both gold and uranium occur in the same ores on the Witwatersrand. Whereas the gold is extracted by cyanidation, uraninite is leached in an oxidative sulphic acid medium. Various flow sheets have been proposed, and many arguments have been raised as to why separation of uranium and gold should be conducted on the processing of uranium ores, especially with reference to the flotation of uranium-bearing minerals. It is the objective of this paper to investigate the behaviour of such uranium-containing minerals during the flotation of a real ore.

There have always been significant obstacles in achieving discardable flotation tailings, i.e. maintaining high recoveries of both uranium and gold. In the Witwatersrand type of quartzitic gold and uranium ores, a varying and significant percentage of the uranium present is freely soluable in acid. On plants that extract both gold and uranium, all processes upstream of the acid leach must be conducted in neutral or alkaline medium in order to avoid sucuable uranium losses.

At Hartbeesfontein Gold Mine treating fresh gold bearing ore, froth flotation is carried out directly after the milling stage so as to produce a high grade gold-bearing pyrite concentrate for intensive treatment and a low grade pulp for milder treatment. This flotation process takes place under neutral or alkaline conditions in the absence of cyanide, which is a powerful pyritic depressant under these conditions. In addition, pyrite flotation at this stage of the process may benefit from the heat generated during the milling process. Very high recoveries of gold (90 per cent) and pyrite (95 per cent) have been attained, but low uranium (50 per cent) recoveries still persist.

During the past 40 years, various attempts have been made on the development of a suitable flotation technique to produce an optimal uranium concentrate. Various problems have been encountered, i.e.:

1. Much of the uranium is present as uraninite, which is inherently difficult to float;
2. The uranium tends to be very finely ground during milling, which makes its selective flotation even more difficult;
3. A small but significant fraction of the uranium is carried by siliceous minerals such as monazite, zircon, leucoxene, titanite and various phyllosilicates, all of which are difficult to float selectively; and
4. Thulcotic floats very readily, but tends to be rather coarse because its low density permits it to escape from milling circuits before being miscast.

Early work indicated that a recovery of uranium of 20 to 30 per cent could be achieved by use of a frother only. The mineral floated was mainly thulcotic. The addition of xanthate permitted additional thulcotic to be recovered along with the significant amounts of uraninite. A further float with oleic acid permitted a total recovery of as much as 80 per cent of the uranium in a concentrate that was 20 per cent by mass of the food (Liebenberg, 1956), but the oleic acid float was sensitive to the presence of lime and iron from the grinding circuit. A combined diphenylthiocarbazide-xanthate float yielded over 60 per cent of the uranium in over 15 per cent by mass of the feed. A combination of a sulphonate and fuel oil gave a recovery as high as 84 per cent in 29 per cent of the food, but required very large quantities of reagents. Various sulphonates were tried, but all tended to float slimes preferentially, so that good recoveries were achieved at the expense of grade (Liebenberg, 1956).

**EXPERIMENTAL**

The ore samples used were rod mill feed obtained from the Hartbeesfontein Gold Mine at Stillfontein in South Africa. The material as received contained about 12.46 g/t of gold, 1.66 per cent sulphur and 15 g/t U\(_3\)O\(_5\). A mineralogical analysis by the Anglo Vat Research Laboratories, showed that 93 per cent of the sulphide minerals present in the ore sample is pyrite, with small amounts (\(\leq 2\) per cent each) of galena, chloropyrite and uraninite.

Before being floated, the ore was ground to 70 per cent - 75 micron in a ceramic mill. For some of the experiments different amounts of powdered metallic iron (purity 2N+) were added to the ore before milling in the ceramic mill. This was done to study the effect of possible galvanic interactions (Van Deventer et al., 1991). After being milled, the ore was transferred to the flotation cell, and deoxygenated tap water (controlled at 25°C) was added to bring the pulp density to 35 per cent solids (1 kg of solids).

Pre-aeration in the bottom driven Leeds-type flotation cell (with induced aeration) was performed on some of the samples as will be explained later. Various flotation experiments were conducted on the ground ore samples after milling.

---

1. Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch, 7600, South Africa

XVIII International Mining Processing Congress Sydney, 23-28 May 1993 929
1. At first the ground samples were floated with a scaled-down version of the reagents used at Hartbeesfontein Flotation Plant (referred to hereafter as Harties circuit). The pH was regulated by addition of NaOH or HCl to a value of approximately 10. The slurry was conditioned at 950 rev/min for ten minutes. The following reagents were then added sequentially: 60 g/t sodium ethyl xanthate, 100 g/t CuSO4, 15 g/t Aeropromotor 3477 (Diisophosphosphate or DTP) and 25 μl/kg Tri-ethoxybutane or TEB. TEB was added mainly to enhance the froth stability.

The ore was then floated for ten minutes. Samples of the concentrate were collected at intervals of one minute by manual scraping, and analysed for gold, sulphur and uranium.

For the following experimental configurations, the procedure as described in (1) above, was repeated except for the conditions as mentioned in each case below.

2. The same reagents as mentioned in (1) for the Harties circuit were used except that prior to addition, the slurry was conditioned with Na2S for three minutes.

3. The same reagents and conditions as for the Harties circuit were used except that no DTP or TEB was added; instead 100 μl/kg Cyanamid AF 65 (frother for pyrite flotation) was used.

4. No xanthate and copper sulphate were added. Only DTP (Aeropromotor 3477) and TEB were used as reagents and the conditions were similar to those described for the Harties circuit.

5. Not one of the reagents mentioned in the Harties circuit were used in the next set of experiments. Oleic acid is normally used for the flotation of oxides. Because of the nature of the very stable froth, all the natural flottable minerals are also floated. Experimental results showed that 0.5 g oleic acid/kg proved to be the most effective addition to use. Smaller concentrations did not sustain the froth stability over the ten minute period of flotation, while higher concentrations caused a huge mass pull to the concentrate, which is:
   i. difficult to handle and
   ii. gives low values of oxides in the concentrate.
   Twenty-five μl of TEB was also added to the samples and the pH was not adjusted to ten, because of the possible formation of salt in solution (pH = 8.5 average).

6. For the last set of experiments, 60 g/t Xanthate, 15 g/t DTP, 25 ml/lon TEB and 0.2 g/kg oleic acid were used. Flotation conditions were the same as those for the Harties circuit.

A summary of the experimental conditions as described above is presented in Table 1, with each combination of reagents being designated by a name given in the legend of each table (see also Table 1).

As can be seen from Table 2 as well as Figure 1, low (10 to 25 per cent) uranium recoveries were obtained during all flotation tests except for the samples pre-leached with sulphuric acid before flotation. Higher uranium recoveries (40 to 74 per cent) were obtained after the pre-leaching with sulphuric acid for the combined float (xanthate, DTP and oleic) and the DTP float. These higher uranium recoveries were most evident when iron

| Table 1 |
| Details of flotation experiments with the addition of various reagents. |

<table>
<thead>
<tr>
<th></th>
<th>Harties Circuit</th>
<th>Modified Harties</th>
<th>Xanthate Float</th>
<th>Oleic Float</th>
<th>DTP Float</th>
<th>Comb. Float</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthate</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>CuSO4</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DTP</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TEB</td>
<td>25</td>
<td>25</td>
<td>-</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Na2S</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cyanamid</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Condition</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Time (min)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Flootation</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

Tables 2 to 6 summarise the per cent recovery of uranium and sulphur, the grades of uranium and sulphur as well as the cumulative solids/cumulative water recovered in the concentrate after ten minutes of batch flotation. Each combination of reagents being used is designated by a name given in the legend of each table (see also Table 1).

As can be seen from Table 2 as well as Figure 1, low (10 to 25 per cent) uranium recoveries were obtained during all flotation tests except for the samples pre-leached with sulphuric acid before flotation. Higher uranium recoveries (40 to 74 per cent) were obtained after the pre-leaching with sulphuric acid for the combined float (xanthate, DTP and oleic) and the DTP float. These higher uranium recoveries were most evident when iron
Cumulative uranium grade (kg/t) after ten minutes of batch flotation for various flotation conditions given in Table 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Haries Circuit Float 1</th>
<th>Xanthate Float</th>
<th>Oleic Float</th>
<th>Comb. Float 2</th>
<th>DTP Float</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.387</td>
<td>0.328</td>
<td>0.202</td>
<td>0.303</td>
<td>0.337</td>
</tr>
<tr>
<td>Fe(2kg/t)</td>
<td>0.352</td>
<td>0.309</td>
<td>0.219</td>
<td>0.151</td>
<td>0.322</td>
</tr>
<tr>
<td>Fe(5kg/t)</td>
<td>0.32</td>
<td>0.295</td>
<td>0.201</td>
<td>0.313</td>
<td>0.29</td>
</tr>
<tr>
<td>Leach</td>
<td></td>
<td>0.078</td>
<td>0.91</td>
<td>0.391</td>
<td></td>
</tr>
<tr>
<td>Leach + Fe(2kg/t)</td>
<td>0.155</td>
<td>0.08</td>
<td>0.41</td>
<td>0.067</td>
<td>0.129</td>
</tr>
<tr>
<td>Burnoff</td>
<td>0.065</td>
<td>0.01</td>
<td>0.308</td>
<td>0.174</td>
<td>0.084</td>
</tr>
<tr>
<td>Burnoff + Fe(5kg/t)</td>
<td>0.068</td>
<td>0.08</td>
<td>0.22</td>
<td>0.193</td>
<td>0.084</td>
</tr>
<tr>
<td>Oxidation</td>
<td>0.341</td>
<td>0.271</td>
<td></td>
<td>0.323</td>
<td>0.323</td>
</tr>
</tbody>
</table>

Cumulative recovery of per cent solids/ per cent H2O after ten minutes of batch flotation for various flotation conditions given in Table 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Haries Circuit Float 1</th>
<th>Xanthate Float</th>
<th>Oleic Float</th>
<th>Comb. Float 2</th>
<th>DTP Float</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>87</td>
<td>90</td>
<td>19</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Fe(2kg/t)</td>
<td>89</td>
<td>93</td>
<td>27</td>
<td>82</td>
<td>87</td>
</tr>
<tr>
<td>Fe(5kg/t)</td>
<td>88</td>
<td>86</td>
<td>19</td>
<td>91</td>
<td>80</td>
</tr>
<tr>
<td>Leach</td>
<td>77</td>
<td>77</td>
<td>82</td>
<td>92</td>
<td>-</td>
</tr>
<tr>
<td>Leach + Fe(5kg/t)</td>
<td>90</td>
<td>89</td>
<td>53</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Burnoff</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Burnoff + Fe(5kg/t)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>89</td>
<td>85</td>
<td></td>
<td>88</td>
<td>86</td>
</tr>
</tbody>
</table>

Cumulative grade (per cent) of sulphur after ten minutes of batch flotation for various flotation conditions given in Table 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Haries Circuit Float 1</th>
<th>Xanthate Float</th>
<th>Oleic Float</th>
<th>Comb. Float 2</th>
<th>DTP Float</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>16.71</td>
<td>13.42</td>
<td>2.4</td>
<td>14.39</td>
<td>15.94</td>
</tr>
<tr>
<td>Fe(2kg/t)</td>
<td>16.55</td>
<td>14.88</td>
<td>2.87</td>
<td>12.4</td>
<td>15.86</td>
</tr>
<tr>
<td>Fe(5kg/t)</td>
<td>15.47</td>
<td>15.59</td>
<td>2.61</td>
<td>16.21</td>
<td>15.55</td>
</tr>
<tr>
<td>Leach</td>
<td></td>
<td>11.42</td>
<td>3.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leach + Fe(5kg/t)</td>
<td>18.28</td>
<td>20.41</td>
<td>4.05</td>
<td>10.01</td>
<td>16.37</td>
</tr>
<tr>
<td>Burnoff</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Burnoff + Fe(5kg/t)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>16.83</td>
<td>16.57</td>
<td>14.81</td>
<td>15.32</td>
<td></td>
</tr>
</tbody>
</table>

Cumulative per cent recovery of sulphur after ten minutes of batch flotation for various flotation conditions given in Table 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Haries Circuit Float 1</th>
<th>Xanthate Float</th>
<th>Oleic Float</th>
<th>Comb. Float 2</th>
<th>DTP Float</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.515</td>
<td>0.481</td>
<td>0.358</td>
<td>0.532</td>
<td>0.495</td>
</tr>
<tr>
<td>Fe(2kg/t)</td>
<td>0.497</td>
<td>0.475</td>
<td>0.331</td>
<td>0.442</td>
<td>0.532</td>
</tr>
<tr>
<td>Fe(5kg/t)</td>
<td>0.503</td>
<td>0.509</td>
<td>0.304</td>
<td>0.490</td>
<td>0.537</td>
</tr>
<tr>
<td>Leach</td>
<td></td>
<td>0.752</td>
<td>0.522</td>
<td>0.498</td>
<td></td>
</tr>
<tr>
<td>Leach + Fe(5kg/t)</td>
<td>0.527</td>
<td>0.550</td>
<td>0.326</td>
<td>0.243</td>
<td>0.276</td>
</tr>
<tr>
<td>Burnoff</td>
<td>0.283</td>
<td>0.13</td>
<td>0.159</td>
<td>0.180</td>
<td>0.120</td>
</tr>
<tr>
<td>Burnoff + Fe(5kg/t)</td>
<td>0.192</td>
<td>0.300</td>
<td>0.199</td>
<td>0.175</td>
<td>0.182</td>
</tr>
<tr>
<td>Oxidation</td>
<td>0.530</td>
<td>0.540</td>
<td>0.319</td>
<td>0.491</td>
<td>0.502</td>
</tr>
</tbody>
</table>

1. Xanthate + DTP
2. Xanthate, DTP + Oleic

---

FIG 1 - Cumulative per cent recovery of uranium during batch flotation for experiments described in Table 1.
was added before flotation. However, the overall uranium grade (Table 3 and Figure 2) was low when the recovery was high. This was probably because of the fact that all leachable uranium was destroyed during the sulphuric acid leach and that the uranium reporting to the concentrate during flotation was mostly associated with carbonaceous material, ie kerogen, thucolite, etc that float relatively easily with xanthate and DTP as reagents.

After roasting the sample to 700°C, a decrease of about ten per cent in uranium recoveries was observed compared to the normal experiment (Harties circuit). There was also a corresponding decrease in uranium grade of the concentrate. Uranium is usually associated with sulphides, either in contact with the sulphides or locked-up in the sulphide minerals. Roasting of the sample at 700°C destroyed all the sulphur, thus exposing the locked and associated uranium. Subsequent flotation tests, however, indicated (as mentioned above) that the exposed uranium did not report to the concentrate during flotation for all surface characteristics of the uranium minerals during tests. This was probably because of a change in the roasting which had a detrimental effect on the uranium recovery. The uranium reporting to the concentrate was probably associated with the thucolite.

Table 6 also reveals very low ratios of cumulative solids/cumulative water recovered in the concentrate when the samples were roasted before flotation. Low ratios correspond usually to low recoveries of iron minerals (Van Deventer et al., 1991), thus indicating that the uranium minerals present are associated with iron minerals or carbonaceous material. Table 6 also indicates higher ratios of cumulative solids/cumulative water recovered in the concentrate when no iron was present, and much higher ratios when the samples were leached with sulphuric acid before flotation. These ratios were also higher than when no metallic iron was present during milling (also when iron was added after leaching), provided that no DTP was added. This indicates slightly poorer drainage of gangue particles from the froth back to the pulp phase.

It is well-known that high concentrations of hydrophobic particles in the froth could destabilise the froth structure (Ross, 1988), which is manifested in the brittle froths observed in most of the experiments except when oleic acid was used. After roasting, during which the sulphur minerals were destroyed, the ratio of cumulative solids/cumulative water recovered in the concentrate decreased drastically (see Table 6). When the sulphides associated with the iron were destroyed (pyrrhotite, pyrite, etc), the iron remained behind, thus decreasing the ratios as would be expected. The high recoveries of water in the experiments where iron was added and where high concentrations of iron was present because of roasting (where larger bubble sizes were observed), correspond well with the fact that the laminer thickness of a bubble increased with increasing bubble size. The drainage of the froth was also greatly improved, as indicated by the slightly lower recoveries of solids in comparison with experiments with no iron present.

It is clear from Tables 4 and 5 and Figures 3 and 4 that the sulphur grades and recoveries for experiments in which a small amount of iron (2 kg/t) was added before milling were slightly higher than those obtained in the absence of iron for some of the reagents tested. Higher iron additions (5 kg/t) have a detrimental effect on sulphur recoveries. It is evident that this influence of iron was less significant with respect to sulphur grades than sulphur recoveries. The high sulphur recoveries (up to 95 per cent) and grades (up to 20 per cent) imply that a high percentage of sulphide minerals was floatable during the various experiments. Even in the case of oleic acid which is a reagent for oxide
Fig 3 - Cumulative per cent recovery of sulphur during batch flotation for experiments described in Table 1.

Fig 4 - Cumulative grade (per cent) of sulphur during batch flotation for experiments described in Table 1.
flotation and therefore gave lower recoveries of sulphur, the addition of small amounts of iron had a positive effect.

From Tables 2 and 3, and Figures 1 and 2, it could be seen that the recovery and grade of uranium were affected adversely by the addition of iron in the case of the Haries and xanthate floats, but that a slightly positive effect was obtained with oleic acid. The combined float gave an enhanced recovery but a substantially lower grade.

Rest potential measurements (Ross and Van Deventer, 1985) suggested that dixanthogen could be formed on sulphide mineral surfaces in pulp after the ore had been milled in the absence of iron. Galvanic contact between steel and gangue minerals such as pyrite and pyrrhotite reduced the rest potential of these minerals (Adam et al., 1984; Natarajan and Iwasaki, 1984), with a concomitant inhibition of their floatabilities. This inhibiting effect of the addition of iron before milling was more severe in the case of non-valuable minerals, which yielded a net increase in the recovery of minerals such as chalcopyrite (Van Deventer et al., 1991). The comprehensive review by Martin et al. (1991) indicated that, in general, the addition of iron affected the floatation of sulphides adversely. However, testwork on the effect of iron on pyrite flotation has led to contradictory results, as it is also clear from Ross and Van Deventer (1985). This contradiction is also clear from the results in Tables 4 and 5.

The addition of iron (2 kg/t) during milling reduced the Eh of the slurry from -120 mV to -210 mV for the oleic acid float and from -260 mV to -320 mV for all the other experiments with the various reagents used. This change in the pulp potential was similar to that observed by Ross (1983) for a complex sulphide slurry. No further lowering in Eh was observed with a corresponding increase in the iron addition (to 5 and 8 kg/t) before milling. There was, however, a slight increase in the Eh (from -320 mV to -300 mV) when the addition of iron was increased to 5 kg/t. This could be attributed to the hydrophobicity of the minerals being affected by the galvanic interaction between the metallic iron and the various minerals.

From the excellent review by Ralston (1991) it is clear that the effect of Eh on flotation is still perplexing to some extent. Ross and Van Deventer (1985) showed that a constant difference existed in a complex sulphide slurry between the Eh and the rest potential of some sulphides. This means that the Eh can be used as an indication of rest potential, which is a relevant indicator of galvanic interaction.

Most of the work on the mechanism of adsorption of oleic acid based collectors has been done on minerals such as fluorite, calcite, barite and haematite (Marinakis and Shergold, 1985; Morgan et al., 1986; Hu et al., 1986). Although the nature of interaction is still uncertain to some extent, coulombic attraction between the carboxylate anions and cationic surface sites followed by the formation of hydrophobic associates, physical adsorption of carboxylate species on a chemisorbed layer of metal soap and the precipitation of multilayers of metal soap on the mineral surfaces have all been suggested as possible mechanisms. It is not clear why a more negative Eh caused by the addition of iron actually resulted in an enhanced notation of both sulphides and uraninite in the present work when oleic acid was used. It should be clear from these results that very little is known about the interaction of the various reagents with uraninite.

CONCLUSIONS

A literature search has revealed that very little is known about the mechanism of flotation of different uranium-bearing minerals. In the present study a wide variety of reagents have been used so as to cater for either the sulphides, carbonaceous material, oxides like uraninite, or combinations thereof. As could be expected, the

Fig 5 - Cumulative recovery of per cent solids/per cent water during batch flotation for experiments described in Table 1.
xanthate based floats gave better selective recovery of sulphides than oleic acid. The latter did not enhance the recovery or grade of uranium either, probably because a substantial fraction of the uranium is associated with pyrite.

Higher uranium recoveries were obtained after pre-treatment with sulphuric acid (which destroyed the uraninite) for the combined float (xanthate, DTP and oleic) and the DTP float. This was most evident when ITOn was added before flotation. Roasting, which destroyed the sulphides and thioenite, caused a significant decrease in uranium recoveries. This is a further indication that a large fraction of these minerals. The sulphur grades were higher when a small amount of iron (2 kg/t) was added before milling. Higher iron additions (5 kg/t) had a detrimental effect on sulphur recoveries. Even in the case of oleic acid which is a reagent for oxide notation and therefore gave lower recoveries of sulphur, the addition of small amounts of iron had a positive effect.

REFERENCES


Proceedings of the XIX International Mineral Processing Congress

Flotation Operating Practices and Fundamentals

Volume 3

Published by
Society for Mining, Metallurgy, and Exploration, Inc.
Littleton, Colorado, USA - 1995
THE DYNAMIC BEHAVIOUR OF COARSE PARTICLES IN FLOTATION FROTHS

W.A. VAN DYK, J.S.J. VAN DEVENTER, AND L. LORENZEN
DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF STELLENBOSCH,
STELLENBOSCH, 7600, SOUTH AFRICA

ABSTRACT

Hydrophobic particles with diameters between 1 and 3 mm are poorly recovered by conventional flotation techniques. A novel reverse flotation technique is described whereby coarse particles with surfaces rendered highly hydrophobic, repel the bubble films in a froth and thus drop through the froth under gravity, to be recovered as a sink product. Conversely, gangue or hydrophilic particles are supported by the bubble films in the froth and are therefore recovered as a floating product.

Tracer tests were conducted in the cell in order to study the dynamic behaviour of solid particles in the froth. The effects of hydrophobicity, density, particle size and particle shape were investigated experimentally. The higher the hydrophobicity of the particles, the lower the recovery of particles as a floating product, while the recovery of particles as a sink product increases with an increase in particle density. Furthermore, a decrease in particle size results in an increase recovery of hydrophobic particles as a floating product. When treating particles of the same mass-to-surface ratio in the froth, flat particles would be recovered as a floating product in preference to cubic, disc-shaped, cylindrical and spherical particles, in that order.

INTRODUCTION

The early recovery of coarse valuable material from a mineral processing circuit could have numerous advantages, such as preventing over-grinding of minerals, reducing conventional flotation time and increasing the recovery of valuable materials. Several researchers have therefore ventured into this field, proposing new techniques, processing circuits and/or alternative flotation reagents.

A system was proposed by Lloyd (1987) in which gold and other valuable minerals could be concentrated underground by coarse milling and flotation. A model of the process, however, indicated that the flotation step would be able to recover only 75 percent of the valuable minerals due to large losses in the coarser particle size ranges. Schubert (1989) investigated the development of an impeller type and impeller-stator flotation system that would recover coarse particles in the treatment of quartz sands and sylvanite. The major criterion that had to be satisfied in this regard was that the coarse particles had to be suspended but not agitated to such an extent that would impose unnecessary turbulent stresses on the bubble-particle aggregates. The design resulted in a lower power consumption but, although it appeared successful for particle sizes of up to 0.4 mm, difficulties were encountered at the coarser size ranges. Other studies were aimed at the use of alternative flotation reagents to improve the yield of coarse coal particles but with limited success (Moxon and Keast-Jones, 1986); (Moxon, Keast-Jones and Aston, 1988).

These investigations have shown that a need exists for a coarse particle separation technique with low operating costs, such as a low power consumption and relatively inexpensive flotation reagents. A technique was developed (Ross, 1993) whereby coarse particles with highly hydrophobic surfaces repel the bubble films in a froth and thus drop through the froth under gravity, to be recovered as a sink product. Conversely, gangue or hydrophilic particles are supported by the bubble films in the froth and are therefore recovered as a floating product.

THEORY

Rupture of bubble films

In a study on the interaction of a solid with a thin liquid film, Dippenaar (1982) found that moderately hydrophobic particles can be transformed into very effective film-breakers if they are coated with a reagent that produces a static contact angle of more than 90° on the solid. When such a particle is introduced into a lamellar froth, the instantaneous contact angle formed at the newly developed three-phase boundary is much smaller than the equilibrium contact angle. The movement of the three-phase boundary over the particle to attain an equilibrium contact angle causes the bubble film to thin and rupture when a critical bubble film thickness is reached. The process of bubble film thinning and rupture occurs in a few milliseconds and could be applied in the selective recovery of highly hydrophobic particles if the right froth conditions are maintained.

Figure 1. Spherical Particle Protruding Through Both Sides of a Bubble Film and the Capillary Pressure-driven Flow Mechanism of Bubble Film Rupture.
Hemmings (1981) postulated a protruding particle theory to explain the effect of hydrophobic particles with diameters greater than the thickness of the supporting liquid films on flotation froth stability. The basis of this theory is a quantification of the tensile and compressive stresses caused by particles protruding through the bubble films. Figure 1(a) gives a schematic representation of a spherical particle protruding through both sides of a bubble film. Interfacial forces tend to cause the particle to protrude further into the gas phase on each side of the film if
\[ \cos \Theta \frac{T}{d_p} < \cos \frac{\Theta}{2} \]  
(1)

where \( \Theta \) is the contact angle, \( T \) is the bubble film thickness (mm) and \( d_p \) is the particle diameter (mm). The equal and opposite reaction to this interfacial force is a destructive compressive stress that promotes film thinning and therefore is a latent cause of froth instability. Interfacial forces tend to cause the particle to submerge itself in the liquid on both sides of the film if
\[ \cos \Theta \frac{T}{d_p} > \cos \Theta \]  
(2)

The equal and opposite reaction to this is a supportive tensile stress that tends to prevent film thinning. From equations (1) and (2) it is obvious that no region of supportive tensile stress exists for \( \Theta > 90^\circ \), which means that a large particle with a contact angle of more than \( 90^\circ \), will cause bubble film thinning and rupture.

Frye and Berg (1989) proposed a mechanism for particle-induced film rupture and performed a hydrodynamic analysis to determine criteria for effective antifoam action by solid particles. They assumed that the mechanism that causes bubble film thinning or stabilisation is driven by capillary pressure. As shown in Figure 1, a coarse particle will bridge the film upon entering the froth, and curvature of the air-water interface will occur in order to satisfy the contact angle requirements at both interfaces. This curvature will result in local pressure variations, the magnitude of which is determined by the Young-Laplace equation:
\[ \Delta P = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  
(3)

where \( \Delta P \) is the pressure drop across the interface, \( \sigma \) is the surface tension and \( R_1 \) and \( R_2 \) are the principal radii of curvature of the surface. The sign of the pressure drop is determined by the direction of the interface curvature, which in turn depends on the contact angle (Figure 1 (a&b)).

Particle and froth characteristics

The capillary pressure-driven flow, and therefore film thinning, depends on the contact angle as discussed above. However, the total dynamic behaviour of the particles in the froth depends on a number of additional particle and froth characteristics. Density, shape, surface characteristics (hydrophobicity or hydrophilicity, and roughness) and size are important particle characteristics, while the bubble size, residence time of the bubbles in the flotation cell and the rigidity and thickness of the bubble films, in turn, are important froth characteristics. A particle in the froth is surrounded by a number of bubbles. Although the particle is not immersed in the film to the same degree as assumed by Dippenaar (1982), Hemmings (1981) and Frye & Berg (1983), the same principles of bubble film stability and film rupturing action would apply at each point where the film and the particle is in contact.

The structure of the froth is another important factor in determining the extent to which particles of various sizes, shapes and hydrophobicities can rupture bubble films. The size of the bubbles increases with increasing height above the froth interface due to bubble coalescence, a decreased hydrostatic head, and froth drainage. The structure of the froth changes accordingly from (a) a bubble swarm at the interface to (b) a packed bubble bed in the intermediate region to (c) a polyhedral structure at the surface. The polyhedral bubble structure is characterised by the fact that the bubbles are separated by rigid liquid films rather than existing as individual mobile entities at the interface, and it is under these conditions that the mechanism of film thinning is most effective. This suggests that the feed particles should therefore be introduced onto the froth surface to maximise the efficiency of the separation.

The stability of a froth is directly related to the stability of the liquid lamellae. As mentioned above, the size of the bubbles in the froth increases with increasing height above the froth-liquid interface. The froth becomes more rigid but less stable with increasing height above the interface, and therefore affects the flotation of particles of various surface characteristics and shapes. This suggests that there is an optimum water-to-air ratio for each particular bubble size for the flotation of particles with a specific hydrophobicity and size. The addition of frothing agents that increase the rigidity of the bubble films would increase the ability of the liquid lamella to support particles in the froth. The water-to-air ratio can therefore be regulated to a large extent by the addition of a frothing agent to the water.

**EXPERIMENTAL**

**Flotation cell**

The original concept, where particles are fed from the top onto a horizontally flowing froth bed, was described by Ross (1993). Various alterations were made to this design in order to minimize froth disturbances. The laboratory-scale flotation cell is illustrated in Figure 2. The cell consists of three tanks arranged alongside one another. To enable the settling of coarse hydrophobic particles through the froth, the vertical velocity component of the bubbles is kept as small as possible by bent weirs forcing the froth in a horizontal direction. The froth is formed in the first tank from where it moves Figure 2. Schematic Representation of the Flotation Cell.
DYNAMIC BEHAVIOUR OF COARSE PARTICLES IN FLOTATION FROTHS

The hydrophilic particles are supported by the bubble films in the froth and are carried over to compartment #3 while the hydrophobic particles break the bubble films and report as a sink product in compartment #1 and compartment #2. The particles are fed by hand onto the froth or by a vibratory feeder which can be installed. The particles are separated from the aqueous phase by screens at the discharge points of compartments #1, #2 and #3, from where the aqueous phase is recycled, via the pump sump, to the buffer tank.

Materials and methods

Density tracers of various specific gravities and shapes were manufactured and used in the testwork. The tracers were coated with candle wax as the coating is stable and easy to apply. The fresh wax is in addition inherently hydrophobic and yields an equilibrium contact angle of 68°. The contact angles were measured by the sessile drop method. However, it was found that the results could not be reproduced as the hydrophobic wax coating seemed to become increasingly hydrophilic with time when soaked in water (the static contact angle reduced to < 40° after 48 hours of soaking). This is in accordance with observations by Adam (1944) on factors modifying contact angles. While this was at first seen as a drawback, it was realised that this property could be very useful to quantify the hydrophobicity in terms of the flotation behaviour of small tracers. However, the above mentioned work is beyond the scope of this paper. The soaking time of the wax-coated tracers is therefore taken as a measure of the particle wettability.

RESULTS AND DISCUSSION

Behaviour of particles in novel cell

All the tests were conducted at an aqueous phase temperature of 25°C, pH of 7, a frother dosage of 1500 ppm Montan LIC40 and spargers with aperture = 50 μm. A further 4200 ppm xanthate was added to the frothing agent to enhance the bubble film stability as well as 2 drops of Teepeol/G3/3 demineralized water. The relevant tendencies are explained in view of the graphs for the recovery of particles to the tailings. The total soaking time of the particles in the aqueous phase (measure of the particle wettability) is plotted on the x-axis, while the percentage of particles reporting to the tailings is plotted on the y-axis.

The effect of particle density is illustrated in Figure 3. Cylindrical tracers with an average length and diameter of 3.38 mm and 2.08 mm respectively, and specific gravities of 3.50, 3.10, 2.90 and 2.70 were used in conjunction with an air flow rate yielding superficial gas velocities of 8.9 m/m/sec in compartment #1A and 8.9 m/m/sec in compartment #1B. As expected, an increased density results in a decreased recovery to the tailings, as can be seen in the S-shaped curve shifting towards the right on the graph of recovery to the tailings. This is expected since the gravitational force on the particles increases while the area available for support by the bubble films remains constant. The particle would thus drop through the froth under the influence of gravity. (Table 1 gives the mass-to-surface-area ratios (M/A) for the various particles.)

Table 1. Applicable Data of Density Tracers.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Dimensions [mm]</th>
<th>SG</th>
<th>M/A Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>cube</td>
<td>3.05 side</td>
<td>3.1</td>
<td>1.58</td>
</tr>
<tr>
<td>cube</td>
<td>3.05 side</td>
<td>2.9</td>
<td>1.47</td>
</tr>
<tr>
<td>cube</td>
<td>3.05 side</td>
<td>2.7</td>
<td>1.37</td>
</tr>
<tr>
<td>cube</td>
<td>2.1 side</td>
<td>3.5</td>
<td>1.23</td>
</tr>
<tr>
<td>cube</td>
<td>2.1 side</td>
<td>3.3</td>
<td>1.16</td>
</tr>
<tr>
<td>cube</td>
<td>2.1 side</td>
<td>3.1</td>
<td>1.09</td>
</tr>
<tr>
<td>cube</td>
<td>2.1 side</td>
<td>2.9</td>
<td>1.02</td>
</tr>
<tr>
<td>cube</td>
<td>2.1 side</td>
<td>2.7</td>
<td>0.95</td>
</tr>
<tr>
<td>disc</td>
<td>2.08 * 1.98</td>
<td>3.5</td>
<td>1.19</td>
</tr>
<tr>
<td>disc</td>
<td>2.08 * 1.98</td>
<td>2.9</td>
<td>0.99</td>
</tr>
<tr>
<td>cyl</td>
<td>2.08 * 3.38</td>
<td>3.5</td>
<td>1.39</td>
</tr>
<tr>
<td>cyl</td>
<td>2.08 * 3.38</td>
<td>3.1</td>
<td>1.23</td>
</tr>
<tr>
<td>cyl</td>
<td>2.08 * 3.38</td>
<td>2.9</td>
<td>1.15</td>
</tr>
<tr>
<td>cyl</td>
<td>2.08 * 3.38</td>
<td>2.7</td>
<td>1.07</td>
</tr>
</tbody>
</table>
However, it is also evident from Figure 3 that the hydrophilicity of the particles affects their recoveries significantly. With an increased soaking time of the coated trays in water prior to flotation, their hydrophilicity increases and this results in an increased recovery of these particles to the tailings. The increased wettability of the particles improves their bubble stabilising properties and they are more readily supported by the bubble films, an observation that correlates with the film rupturing theory of Hemmings (1981). It is also evident that, the larger the M/A ratio of the particles, the longer the soaking time that is required to improve their wettability to such an extent that they can be recovered in the tailings.

The influence of particle size on the recovery of particles is depicted in Figure 4. Cubical particles with side lengths of 2.10mm and 3.05mm respectively were used. Tests were conducted using tracers of three specific gravities (3.10, 2.90 and 2.70) and an aeration rate yielding superficial gas velocities of 8.9 mm/sec for compartment #1A and 8.9 mm/sec for compartment #1B. Similar trends are observed as for the cylindrical tracers in Figure 3, viz the recovery to the tailings decreases with an increase in particle size as portrayed in the S-shaped curves shifting towards the right on the graph. The M/A ratio increases with particle size, and it can thus be expected that the recovery to the tailings will decrease accordingly. Similar to the case of a decrease in density, the gravitational force on the particles will decrease with decreasing particle size, and the particles could thus be supported by the liquid lamella.

In the case of smaller particle sizes, the recovery of particles to the tailings is less sensitive to a change in particle density. The 3.05mm cubes display a distinct recovery curve for each density fraction, while the recovery curves for the 2.10mm cubes virtually coincide. This trend can again be explained in view of the M/A ratio difference between the particles of each density fraction and particle size. The M/A ratio of a particle in each density fraction is presented in Table 1. The ratio difference between individual 2.1mm particles of the various density fractions is only 0.07 while the ratio difference for the 3.05mm particles is 0.1. The much larger ratio difference for the 3.05mm particles would result in the distinct recovery curves as shown in Figure 4.

To demonstrate the influence of particle shape on the recovery of particles to the tailings, experiments were conducted with various particle shapes at the same aeration rate used in the previous experiments. The associated recovery curves are presented in Figure 5. Three shapes were investigated, i.e. 2.1mm cubes, 2.08 x 3.38mm cylinders and 2.08 x 1.98mm discs. The expected trends as obtained with the results of the experiments described above, are followed for each individual particle shape in that the recovery to the tailings decreases with an increase in the M/A ratio. However, when the M/A ratios for the various shapes are compared, it is found that these trends are not continued. For example, although the M/A ratio of the 3.5G cubes is higher than that of the 2.9G cylinders (1.23 and 1.15 respectively), the cubes are more easily recovered to the tailings. This clearly shows that the bubble films have less “grip” on the rounded area of the cylinder, while the shape of the cube lends itself more to support by the bubble films.

This observation is substantiated by comparison of the results for the 3.5G disk and the 2.7G cylinder (M/A ratios of 1.19 and 1.07 respectively). Although it is expected that the recovery of the disc-shaped particles to the tailings would be less than that of the cylinders because of their larger M/A ratios, the opposite is true. This can be attributed to the fact that the cylindrical area of the disc constitutes 65 percent of its total surface area, while the corresponding figure for the cylinder is 76 percent. Based on these observations, it can be expected that when treating particles of the same M/A ratio in the froth, flat particles would be recovered to the tailings in preference to cubic, disc-shaped, cylindrical and spherical particles, in that order.

Figure 5. The Effect of Particle Shape on the Recovery of Particles to the Tailings.

By varying the aeration rate of the cell, various froth characteristics such as the rigidity and thickness of bubble films and the residence time of the bubbles in the cell can be modified. The effect of aeration rate on the recovery of 3mm cubes to the tailings was investigated. Tracers with specific gravities of 3.10, 2.90 and 2.70 were used in conjunction with two aeration rate settings: (1) superficial gas velocity of 12.7 mm/sec for compartments #1A and #1B and (2) superficial gas velocity of 8.9 mm/sec for compartments #1A and #1B.

As can be seen in Figure 6, an increased aeration rate results in an increased recovery of hydrophobic particles to the tailings. It can be expected that the aeration rate will have some influence on the recovery of even highly hydrophobic particles, seen in the light of the previous work on bubble film thinning and rupture (Dippenaar, 1982) (Hemmings, 1981). The characteristics of the froth such as the rigidity and the thickness of the bubble films, as well as the size...
and the residence time of the bubbles, are closely related to the aeration rate. An increased aeration rate would firstly increase the thickness of the bubble films in the froth since there is less time for bubble film drainage, and secondly would decrease the residence time of the bubbles. The increased bubble film thickness would increase the time taken for bubble film thinning and this would result in an increased recovery to the tailings. In addition, the recovery to the tailings would increase if the particles do not have sufficient time to settle through the froth before they reach the splitter plate. It can therefore be expected that the aeration rate would be a very important control parameter in the reverse froth flotation technique.

There does not appear to be any relationship between the aeration rate and the hydrophobicity of particles in terms of their recovery to the tailings. As can be seen from Figure 6, the results follow the same trends for the particles of various densities. Although the curves move to the left with an increased aeration rate, they do so in a uniform manner, i.e. their S-shape remains.

CONCLUSIONS

A novel separation technique that could treat coarse hydrophobic particles at a low power input and without the addition of alternate flotation reagents, has been developed. The concept is based on the fact that a coarse particle with a highly hydrophobic surface will repel the bubble films in a froth and thus drop through the froth under the influence of gravity. The gangue or hydrophilic particles, in turn, are supported by the bubble films in the froth and are therefore recovered as the floating product.

The results of the work have shown that prolonged soaking times of the coated tracers in the water-frother mixture result in an increase in particles reporting to the tailings due to a decrease in particle wettability. The recovery of particles to the first concentrate increased as the particle density and size increased. It was also found that the effect of density on the particle behaviour increased as the particle size increased due to the greater difference between the mass to area ratios (M/A) of the particles in each density fraction. The shape of the particles also influenced their recovery significantly - it was noted that in addition to the M/A ratio of the particle, its sphericity contributed to its behaviour. It can therefore be expected that when treating particles of the same M/A ratio, spherical particles would be recovered to the first concentrate in preference to (in recovery order) cylindrical, disk-shaped and cubical particles.

An increased aeration rate decreased the recovery of particles to the underflow product, presumably due to a decrease in residence time of the bubbles, and therefore the particles in the froth, and the increased bubble film thickness. It can therefore be expected that the aeration rate would be a very important control parameter in the reverse froth flotation technique.

REFERENCES


INTRODUCTION

The probabilities of collision and attachment in conventional flotation cells are low owing to the relatively low intensity of turbulence. Consideration of these constraints led to the development of an air-sparged hydrocyclone (ASH) in the late seventies at the University of Utah [1]. This device was designed to utilise the powerful centrifugal force developed in a cyclone, together with a high concentration of small bubbles, to achieve effective flotation of fine particles at an increased rate. Bubble attachment, rather than the collision rate or air flow, limits the rate of flotation in an ASH [2].

The ASH consists of a vertical porous cylinder with slurry fed tangentially at the top, froth overflowing through the central vortex finder, and tailings flowing downward through a spigot. Air bubbles sparged radially through the porous wall are dispersed by the high velocity of slurry in swirl flow countercurrent to the rising froth phase. Separations can be achieved in about one second rather than minutes as in conventional cells.

Miller and co-workers have demonstrated their concept successfully in the flotation of oil shale [3], fine coal [4], copper sulphide ore [5] and fine gold [6]. Previous work by Van Deventer et al. [7] has shown that the ASH can be used successfully to separate gold-bearing pyrite from a Witwatersrand quartzitic ore. A spigot where flow is restricted by an orifice was found to be more successful in preventing blockage by wood chips than an annular opening between a pedestal and the cylinder wall [7,8].

This paper presents the results of recent testwork on a low-grade pyritic ore containing 0.14%, and suggests improvements in the design of an ASH. These results are compared with those obtained for an ore containing 1.74%.

EXPERIMENTAL

Two different cyclones, I and II, were used. Cyclone I consisted of a porous ceramic cylinder, had a length of 410mm, an internal diameter of 50mm, slurry inlet of 15.8x5.4mm, vortex finder of length 50mm and diameter 12.7mm, porosity of 1 micron, and a pedestal of diameter 46.5mm above the spigot of diameter 15mm. More details are given elsewhere [7,8].

Cyclone II consisted of a porous sintered stainless steel cylinder. Except where the influence of a specific parameter was studied, cyclone II had a length of 500mm, an internal diameter of 46mm, slurry inlet of 15x6mm, vortex finder of length 50mm and diameter 12.7mm, porosity of 2 or 18 micron, and a spigot of diameter 14mm. The flow rate of air was normally 200 l/min.

Two different batches of ore, A and B, obtained from the reclaimed dumps of ERGO Ltd on the East Witwatersrand, were used. Table I gives the distribution of total mass and sulphur in the particle size fractions. It is clear that ore B was coarser than A. Except where the influence of a specific parameter was studied, 160 g/ton of PAX collector and 35 mg/l of Dowfroth 250 were added to a slurry of A containing 10 mass% solids. Slurry containing 10 mass% B was conditioned by 160 g/ton SIBX collector and 40 mg/l Dowfroth 250E at a pH of 4.5. Batch flotation tests on ore yielded an optimal sulphur recovery of 95% and an associated grade of 41%, while the corresponding values for ore B were 63% and 11% respectively.
RESULTS AND DISCUSSION

INFLUENCE OF OPERATING VARIABLES

By using ore A in cyclone I, Burger(8) showed that the recovery of solids decreased sharply as the feed rate of slurry to the ASH increased. The recovery of +38 micron sulphide particles was inhibited at higher feed rates of slurry, while the opposite applied to -38 micron particles. At lower feed rates of slurry the grade of sulphur in the concentrate increased with an increase in centrifugal force. A maximum grade was attained near the slurry feed rate which yielded the minimum recovery of water. Some of these experimental data of Burger(8) are shown in Table II. For the ore containing 1.74% sulphur, cyclone I was capable of producing over 80% recovery of pyrite and a concentrate grade of 40% at slurry feed rates between 30 and 40 L/min. Such results compare favourably with those normally obtained for rougher flotation in plants operating on this ore.

An increase in the solids content of the feed enhanced the recovery of total solids and pyrite (Table II), decreased the sulphur grade, and increased the recovery of water significantly. Van Deventer et al.(7) explained that increased addition of collector exerted an influence on the water recovery only at higher feed rates of slurry where high centrifugal forces became operative. According to Table I, this was accompanied by an increase in the recovery of pyrite at all feed rates of slurry. It is difficult to draw a general conclusion about the effect of collector addition on the grade. An addition of 120 g/ton appeared to be sufficient for this type of ore. Owing to the high shearing forces on the particle-bubble aggregates in the cyclone, a dosage of 40 g/ton used in conventional plants was inadequate.

As could be expected, increased additions of frother enhanced the recovery of both water and solids, and lowered the grade of sulphur(8). At feed rates of slurry above 40 L/min, this resulted in enhanced recovery of pyrite, as could be expected. However, at slurry feed rates below 40 L/min the recovery of pyrite decreased with an increase in frother addition.

At slurry feed rates higher than 40 L/min, an increase in the air flow rate enhanced the recovery, but decreased the grade of pyrite. Burger(8) gives more details in this regard.

INFLUENCE OF DESIGN VARIABLES

Table III shows data obtained by feeding slurry B at a flow rate of 45 L/min to Cyclone II. These tests were also repeated at a variety of other flow rates between 10 and 60 L/min. It is clear that the recoveries and grades in both the cyclone and batch tests were significantly lower than those obtained for slurry A. Furthermore, the discrepancy between cyclone and batch results was more severe than in the case of slurry A. This could possibly be explained in terms of the extremely low head grade of slurry B, and the occurrence of more pyrite particles in the coarse fractions in slurry B (Table I). As shown by Burger(8), both the grade and recovery are significantly lower for particles above 75 micron.

Table III indicates that an increase in either the length or diameter of the vortex finder yielded lower grades. It appears that the recovery of pyrite reached an optimum value at certain values for the length and diameter of the vortex finder.
The larger the diameter of the orifice, the lower the recoveries of both water and solids. Figures 1 and 2 show that this was accompanied by an increase in the concentrate grade, and a more complex behaviour of the recovery of pyrite. It appears that relatively high grades and reasonable recoveries could be obtained at high feed rates and an orifice diameter of 22mm. In this case the froth must have had a cleaning action significantly better than that attained in the batch tests.

By comparing experiments 11 and 20, and 17 and 18, in Table III, it is evident that an increase in the area of the tangential slurry inlet caused the grade to decrease, while no conclusion could be drawn about the recovery. These runs also show that an increase in the porosity of the cylinder enhances the grade, but lowers the recovery, presumably owing to the lower bubble surface area.

The effect of a pedestal, as suggested by Miller and Kinneberg[2], and used by Burger[8], was investigated by feeding slurry B to cyclone I with and without a pedestal. In the case of the pedestal, the underflow was limited by an orifice below the pedestal, and not by the annular opening between the pedestal and the cylinder. Orifice diameters of 10 and 15mm were used. When this pedestal was removed, the recoveries of water and solids changed very little, while the recovery of pyrite increased slightly. The concentrate grade changed very little at an orifice diameter of 10mm, but increased significantly at 15mm. Hence, it could be concluded that a pedestal is not required in the ASH.

Figures 3 and 4 present the grades and recoveries when one quarter of the porous cylinder was replaced by inert sections at different positions. The total flow rate of air remained constant at 200 l/min, so that the flux of air increased through the remaining porous sections. Inert sections above the centre of the cylinder yielded the highest recovery of sulphur, but did not enhance the grade significantly. Inert sections below the centre of the cylinder yielded a more moderate increase in recovery, but enhanced the grade to levels comparable to that obtained in batch tests. An increase in the flow of air did not produce these effects, which means that the efficiency of the cyclone was sensitive to the distribution of air along the length of the cyclone.

**CONCLUSIONS**

Flotation with an ASH recovered pyrite effectively from a quartzitic ore containing 1.74 %S. Recoveries of over 80% and grades of over 40 % could be achieved. A coarse low-grade quartzitic ore, which contained only 0.14 %S and yielded an optimal sulphur recovery of 83% and an associated grade of 11 %S in batch flotation, was much more difficult to separate. Grades higher than 10 %S but with recoveries of 25%, or recoveries higher than 40% but with grades of 3.3 %S could be achieved.

Contrary to Miller and Kinneberg's[2] suggestion of an annular discharge and a froth pedestal, it was found here that a simple orifice spigot yielded the best results. Significantly improved performance could be achieved by sealing off the lower part of the porous cylinder. Research is continuing to optimize the design of the ASH.

The ASH has potential as a rougher cell in closed circuit with a mill, to produce concentrate as feed to a column flotation cell, and to be used where the higher capital costs of a conventional flotation plant could not be justified.

**REFERENCES**


5. Kinneberg, D.J. and Miller, J.D., Copper sulphide flotation in an air-sparged hydrocyclone, USBM Final Report on Grant G1115492, Dept. of Metallurgy, Univ. of Utah, Salt Lake City, May 1983.


FIGURE 1 - RECOVERY OF PYRITE FROM SLURRY B IN CYCLONE II AT DIFFERENT DIAMETERS OF THE ORIFICE SPIGOT.

FIGURE 2 - GRADE OF CONCENTRATE FROM SLURRY B IN CYCLONE II AT DIFFERENT DIAMETERS OF THE ORIFICE SPIGOT.
FIGURE 3 - RECOVERY OF PYRITE FROM SLURRY B WITH INERT SECTIONS AT DIFFERENT POSITIONS ALONG THE LENGTH OF CYCLONE I.

FIGURE 4 - GRADE OF CONCENTRATE FROM SLURRY B WITH INERT SECTIONS AT DIFFERENT POSITIONS ALONG THE LENGTH OF CYCLONE I.

ACKNOWLEDGEMENTS

This paper is published with permission of the Council for Mineral Technology, whose financial assistance is greatly appreciated. Thanks are extended to Dr W A H Te Riele for valuable discussions during the course of this work.
Section 13  Publications on

Fluid Mechanics
TECHNICAL NOTE
SEGREGATION OF PARTICLES DURING FLOW-SPLITTING OF SLURRY

A.J. BURGER, J.S.J. VAN DEVENTER and F.L.D. CLOETE
Dept. of Metallurgical Engng., University of Stellenbosch
Stellenbosch 7600, South Africa
(Received 27 January 1988)

ABSTRACT
The segregation of particles during flow-splitting is a common occurrence in mineral processing operations. Many flow dividers generate force fields from changes in velocity and act as inefficient classifiers.

Data were obtained on the performance of various T- and Y-pieces dividing a slurry of ore containing pyrite. It was shown that segregation could be avoided by using a Y-piece with equal velocities in the two branches.

Keywords
Slurry; segregation; flow-splitting; sampling

INTRODUCTION
It is well known that problems arise in obtaining representative samples of dusty gas and in the sampling of flowing slurries. Segregation of particles, as well as solid-fluid separation, may occur when the velocity of flow into a sampling probe differs from that in its immediate vicinity. Classifiers such as hydrocyclones create a force field through changes in velocity or direction in the fluid to cause the segregation of particles desired.

Segregation of particles may occur when a stream of slurry is split in such a way that the velocities in the branched streams are different. Although this is a problem which is recognized in practice, no quantitative information could be found in the literature. Segregation of particles may occur when a slurry is pumped from a mixing tank with a fraction being recycled. This problem arose in the handling of a coarse quartzitic slurry, and was solved by a simple method described below.

EXPERIMENTAL PROCEDURE
Figure 1 illustrates the flow diagram of the equipment. Slurry was pumped from the bottom of an agitated tank containing 450 L of slurry at the start of a run, and flowed vertically upward through the flow-splitter to be divided into a recycle and a feed stream. Valves in the recycle to the agitated tank and in the feed stream from the flow-splitter could be used to control the flow rate of the feed to a downstream processing unit. A feed rate of 45 L/min was associated with a recycle rate of 200 L/min.

The three flow-splitters used are shown in Figure 2. Flow-splitters A and B were the same T-piece in two different orientations with equally-sized connections. In configuration A the slurry was split into a vertically upward recycle stream of 170 to 250 L/min and a lateral feed stream of 0 to 70 L/min. In configuration B both the recycle and the feed streams left the splitter horizontally.

Flow-splitter C was designed on the principle that fluid entering either the recycle or feed stream should undergo the same change in velocity. The two limbs of the Y-piece should divert through equal angles. The cross-sectional
Fig. 1 Flow diagram of experimental equipment

Fig. 2 Three different configurations of flow-splitting
areas of the two discharge limbs should be proportional to the respective flow rates.

Table 1 gives the distribution of particle size and sulphur grade in the quartzitic pyrite ore used. The solids content of the slurry in the tank was 10 mass% at the start of a run. Samples of the recycle taken with the feed stream being closed off also revealed a solids content of 10 mass% and a sulphur grade of 1.74%. Hence, mixing in the agitated tank was assumed to be adequate.

### TABLE 1 Distribution of Particle Size and Grade of Sulphide in Ore

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass %</th>
<th>Mass % in size range</th>
<th>Mass % of total S in ore in size range</th>
</tr>
</thead>
<tbody>
<tr>
<td>+212</td>
<td>11.5</td>
<td>0.322</td>
<td>2.13</td>
</tr>
<tr>
<td>+150</td>
<td>30.0</td>
<td>0.748</td>
<td>13.0</td>
</tr>
<tr>
<td>+106</td>
<td>22.4</td>
<td>2.08</td>
<td>26.9</td>
</tr>
<tr>
<td>+75</td>
<td>15.5</td>
<td>2.70</td>
<td>24.2</td>
</tr>
<tr>
<td>+53</td>
<td>9.3</td>
<td>3.14</td>
<td>16.8</td>
</tr>
<tr>
<td>+38</td>
<td>2.8</td>
<td>3.61</td>
<td>5.82</td>
</tr>
<tr>
<td>-38</td>
<td>8.5</td>
<td>2.29</td>
<td>11.2</td>
</tr>
<tr>
<td>all fractions</td>
<td>100.0</td>
<td>1.74</td>
<td></td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

Figures 3 and 4 illustrate the solids content and sulphur grade of the feed stream using flow-splitters A and B. Experiments were conducted at increasing flow rate of the feed stream. Flow-splitter A yielded a solids content slightly below 10%, and a sulphur grade below 1.74% at lower velocities in the feed stream. This segregation of particles was caused by the lower tendency of the heavy particles to change direction. The increase in the velocity of the feed stream had a more pronounced effect on the more dense pyrite than on the quartzite, with a resulting increase in the sulphur grades.

![Fig.3 Solids content of feed stream at different flow rates using flow-splitters A and B](image)

In flow-splitter B both the recycle and the feed streams had to change direction by 90° relative to the inlet of the splitter. This means that segregation of particles was caused more by differences in flow speed than direction of flow. Particles were expected to settle more easily in areas of low velocity, so that a higher solids content and sulphur grade could be expected at low feed rates. Figure 3 and 4 confirm this, and reveal that less segregation occurred at the higher feed rates. For both configurations A and B
it appeared as if a feed stream with acceptable composition could be obtained at higher feed rates only.

![Graph showing sulphur grade of feed stream at different flow rates](image)

Fig. 4 Sulphur grade of feed stream at different flow rates using flow-splitters A and B.

Figures 5 and 6 show that significantly improved performance, and hence less segregation, could be achieved at all feed rates by use of flow-splitter C. Although the splitter was designed to yield equal velocities of the recycle and feed streams at a feed rate of 45 L/min, acceptable results were also obtained at other flow rates. The sequence of tests did not affect results significantly, which indicates that a change in the recycle had little influence on the mixing efficiency in the tank.

![Graph showing solids content of feed stream at different flow rates](image)

Fig. 5 Solids content of feed stream at different flow rates using flow-splitter C.

**CONCLUSIONS**

1. Serious segregation of particles can occur when a slurry is split into two streams by use of a T-piece and the velocities in the branched streams are significantly different.

2. In order to overcome this problem, the cross-sectional areas of the branched pipes should be such that the velocities in both branched streams are equal. Furthermore, the two branched pipes should divert from the inlet branch through equal angles.
Fig. 6 Sulphur grade of feed stream at different flow rates using flow-splitter C

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial and technical assistance from the Council for Mineral Technology. Thanks are extended to Mr. R. C. Dunne and Dr. W. A. M te Riele for valuable discussions during this investigation.
Communications

Observations on the Effect of Medium Density and Viscosity on the Rate of Induced Aeration in Agitated Vessels

C. ALDRICH and J.S.J. VAN DEVENTER

Induced aeration in agitated vessels is used widely in the metallurgical industry, e.g., in the bioleaching of minerals and flotation, due to its efficiency in facilitating contact between liquids and gases in reactors. Although the mechanism and associated hydrodynamic phenomena of gas induction in stirred vessels (such as the formation of cavities behind the rotating impeller blades) are too complicated for a detailed fundamental description, the induction of gas is considered to be directly proportional to the pressure-driving force generated by the rotating impeller in the fluid. When the impeller is at rest, for example, the static pressure at any point on the impeller is equal to both the static pressure in the fluid at that point and the pressure of the gas above the liquid surface. When the impeller rotates with velocity \( \nu \) at the point considered, Bernoulli's equation holds, i.e., in an inviscid fluid,

\[
d\left( \frac{1}{2} \rho \nu^2 \right) + dp = 0
\]  

Gas induction commences when the pressure, \( p \), is equal to the pressure in the gas space above the fluid, with density \( \rho \). A further increase in the impeller speed beyond this critical point results in an increase in the rate of gas induction under the influence of the higher pressure-driving force generated by the rotation of the impeller in the fluid.

Previous research has underlined the importance of the viscosity and density of the fluid, but the fact that variations in density and viscosity have often been investigated concurrently complicates the interpretation of results on induced aeration found in the literature. Some authors observed an increase in the rate of induced aeration with an increase in viscosity, while others reported a decrease in the rate of gas induction with an increase in the viscosity of the fluid.

Zlokarnik, working with hollow shaft contactors, and Kind, experimenting with Wemco laboratory flotation cells (Wemco, Envirotech Corporation, Menlo Park, CA), found that an increase in the density of the fluids had an adverse effect on aeration. Joshi modified a pipe impeller and studied the effect of liquid density on gas induction by adding isopropanol to water, so as to vary the density from 900 to 1000 kg/m\(^3\). By allowing for corrections in the liquid viscosity, he concluded that changes in the density did not affect gas induction. The corrections that he used for the effect of viscosity were based on the work of Joshi and Sharma, but in that work, viscosity effects were investigated without accounting for concomitant density effects in the first place.

The objective of this communication is consequently to determine the effects of density and viscosity on the rate of induced aeration in liquids in agitated vessels for conditions where either the density or the viscosity of the liquid phase is kept reasonably constant. It is not the aim of this article to explain the results quantitatively, or to provide data for scale-up purposes, but rather to reconcile opposing views in a qualitative manner.

Experiments were conducted with two turbine impellers in a small Perspex vessel with an inner diameter of 190 mm. The height of the fluid in the vessel was approximately 200 mm. The vessel, moreover, was equipped with four evenly spaced baffles, each of which protruded 20 mm into the bulk fluid. The baffles were each approximately 2-mm-thick. Six-bladed and 12-bladed Rushton turbines were enclosed in two draft tubes of different sizes (Figure 1) and immersed in the fluid contained in the vessel. A variable-speed motor was used to vary the speed of the turbine impellers in the four rotor-stator combinations, viz, the six-bladed turbine in 74 mm (T6S80) and 94 mm (T6S100) stators, as well as the 12-bladed turbine in the 74 mm (T12S80) and 94 mm (T12S100) stators. Air entered through a sealed unit at the top of the agitator and was dispersed through vertical slots at the bottom of the draft tube at sufficiently high impeller speeds. Details of the impellers are provided in Figure 1.

In order to study the effect of density on the rate of induced aeration, experiments were conducted with a 95 percent aqueous ethyl alcohol solution (density 798 kg/m\(^3\), viscosity 1.4 cP) and tap water (density 1000 kg/m\(^3\), viscosity 1.05 cP). The small differences in viscosity between these liquids were disregarded, as were the differences in surface tension, based on both the results of other investigators and our own earlier experimental work. In addition, the selected fluids were both nonelectrolytic in order to eliminate the possible effects that the ionicity of the liquid phase could have on the dispersed gases. To facilitate a comparative study of the effect of viscosity on induced aeration in agitated vessels, liquids of approximately constant densities, but widely ranging viscosities, were used. This was accomplished by aerating tap water and an aqueous sucrose solution in the Perspex vessel at temperatures ranging from 20 °C to 85 °C. In this way, viscosity ranges from 0.35 to 1.05 cP in tap water and 4 to 60 cP in a 60 percent aqueous sucrose solution could be investigated, with a simultaneous variation in density on the order of only 2 percent for the tap water and 3 percent for the sucrose solution. The variation in the surface tension of the sucrose solution was on the order of 6 percent, while that of the tap water was approximately 14 percent over the entire temperature range. These parameter variations are considered to be sufficiently small, so as to have only a marginal influence on gas induction. Variations in the observed rates of induced aeration at any stage of experimental measurement were on the order of 5 percent.

\[C. \text{ ALDRICH, Senior Researcher, and J.S.J. VAN DEVENTER, Head of Department, are with the Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7599, South Africa.}\]

In addition to these experiments, a similar investigation was undertaken with pure glycerine in a Wemco laboratory flotation cell with induced aeration. The viscosity of the glycerine was varied by heating it to temperatures between 20 °C and 190 °C. In this temperature range, the density of the glycerine did not vary more than 4 pct and its vapor pressure did not exceed 40 mmHg (an increase of less than 5 pct). The Wemco unit was equipped with a shrouded turbine impeller, the speed of which was determined stroboscopically. The rate of air induced into the liquid through an aperture in the shroud was measured with a rotameter connected to the air inlet and did not vary by more than approximately 20 pct.

In support of Zlokamik's viewpoint, an increase in the density of the liquid appears to have an inhibitive effect on aerodynamic forces on the gas bubbles in the fluid, making induction into the bulk liquid more difficult. At 1000 rpm, the increase in density in Figure 2 yields a decrease in aeration rate of about 30 pct, while the adverse effect of the concomitant decrease in viscosity is estimated at only about 7 pct. However, owing to the change in viscosity and the narrow range of the densities investigated, these conclusions can only be tentative.

Of particular interest were the observations made with regard to the effect of viscosity on gas induction. In the tap water with a viscosity ranging from 0.35 to 1.05 cP during aeration, the rate of gas induction in the Perspex vessel was observed to increase continuously with an increase in the viscosity of the liquid, as illustrated in Figures 3 and 4. In the 60 mass pct aqueous sucrose solution with a viscosity ranging from 4 to 60 cP during the investigation, the aeration rate in the Perspex vessel was found to increase with an increase in viscosity up to approximately 12 cP, after which the trend was reversed and a gradual but significant decrease in aeration followed further increases in the liquid viscosity, as illustrated in Figures 5 and 6. The complex relationship between viscosity and the rate of induced aeration in agitated vessels was also exhibited with the aeration of pure glycerine in the Wemco unit, where the rate of aeration increased from approximately 3 to 9 L/min with an increase in the viscosity of the glycerine from approximately 0.34 to 19 cP, after which it remained essentially the same from 19 to approximately 180 cP and decreased sharply to zero from 180 to approximately 740 cP, as shown in Figure 7.

Although the tap water and the sucrose solutions exhibited relatively high vapor pressures at higher temperatures (associated with comparatively low viscosities and low rates of induced aeration), the effect of vapor pressure on gas induction appears to be insignificant when the behavior of the pure glycerine is considered (as mentioned earlier, the glycerine’s vapor pressure did not exceed 40 mmHg at any given point in the experiments). Furthermore, the maximum pressure reduction owing to impeller action in the agitated vessels did not exceed 150 mmHg (i.e., an absolute pressure of approximately 600 mmHg), which was substantially higher than the vapor pressures of the aerated liquids. It is thus unlikely that these small variations in the vapor pressure of the glycerine could have affected the cavities behind the impeller blades to such an extent, so as to explain the observed trends in the gas induction rate in the fluid.

Since variations in the densities, ionicity, and surface
tension (and in the case of the glycerine, variations in the vapor pressure) of the liquids at the different temperatures were slight, the only important variable influencing the rate of gas induction in the liquid appears to be the viscosity of the fluid.

The following conclusions can be drawn from the preceding discussion.

1. An increase in the density of a fluid medium appears to adversely affect the rate of induced aeration in agitated vessels.
2. An increase in the viscosity of a medium reveals a maximum rate of induced aeration, depending on both the viscosity of the medium and the geometry of the agitated vessel. If the viscosity of the fluid is low, an increase in viscosity is likely to result in an increase in the rate of gas induction, while an increase in the viscosity of a more viscous fluid, such as a concentrated aqueous sucrose or glycerine solution, is likely to lead to a decrease in the rate of induced aeration in agitated vessels.

METALLURGICAL AND MATERIALS TRANSACTIONS B
Equilibrium Values for the Dissolution of Solid Copper into FeS-Na₂S Mattes

Y. ZHANG, T. NAGASAKA, A.W. CRAMB, and R.J. FRUEHAN

Recently, there has been an interest in the removal of solid copper from ferrous scrap at low temperatures to eliminate the increasing residual copper content problem in recycled steels. Treatments of liquid steel, although thermodynamically feasible, are too expensive, and methods of solid scrap treatment are now under development. Physical separation, acid treatment, dissolution with liquid aluminum, and reaction with an FeS-Na₂S matte have all been discussed in the open literature as potential processes for the separation of solid copper from ferrous scrap.1-12

Solid ferrous scrap treatment with a liquid matte to separate copper was recently developed at Carnegie Mellon University.13 This process is based upon four principles: (1) the majority of the copper found in scrap is present as solid copper; (2) the removal of solid copper, of activity close to unity, from solid scrap by reaction is more thermodynamically favorable than the removal of copper dissolved in liquid iron; (3) the solid copper is transformed by reaction into a liquid sulfide; and (4) the copper containing liquid can be separated (by drainage) from the scrap. In this manner, solid copper can be separated from solid scrap. The chemistry of the process is based upon the following reaction:

\[ 2\text{Cu(s)} + \text{FeS(l)} = \text{Cu}_2\text{S(l)} + \text{Fe(s)} \quad [1] \]

where solid copper reacts with FeS to form Cu₂S while precipitating solid iron at the temperature of interest (<1000 °C). Reaction [1] is the reaction which was the basis for the ladle sulfide slagging process originated by Jordan in 1950.14 However, in the solid scrap treatment process, the reaction takes place at a much lower temperature while the scrap and copper are solid and separate. At 1000 °C, the equilibrium constant of Reaction [1] has a value of five and solid copper can reduce FeS. The process can be initiated with a liquid matte containing a mixture of FeS and Na₂S.14,5

As the reaction proceeds, FeS in the matte is replaced by Cu₂S in an ionic exchange reaction where solid iron is precipitated and copper ions enter the matte phase. The solid copper is transformed into copper ions dissolved in the liquid matte until either the Cu₂S solubility limit in the matte or the equilibrium condition of Eq. [1] is reached. Fortunately, Cu₂S is almost completely miscible in the liquid FeS-Na₂S at process temperatures. This is important, as process success depends upon not only reaction of copper with the matte but subsequent drainage of the matte in order to allow separation of the copper from the scrap. The equilibrium constant for Reaction [1] can be written as follows:

\[ K = \frac{a_{\text{Cu}_2\text{S}}a_{\text{Fe}}}{{a_{\text{Cu}}a_{\text{FeS}}}} = \frac{a_{\text{Cu}_2\text{S}}X_{\text{Cu}_2\text{S}}}{{a_{\text{Cu}}a_{\text{FeS}}}} \quad [2] \]

where \( a \) and \( \gamma \) indicate the activity and the activity coefficient with respect to pure materials, respectively, and \( X \) denotes the mole fraction. According to the phase diagram of Fe-Cu system, iron and copper are almost immiscible below 1000 °C. Therefore, their activities are reasonably approximated as unity and Eq. [2] can be simplified as

\[ X_{\text{Cu}_2\text{S}} = \frac{a_{\text{FeS}}}{{\gamma_{\text{Cu}_2\text{S}}}} \quad [3] \]

According to Eq. [3], to maximize the amount of copper in the matte, it is necessary to maximize the activity of FeS and to minimize the activity coefficient of Cu₂S in the starting matte. As Na₂S reduces the melting point of FeS and, in addition, the activity coefficient of Cu₂S in the matte, it aids in improving the thermodynamics of copper removal. An FeS-Na₂S matte of weight ratio 82/18 was chosen as the starting matte composition for pilot studies.15

Previous work16 has shown that the reaction rate for copper dissolution is controlled by liquid phase mass transfer. As all rate equations contain a mobility term and a driving force, it is important to know not only the fluid flow characteristics of the system but also the equilibrium condition of the reaction to fully determine the reaction rate kinetics. The purpose of this communication is to document a study of the dissolution equilibrium of copper in contact with an FeS-Na₂S matte. The equilibrium Cu₂S content in the matte was determined at temperatures ranging from 830 °C to 1050 °C.
Short Communication

Observations on induced aeration in agitated slurries

C. Aldrich and J.S.J. van Deventer
Department of Metallurgical Engineering, University of Stellenbosch, Private Bag X5018, Stellenbosch 7600 (South Africa)

(Received February 13, 1992; in final form November 23, 1993)

Abstract

Despite its importance as a fundamental operation, research on induced aeration in slurries in agitated vessels has received little attention up to the present. In experiments conducted with a hollow pipe and shrouded Rushton turbine impellers and slurries composed of ore as well as synthetic particulates, it is shown that the onset of gas induction is not affected by solids concentrations of less than approximately 15% by mass. Beyond this critical point induced aeration decreases with an increase in the solids concentration, particle size and particle density of the slurry. These effects can be interpreted in terms of the effect of the solids on the apparent properties of the fluid, i.e. the viscosity and density.

1. Introduction

Since it is a convenient way of contacting gases and liquids in chemical engineering operations such as the treatment of waste water and fermentation processes, induced aeration in agitated vessels has been studied in a variety of contactor designs and aeration conditions. Despite its importance as a fundamental operation, research has been focused mainly on gas induction in homogeneous liquids, and little attention has been paid to slurries. Sawant et al. [1] investigated the effect of an aqueous suspension of fine dolomite particles (smaller than 60 \( \mu \)m) on the rate of gas induction in a Denver-type flotation cell and concluded that solids loadings of up to 20% had no appreciable effect on aeration. In a similar investigation, Arbiter et al. [2] experimented with glass beads and haematite ore of various sizes in a Fagergren and a Denver flotation machine and solids mass loadings of up to 50%,
that the slurry particles were fully suspended in the vessel prior to the onset of aeration, it was difficult to conduct comparative experiments on an extended scale.

Since the actual mechanism is poorly understood, no fundamental analysis of gas induction is available in the literature, and this communication presents similarly semiquantitative relationships between rheological parameters and gas induction in slurries, rather than a mathematical description of induced aeration.

3. Critical aeration

The critical point of gas induction, i.e. the point at which minute quantities of gas are induced into the fluid (manifested by the first few bubbles to emerge on the bulk fluid surface), was not affected significantly by solids loadings below approximately 15\%, as shown in Figs. 3–5, where the onset of gas induction in aqueous slurries is compared with water.

Above loads of about 20–25\%, the solids loading appears to have a more pronounced effect on the onset of gas induction, as is illustrated by the 50\% quartz, 25\% calcium fluoride and 38\% resin suspensions in Figs. 3–5. This is to be expected since, at these solids concentrations, interparticle effects probably contribute considerably to the apparent viscosity of the fluid [3, 4], which is known to have an effect on the onset of induced aeration [1, 5, 6]. Figures 3 and 4 also show that the onset of aeration is inhibited by an increase in viscosity in

---

**Table 1. Properties of liquids and slurries used**

<table>
<thead>
<tr>
<th>Slurry*</th>
<th>( \varphi ) (mass%)</th>
<th>( d_s ) (( \mu )m)</th>
<th>( \rho_f ) (kg m(^{-3}))</th>
<th>Shape(^b)</th>
<th>( \mu ) (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>–</td>
<td>–</td>
<td>998</td>
<td>–</td>
<td>1</td>
</tr>
<tr>
<td>25 Mass% aqueous brine solution</td>
<td>–</td>
<td>–</td>
<td>1190</td>
<td>–</td>
<td>2.2</td>
</tr>
<tr>
<td>63 Mass% aqueous sucrose solution</td>
<td>–</td>
<td>–</td>
<td>1304</td>
<td>–</td>
<td>60</td>
</tr>
<tr>
<td>65 Mass% aqueous sucrose solution</td>
<td>–</td>
<td>–</td>
<td>1315</td>
<td>–</td>
<td>178</td>
</tr>
<tr>
<td>Resin</td>
<td>11; 13</td>
<td>710</td>
<td>1270</td>
<td>S</td>
<td>–</td>
</tr>
<tr>
<td>Quartz</td>
<td>23; 38</td>
<td>63</td>
<td>2500</td>
<td>I</td>
<td>–</td>
</tr>
<tr>
<td>Baddeleyite</td>
<td>50</td>
<td>63</td>
<td>2650</td>
<td>I</td>
<td>–</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>10</td>
<td>142</td>
<td>3730</td>
<td>I</td>
<td>–</td>
</tr>
<tr>
<td>Nylon</td>
<td>9</td>
<td>800</td>
<td>1020</td>
<td>S</td>
<td>–</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>25</td>
<td>1790</td>
<td>3180</td>
<td>C</td>
<td>–</td>
</tr>
<tr>
<td>Siliceous ore(^c)</td>
<td>20</td>
<td>108</td>
<td>2170</td>
<td>I</td>
<td>–</td>
</tr>
</tbody>
</table>

*All solids are suspended in water, unless indicated otherwise.

\(^b\)C, cylindrical; I, irregular; S, spherical.

\(^c\)Suspended in an aqueous sucrose solution with a density of 1315 kg m\(^{-3}\) and viscosity of 178 cP, denoted by S.
4. The rate of induced aeration

Previous research [1, 5, 7] has established that the only physical properties of homogeneous fluids affecting induced aeration are the density and the viscosity of the fluid. On the basis of these observations, it can be expected that the apparent density and viscosity of multiphase media affect the rate of induced aeration similarly.
4.1. Solids loading

The presence of solids in the medium affects the apparent viscosity of the medium and, if the density of the solids differs from that of the fluid, the apparent density of the slurry is affected as well. It is well known that an increase in the solids loading of slurries results in an increase in the apparent viscosity of the fluid [3] and, depending on the density of the particles, also increases the apparent density of the fluid. The apparent viscosity of the fluid is furthermore dependent on the density of the particles and the size of the particles, as well as on the shapes of the particles and the prevailing shear rates in the flow [3]. The adverse effect of an increase in the solids loading on induced aeration above the critical point, however, was clearly observed in experiments with both the pipe and the turbine impellers, as indicated in Figs. 6–10, where

---

Fig. 5. Critical aeration in slurries agitated with the pipe impeller: —, water; PS, polystyrene.

Fig. 6. Induced aeration in slurries using the T6S80 impeller–stator assembly.
all the curves representing slurries lie below the curves representing water (i.e. show lower rates of gas induction).

For comparative purposes the rates of gas induction in a 25 mass% aqueous brine solution with a viscosity of 2.2 cP and a density of 1190 kg m$^{-3}$, as well as an aqueous sucrose solution with a viscosity of 60 cP and a density of 1304 kg m$^{-3}$ have been included in Figs. 6–10. Owing to the small difference in their viscosities (see Table 1), the difference in the rates of induced aeration in the brine solution and the water can be attributed almost entirely to the difference in the densities (approximately 20%) of the fluids. No direct comparison between the water and the aqueous sucrose solution is possible, however, since both the density and the viscosity of the sucrose solution differ significantly from those of water. None the less inclusion of the sucrose data in Figs. 6–10 serves as a useful reference to the behaviour of the slurries.
investigated. The decrease in the rates of gas induction with an increase in the solids loading in the slurry can probably be ascribed to the increase in the apparent density of the fluid in the presence of higher solids concentrations, as well as to the increase in the apparent viscosity of the fluid. The effect is especially noticeable at slurry concentrations above approximately 20%, probably owing to the effect of interactions between the particles that become significant above this concentration level. This increases both the apparent viscosity of the medium as well as the buoyancy of the gas in the liquid and impedes prolonged entrainment of the gas in the liquid, in turn hindering dispersion of the gas into the bulk liquid.

A further contributing factor is the lower fraction of liquid available to aeration owing to the space occupied by the particles. As is shown in Figs. 6 and 10, the rate of gas induction in the polystyrene and nylon slurries which have essentially the same
densities as water is lower than would have been expected if only the dilution effect (approximately 10%) of the solids were to be taken into account.

4.2. Particle size

If the effects of the 25% calcium fluoride and the 23% resin slurries on the rate of induced aeration are compared in Figs. 7–9, it can be seen that the resin has a more inhibitive effect on the rate of gas induction than the calcium fluoride, despite its slightly lower solids concentration and its lower particle density. The same trend is observed when the nylon and polystyrene slurries are compared in Fig. 10. The nylon particles (1790 μm) are considerably larger than the polystyrene particles (800 μm) and are therefore associated with a commensurately lower rate of gas induction. (These observations are not definitive, since the different sphericities of the nylon and polystyrene particles cannot be entirely discounted.) From these observations it can be concluded that a larger particle size has an adverse effect on the rate of induced aeration in slurries.

4.3. Particle density

Too few data were obtained to establish the effect of particle density on induced aeration but, from the limited data available, it would appear as if higher particle densities result in decreased rates of gas induction. This effect is best illustrated in Fig. 7, where the 15% baddeleyite slurry had a significantly stronger suppressive effect on induced aeration than the 23% resin slurry, for example. The baddeleyite had both a lower solids content and particle size than the resin, but a much higher particle density.

5. Conclusions

The induced aeration of slurries decreases with an increase in (a) the solids content, (b) the particle size and (c) the particle density of the slurry. These effects can be interpreted in terms of the effects of the solids on the apparent properties of the fluids, namely viscosity and density. The apparent viscosity of the medium is a complex function of the physical properties of the constituents of the medium, as well as the prevailing flow conditions in the medium, and can be expected to be increased by an increase in the solids content of the slurry. An increase in the apparent density of the fluid medium leads to a decrease in the rate of gas induction and the apparent density of the slurry is directly affected by the concentration of solids present, as well as by the relative densities of the solids with regard to the liquid phase.

References


Appendix A: Nomenclature

\[ \begin{align*} 
\text{Ac} & = \frac{Q}{N d^3}, \text{ aeration number (}) \\
\text{d} & = \text{impeller diameter (m)} \\
\text{d}_p & = \text{particle size of slurry solids (m)} \\
\text{Fr} & = \text{Froude number (}) \\
\text{Frc} & = N^2 d^2 g f h, \text{ critical Froude number (}) \\
\text{g} & = \text{gravitational acceleration (m s}^{-2}) \\
\text{h} & = \text{impeller immersion depth (m)} \\
\text{N} & = \text{impeller speed (rad s}^{-1}) \\
\text{Nc} & = \text{impeller speed at onset of aeration (rad s}^{-1}) \\
\text{PIPE} & = \text{pipe impeller (}) \\
\text{Q} & = \text{rate of induced aeration (m}^3 \text{ s}^{-1}) \\
\text{S80} & = \text{stator with inner diameter of 74 mm (outer diameter 80 mm) (}) \\
\text{S100} & = \text{stator with inner diameter of 94 mm (outer diameter 100 mm) (}) \\
\text{T6} & = \text{six-bladed turbine impeller (}} \\
\text{T6S80} & = \text{T6 impeller combined with stator with inner diameter of 74 mm (outer diameter 80 mm) (}} \\
\text{T6S100} & = \text{T6 impeller combined with stator with inner diameter of 94 mm (outer diameter 80 mm) (}} \\
\text{T12} & = \text{12-bladed turbine impeller (}} \\
\text{T12S80} & = \text{T6 impeller combined with stator with inner diameter of 74 mm (outer diameter 80 mm) (}} \\
\text{T12S100} & = \text{T12 impeller combined with stator with inner diameter of 94 mm (outer diameter 100 mm) (}} \\
\end{align*} \]

Greek letters

\[ \begin{align*} 
\mu & = \text{viscosity (cP)} \\
\rho_p & = \text{particle density (kg m}^{-3}) \\
\phi & = \text{solids mass fraction in slurry (}} \\
\end{align*} \]
THE EFFECT OF JET REACTORS ON THE LEACHING OF GOLD FROM ORES

L. LORENZEN§, B.M. LOFTUS§, K.R.P. PETERSEN§ and J.SJ. VAN DEVENTER†

§ Department of Chemical Engineering, University of Stellenbosch, Private Bag X1, Matieland, 7602, Stellenbosch, South Africa. Email: lll@maties.sun.ac.za
† Present address: Dept. of Chemical Eng., University of Melbourne, Parkville, Vic.3052, Australia
(Received 20 March 1997; accepted 20 May 1997)

ABSTRACT

The extraction of metals from ores by means of appropriate solvents has been practised for many years. A number of methods involve leaching of crushed ores held in tanks or ponds in which the solvent is sprayed over the ore, of which effectiveness is enhanced by mechanical agitation and increased temperature and pressure. In contrast, this investigation uses a high-velocity impinging stream reactor to induce micro-cracking in the ore phase, and consequently enhance leaching kinetics by improved solvent/ore contact. Initial tests show that jet reactor leaching of a free milling ore can increase gold recovery by 10% while decreasing leaching time by up to 90%. Further investigation is required regarding refractory ores, taking into account the complex mineralogy of each ore. The three refractory ores that were tested, all behaved very similarly when subjected to jet reaction. There is no apparent improvement in recovery. However, leaching kinetics are dramatically increased when these ores are subjected to jet reaction prior to agitation. © 1997 Elsevier Science Ltd

Keywords
Cyanidation; sulphide ores; liberation; leaching; gold ores

INTRODUCTION

Many metallurgical industries are experiencing the reality of becoming marginal profit operations due to lower ore grades, high energy operation costs, unstable markets, an unpredictable economic climate and increasing pressure placed on the industry by environmentalists. Technological improvements, specifically directed towards higher recovery of precious minerals, is pivotal to the future of mineral processing. This is particularly applicable to the South African minerals industry, where approximately R500 million per annum is lost due to valuable minerals reporting to tailings streams [1]. In most South African ores more than 97% of the gold is dissolved in a cyanide medium after a residence time of about 16 to 24 hours in Pachuca tanks [2]. This apparently high recovery percentage may be the reason why so little attention has been given to techniques to improve leaching kinetics and the treatment of ore types that have been traditionally more difficult to treat.

Presented at Complex Ores '97, Bulawayo, Zimbabwe, March 1997

909
One of the major challenges in the gold industry lies in the treatment of refractory ores, i.e. ores which are not readily treated by simple cyanidation. Previous methods developed for these ores include the roasting of sulphidic ores; chlorination of carbonaceous ores; pressure oxidation of sulphidic, pyritic and arsenopyritic ores; and bacterial oxidation of sulphide ores. The use of lixiviants other than cyanide have also been investigated, but cyanidation still proves to be the most practical option. The use of intensive cyanidation methods, either by increasing pressure, temperature, cyanide concentration or oxygen concentration, are seldom advantageous.

A promising new approach in the enhancement of mass transfer kinetics of multiphase fluid streams is based on impinging stream jet reaction, which has shown to significantly improve mass transfer in gas–liquid, liquid–liquid and liquid–solid systems [3]. In this investigation, jet reactor technology is applied to the leaching of gold from ores. By bringing gold bearing ore into contact with a high velocity jet of cyanide prior to mechanical agitation, gold recovery is increased and leach time dramatically reduced. The increase in dissolution kinetics can be ascribed to the enhanced mass transfer due to high pressure jet mixing, coupled with possible micro-cracking of the particle as a result of the high velocity collisions within the reactor. The expected benefits arising from the use of jet reactors in leaching are energy savings, smaller leach tank requirements, high throughput and greater profitability due to increased gold production per unit of ore processed. Jet leaching has the potential to be a truly value-added technology since costs and space requirements are relatively low, while modifications to existing plant design would be minimal.

LEACHING

Ores are termed refractory when direct treatment by cyanidation gives unacceptably low gold recoveries or is uneconomic for the following reasons [4]: gold is locked in gangue minerals, often sulphides, and cannot adequately be liberated, even by fine grinding; or gold occurs with minerals that consume unacceptable quantities of reagents, e.g. pyrrhotite, arsenopyrite; or gold occurs with carbonaceous materials which adsorb gold during leaching; or any combination of the above. In the case of sulphidic ores, oxidation may be necessary to dissolve some, or all of the sulphide components in order to expose gold values and/or to passivate their surfaces, thereby preventing excessive consumption of reagents. The current means of scavenging gold sulphide concentrates from tailings at conventional gold plants is by flotation and consequent roasting of the sulphides. The concentrate is normally produced at a grade of 30% sulphur so that it is amenable to subsequent roasting. The sulphur is mostly present in the pyrite (FeS$_2$) although there is also some present in the pyrrhotite and several base metal sulphides. Calcination, one of the most popular roasting processes by which gold is recovered from refractory sulphides only renders about 60% of the refractory gold amenable to subsequent cyanidation.

Other techniques developed for the treatment of sulphide refractory gold ores include pressure oxidation processes and bacterial oxidation. Throughout the 1970's and 1980's Gencor (South Africa) worked on the development of bacterial oxidation for sulphide refractory gold ores and in 1986 a 10 ton/day plant was commissioned at Fairview (South Africa) to treat flotation concentrates and has since been operating successfully. The continued interest in bio-oxidation processes is due to the potential cost savings over pressure oxidation and the considerable environmental advantages over roasting [4].

Carbonaceous ores contain organic carbon (> 1%), and has a strong gold-absorbing tendency and severely reduces gold extraction to less than 80% during leaching. The carbonaceous constituents in these ores must either be passivated by chlorine or destroyed by roasting to enable gold extraction by cyanide leaching.

The first step in the design of a process to treat a possible economic gold residue should be an examination of the refractive nature of the ore in the residue. Factors affecting the extraction of gold are usually of a mineralogical nature [5]. In the field of precious metal metallurgy, little emphasis is placed on the mineralogical information available to the metallurgist, and consequently the optimum grind size of the ore is determined for the liberation of the gold.
Diagnostic leaching was developed at the Anglo American Research Laboratories [6,7], and has since been a useful tool to the metallurgist in determining the gold deportment in refractory gold ores. Diagnostic leaching determines with which minerals the gold is associated and how this will affect the extraction route. Diagnostic leaching combines sequential selective oxidative leaches of an ore or concentrate. The process is varied according to the mineralogy of the matrix material and aims to destroy selectively the minerals associated with the gold. Although a useful tool on a bench scale, a multistage chemical leach operation may not be practical industrially due to high chemical costs and environmental concerns. For these reasons, the benefits associated with physical manipulation of refractory ores in conjunction with normal cyanidation methods are increasingly becoming more apparent.

**JET REACTORS**

The underlying principle of jet reaction is based on enhancing mass transfer kinetics in gas–liquid, liquid–liquid and liquid–solid systems through improved contact of the constituent fluid phases. Processes in industry include the dissolution of solids, the selective exchange of ions between a solid and a solution, or leaching. In general mass transfer in such processes is governed by three resistance’s: the internal resistance to diffusion of the solute in the solid phase, an interfacial resistance between the phases, and the diffusion resistance in the liquid phase. The aim is to reduce all or part of the above resistance’s in order to intensify the exchange process [3]. Work done by Tamir [3] on solid–liquid systems using impinging stream reactors include: dissolution of solids, ion exchange and electrochemical mass transfer.

The use of waterjet technology in mining and metallurgical industries has thus far been limited to waterjet and abrasive waterjet drilling [8], granite cutting with abrasive waterjets [9], waterjet assisted excavation tools in coal mining [10] and granite quarrying [11]. In this investigation the properties of high velocity jet streams are used to assist in both the chemical and physical processes involved in the extraction of a valuable mineral, namely gold.

**JET REACTOR SETUP**

The experimental set-up is shown in Figure 1. The cyanide solution concentration is made up to 1kg of KCN per ton of ore and is contained in a storage vessel. The cyanide solution is pumped to the reactor by way of a high pressure reciprocal pump. Typical pressures produced vary between 200 and 300 bar.

![Experimental Set-up Diagram](https://scholar.sun.ac.za)
The ore slurry is contained in a stainless steel mixing drum and is pumped to the reactor by way of a slurry pump. Typical flow rates for the cyanide and the slurry are 1.5–2.0 l/min and 12–15 l/min respectively. The cyanided pulp exits the reactor and is then agitated in a plastic holding drum, from which samples are taken.

The compact stainless steel reactor cavity is designed in such a way that contact between ore particles and cyanide is maximised and a milling action within the reactor is induced. A cross-flow of two ore slurry streams is introduced perpendicularly to a high velocity cyanide jet for intensive leaching action to take place. The high velocity cyanide jet is produced using a high pressure pump and passing the solution through an appropriate nozzle. The velocity and volumetric flow rate of the cyanide jet can be varied by regulating the pressure produced by the pump or varying the nozzle diameter.

EXPERIMENTAL RESULTS

(1) Physical parameters

In initial experiments, a free milling ore (President Brand) was used to determine optimum operating conditions. All the results are compared to the leaching result obtained by leaching the ore in an agitated vessel (kinetic run). A typical leaching result obtained from the jet reaction is shown in Figure 2 where it is clearly visible that gold recovery increases and leach time is reduced when the ore is first subjected to a jet of cyanide prior to agitation in the holding tank. In both experiments 1 kg/t NaCN, pH of 10 and 40% solids were the standard leaching conditions.

![Fig.2](https://scholar.sun.ac.za)

Fig.2  Typical graph of recovery versus time (the inclusion of the jet reactor shows a 10% improvement in the final amount of gold recovered).

Flat spray tungsten carbide tipped nozzles were selected to produce the cyanide jet. Optimum operating conditions were determined by varying pressure, nozzle diameter and spray-angle. The relevant increases in recovery compared to that of a kinetic run are shown in Tables 1 to 3.

An increase in cyanide pressure results in an increase in gold recovery. This can be attributed to the increase in both the flow rate and velocity of the cyanide jet. The results obtained for a set of experiments where the nozzle diameter and spray angle are kept constant, while pressure is varied, are shown in Table 1. There is a substantial increase in recovery from 2% to 18% for 10 and 20 MPa respectively.

The small increase in recovery at 30 MPa can be ascribed to the high viscous pressure forces encountered
in the nozzle which negates any further major increase in flow rate \((Q = \sqrt{P})\) and eventually leads to a physical degradation of the nozzle. It is likely that the increase in flow rate from 1.17 to 1.46 l/min for a pressure change from 20 to 30 MPa is partly due to nozzle failure.

**TABLE 1** The effect of cyanide pressure on gold recovery

<table>
<thead>
<tr>
<th>Pressure, (P) [MPa]</th>
<th>Flow rate, (Q) [l/min]</th>
<th>Velocity, (V) [m/s]</th>
<th>Recovery [% increase]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.83</td>
<td>161</td>
<td>2%</td>
</tr>
<tr>
<td>20</td>
<td>1.17</td>
<td>227</td>
<td>18%</td>
</tr>
<tr>
<td>30</td>
<td>1.46</td>
<td>284</td>
<td>20%</td>
</tr>
</tbody>
</table>

The results obtained for a set of experiments where pressure and spray angle are kept constant, while nozzle diameter is varied, are shown in Table 2. As the diameter increases, the flow rate increases, while velocity decreases. Note that there is an increase in recovery with a decrease in nozzle diameter. This indicates that jet velocity (a result of flow rate and nozzle diameter) is pivotal to effective leaching. However, the effect of cyanide concentration needs to be evaluated, since lower cyanide concentrations were used at high flow rates through the reactor to maintain continuity in cyanide concentration in the holding tank.

**TABLE 2** The effect of nozzle diameter on gold recovery

<table>
<thead>
<tr>
<th>Diameter, (\phi) [in. (x) 10(^{-3})]</th>
<th>Flow rate, (Q) [l/min]</th>
<th>Velocity, (V) [m/s]</th>
<th>Recovery [% increase]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1.17</td>
<td>227</td>
<td>18%</td>
</tr>
<tr>
<td>18</td>
<td>1.42</td>
<td>145</td>
<td>8%</td>
</tr>
<tr>
<td>31</td>
<td>6.11</td>
<td>209</td>
<td>7%</td>
</tr>
</tbody>
</table>

The effect that the spray angle has on recovery can be seen from Table 3 and Figure 3. Gold recovery is best for a spray angle of 40° where the jet cuts the entire face of the slurry entering the reactor. At a wider spray angle of 110° the energy of the cyanide jet is absorbed largely by the reactor walls.

**TABLE 3** The effect of spray angle on gold recovery (large spray angles cause much of the spray energy to be dissipated into the reactor wall).

<table>
<thead>
<tr>
<th>Spray angle, (\theta) [degrees]</th>
<th>Flow rate, (Q) [l/min]</th>
<th>Velocity, (V) [m/s]</th>
<th>Recovery [% increase]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°</td>
<td>1.56</td>
<td>158</td>
<td>3%</td>
</tr>
<tr>
<td>40°</td>
<td>1.42</td>
<td>145</td>
<td>8%</td>
</tr>
<tr>
<td>110°</td>
<td>1.45</td>
<td>147</td>
<td>1%</td>
</tr>
</tbody>
</table>

**Fig. 3** The effect of the Spray Angle (larger spray angles only serves to dissipate fluid energy into the reactor walls).
(2) Chemical parameters

The effect that various chemical parameters such as cyanide concentration, slurry flow rate, slurry density and pH may have on leaching kinetics was investigated. A free milling ore (President Brand) was used in these tests. Optimum physical operating parameters were selected based on the previous findings. The nozzle used throughout these experiments had a diameter of 0.018 inches and a spray angle of 40° (C1840). All experiments were conducted at 30 MPa. The results of the sensitivity analysis are summarised in Figure 4. The kinetic run (in an agitated vessel) was done under the following conditions: KCN = 1 kg/t; pH = 10; and slurry density = 40% solids.

From Figure 4 it is evident that slurry flow rate and pH do not have any notable effect on the leaching kinetics for jet reaction. However, cyanide concentration and slurry density drastically affect leaching kinetics.

![Figure 4: Sensitivity analysis done for a free milling ore. The effect of cyanide concentration, pH, slurry density and slurry flow rate are investigated.](https://scholar.sun.ac.za)

Leaching kinetics are sensitive to cyanide concentration. There is a large increase in the amount of gold leached for cyanide concentrations of 0.2 and 1.0 kg/t respectively. There is no increase in gold dissolution when the cyanide concentration is increased to 2.0 kg/t, since there is already an excess of cyanide at a concentration of 1.0 kg/t. Gold dissolution decreases sharply with an increase in slurry density. This is due to particle-interaction and poorer contact with the cyanide, associated with an increase in slurry density.

(3) Refractory ore testing

Kinetic and jet reactor leaching tests were performed on various refractory ore types. The following ores were tested: (1) mixed run of the mill ore from Free State Geduld Mine (F.S.G.) (2) a pyritic floatation concentrate from Barberton and (3) calcine from President Brand Gold Mine. Although many of the results obtained were quantitatively inconclusive, the use of jet reaction with refractory ores is promising.

All the ore types mentioned above produced very similar results when subjected to jet reaction. A typical leaching result is shown in Figure 5. Results obtained show a definite increase in the leaching kinetics, therefore reduced leach time. However, increase in recovery is not evident over a 24 hour leaching time, and it appears that the same recovery will be obtained for the kinetic run after continued agitation. The complex mineralogy of these ores needs to be taken into consideration, that together with jet reaction a process to overcome the leaching problems associated with these ores can be developed.
adequate for comparing the performance of reactors on a relative basis, because the more efficient a reactor is, the higher the percentage of reacted hydroxide ions would be. However, the reactors behaved like mixed tank reactors, so that the absorption of gas took place at a hydroxide concentration equal to the outlet concentration. Therefore, the extent by which chemical reaction enhanced the absorption process varied with varying outlet concentrations. Since the extent of enhancement varied throughout the absorption experiments (and could not be determined either), it is clear that the percentage of reacted hydroxide ions is not an absolute measure of the efficiency of a reactor. In some cases it is difficult to judge from the preliminary results if one reactor is significantly or merely marginally better than another. It is also clear that only general, qualitative conclusions could be drawn from the preliminary results.

5. DISCUSSION OF THE PRELIMINARY RESULTS

Since some of the preliminary reactors were manufactured from perspex, it could be observed visually that gas–liquid separation started as soon as the two phase mixture entered the reactor outlet tube. This separation occurred despite the fact that the flow velocity through the outlet tube was fairly high. Jet reactors must thus be designed to maintain high levels of turbulence throughout the reactor and to ensure that there are no plug flow regions in the reactor.

It should be noted that the absorption rate in a jet reactor, operated in the bubble mode, is expected to increase as the gas pressure in front of the nozzles is raised. A higher gas flow rate results in a greater gas holdup, which affects the absorption rate in two ways. Firstly, the number of bubbles in the reactor might increase as the gas holdup increases, so that the interfacial area for mass transfer is larger. Secondly, the liquid holdup in the reactor decreases as the gas holdup increases, but the rate at which energy is dissipated by the liquid stays constant. Consequently, the rate of energy dissipation per unit mass of liquid increases, giving rise to higher levels of turbulence in the liquid. This enhances the rate of mass transfer to the liquid.

5.1. The Opposing Jets Reactor

The comparative absorption efficiencies of the two configurations of the opposing jets reactor (GG and GL) are presented in Figure 3. These results
were obtained from experiments performed at liquid flow rates of 18 and 22 (rotameter readings), respectively. As expected for a jet reactor operated in the bubble mode, the absorption rates increased as the gas pressure was increased. It is evident from the results that the GL-configuration is significantly more efficient than the GG-configuration. When the reactor is operated in the GL-configuration, the absorption rate is also slightly more affected by an increase in the gas pressure. This suggests that the impinging effect is more pronounced for the case of the GL-configuration than for the GG-configuration. The reason for this might be that, in the GL-configuration, each liquid nozzle sprays liquid past the gas nozzle situated at 90° from it. Consequently, a forceful, directed flow pattern is generated, which shears off small bubbles from the gas stream at the gas nozzle’s orifice. In the case of the GG-configuration, the two liquid nozzles face one another, so that their sprays collide almost head-on in the vicinity of the gas nozzles’ orifices. This would generate random turbulence instead of a directed flow pattern. As a result, lumps of gas, rather than small bubbles, enter the reactor. The lumps of gas represent dead regions in the reactor, which has a negative influence on the efficiency of the reactor.

5.2. The Hemispherical and Spherical Reactors

The results of the hemispherical and spherical reactors are compared in Figure 4. Once again the absorption rates increased as the gas pressure was
increased. At gas pressures above about 90 kPa, the absorption rates in the spherical reactor were much higher than that in the hemispherical reactor. This is attributed to the fact that the reactor volume of the spherical reactor was about twice as large as that of the hemispherical reactor. What is more significant about these results are the very similar dependencies of the absorption rates on the inlet gas pressure. This is a direct result of the fact that the same arrangement of nozzles was used for the two reactors, giving rise to the same degree of impingement.

5.3. A Comparison between the Opposing Jets Reactor and the Hemispherical Reactor

In Figure 5, the results of the opposing jets reactor in the GL-configuration are compared to the results of the hemispherical reactor. The volume of the hemispherical reactor was almost three times as large as the volume of the opposing jets reactor, but the difference in absorption rates in the two reactors did not reflect this. It even seems that the absorption rate in the opposing jets reactor might surpass the absorption rate in the hemispherical reactor at high gas inlet pressures. It is also evident that the performance of the opposing jets reactor is more dependent on the gas pressure than the performance of the hemispherical reactor, which implies that there is a greater impinging effect in the former reactor than in the latter one.
5.4. Conclusions of the Initial Experiments

From the results of the preliminary experiments, it was concluded that the opposing jets reactor in the GL-configuration was the most efficient of all the reactor geometries tested. This reactor brought about a greater impinging effect between the feed streams than any of the other reactors. Despite its very small size, it compared favourably to the other large reactors on the basis of absorption rates. This once again proves that there are definite benefits to the intensification of the mixing process, but that the design of the reactor is crucial to its efficiency.

It was also found that the arrangement of the nozzles had an enormous influence on the efficiency of the reactor. The nozzles must be arranged in such a way that liquid is sprayed past the orifices of the gas nozzles, to create a forceful, directed flow pattern past the gas nozzles. This would ensure that small bubbles are sheared from the entering gas stream. Thus, dead reactor zones (created by gas bubbles lumping together in parts of the reactor) would be eliminated. The impinging effect can only come to its full potential if the correct nozzle arrangement is used.

Gas–liquid separation starts as soon as the two phase reacting mixture enters a plug flow region. Therefore, it is essential to design reactors so that plug flow regions are eliminated as far as possible. The nozzles must be situated in such a way that the reactor feed streams are injected from diverse directions to sustain high levels of turbulence throughout the reactor.
Finally, it was found that the results of the preliminary experiments were not conclusive, because the basis on which the absorption efficiency of the reactors was evaluated, was not an adequate measure of a reactor's performance. By comparing the absorption rates of different reactors directly with each other, certain trends were observed, but these findings were not proven beyond doubt. The result did not give any indication whether or not the new jet reactors were an improvement on other phase contacting devices, such as other jet type reactors or absorption columns. In view of the above, it was decided to continue the experimental investigation and to conduct the final experiments in such a way that the mass transfer parameters of every experimental run could be determined. The main aims of the final experiments were to verify the findings of the preliminary experiments and to prove that the newly developed jet reactors performed better than other existing fluid contacting devices.

6. THE FINAL EXPERIMENTS

6.1. The Final Reactors

Because of the high efficiency displayed by the GL-configuration of the opposing jets reactor during the preliminary experiments, the final three reactors were all derivatives of this configuration. However, the angle of impingement between the gas and liquid streams is different for each of the three reactors, in an attempt to optimise the arrangement of the nozzles. Although all the reactors were 20 mm thick, they had different shapes as shown in Figures 6(a)–(c). The dimensions of the different reactors were such that all three reactors had exactly the same volume (0.00842 litres). The reactors were mounted in the vertical plane. Liquid was injected through the top nozzles and gas through the bottom ones. Since it was visually observed during the preliminary investigation that phase separation started as soon as the gas–liquid mixture entered the outlet tube, it was decided to use a shorter outlet tube for the final reactors. Consequently, the outlet tubes of the final reactors were 15 mm long and 6 mm in diameter. It ran along the horizontal axis which went through the centroid of the reactor.

6.2. Determination of the Mass Transfer Parameters by means of a Chemical Technique

The method used to determine the mass transfer parameter (i.e., the mass transfer coefficient and the interfacial area) was similar to that used by
Herskowits (1990). Herskowits absorbed carbon dioxide in water and a sodium hydroxide solution, respectively, under identical operating conditions. Since it was assumed that the hydrodynamic behaviour of the two liquids was the same, the mass transfer coefficient had the same value for the two experimental runs and the difference in absorption rates was attributed to the effect of chemical reaction. The chemical absorption rate was divided by the purely physical absorption rate to obtain the value of the enhancement factor, $E$. The value of the mass transfer coefficient, $k_L$, could then be calculated by solving the equation,

$$E = \frac{\sqrt{M(E_i - E)/(E_i - 1)}}{\tanh\sqrt{M(E_i - E)/(E_i - 1)}}$$  \hspace{1cm} (2)$$

where

$$M = \frac{D_4 k_2 C_{BO}}{k_L^2}$$  \hspace{1cm} (3)$$

iteratively. It should be kept in mind that Eq. (2) is merely an approximation, since it was obtained by fitting a function to the numerical solution of a differential equation (Danckwerts, 1970). The error of this approximation can be as high as 12 percent.
When a gas is physically absorbed into a liquid without any chemical reaction, the gas merely dissolves in the liquid. It is very difficult to accurately determine the concentration of a dissolved gas in a liquid sample. Apart from this, the solubility of a gas in a liquid is very sensitive to the liquid temperature, as well as the partial pressure of the gas above the liquid. Changes in these parameters can cause the concentration of the dissolved gas to change before the sample has been analysed, resulting in inaccurate absorption data. If a gas reacts chemically in the liquid phase, it usually forms an ion of which the concentration can be determined quite readily. Also, the ion concentration is much less subject to change than the concentration of a dissolved gas. It is clear that, in general, concentration measurements are much more reliable for chemical absorption than for purely physical absorption.

In view of the above, it was decided to modify the method used by Herskowits. According to the new approach, carbon dioxide is absorbed under identical operating conditions into two sodium hydroxide solutions of different concentration. Since it was assumed that the two solutions had similar hydrodynamic properties, the mass transfer coefficients of the two experimental runs were the same. Thus, the difference in absorption rates of the two experimental runs was attributed to the difference in the enhancement factors of the two runs. Although absolute values of the enhancement factor could not be determined, the ratio of the $E$-values for the two runs could be calculated as the ratio of absorption rates. Thus, for each pair of experimental runs, there were three unknown variables, namely the enhancement factors of the two runs ($E_1$ and $E_2$) and the mass transfer coefficient ($k_L$). However, since $E_1$ and $E_2$ are related by the experimentally determined ratio of the enhancement factors, there were only two independent variables. Equations (2) and (3) imply that the enhancement factor and the mass transfer coefficient are related by an implicit function of the form

$$E = f_1(E, k_L)$$

(4)

This equation applied to both experimental runs; thus two governing equations could be obtained from Eq. (4). Since the system contained two independent variables and was governed by two independent equations, it was defined unambiguously in mathematical terms and would yield a unique solution of the variables. An iterative mathematical strategy was followed to determine the value of $k_L$. At the start of the procedure, $k_L$ was assigned an initial value. The two implicit governing equations were then solved to yield
the values of $E_1$ and $E_2$ for this arbitrary value of $k_L$. The ratio of the calculated $E$-values was compared to the experimentally determined ratio and a better value was assigned to $k_L$. By repeating this procedure until the calculated $E$-ratio was sufficiently close to the experimentally determined ratio, the correct value of the mass transfer coefficient was obtained. With the values of $E_1$, $E_2$ and $k_L$ known, the value of the interfacial area for mass transfer could be calculated from the mass transfer equation:

$$\dot{n} = k_L a (C_A - C_{AO})$$ (5)

A sensitivity analysis was performed on the computer program used to process the absorption data to determine the response of the calculation technique to small variations in the input variables. The input variables of the computational routine are the inlet and outlet hydroxide concentrations, temperatures and liquid flow rates, of both runs. During the sensitivity analysis, typical sets of experimental data were corrupted by changing one of the input variables of one of the experimental runs by either one percent, or by one degree Celsius in the case of temperature. The change that this variation brought about in the values of the mass transfer parameters, was recorded. For the case of each input variable, four typical responses of the three mass transfer parameters ($k_L$, $a$ and $k_L a$) are displayed in Figures 7(a), (b) and (c), respectively. From the results of the sensitivity analysis, it is clear that the value of $k_L$ is more sensitive to variation in the input variables than

![Figure 7(a) Response of mass transfer coefficient ($k_L$).](https://scholar.sun.ac.za)
the values of $a$ and $k_La$. The reason for this phenomenon is that there is an inverse relationship between $E$ and $k_L$. If the input data is corrupted, the values of $E$ and $k_L$ are affected inversely (i.e., $E$ increases if $k_L$ decreases and vice versa) so that the change in the product $k_LE$ is less notable than the change in $k_L$ alone. Recalling that the value of the mass transfer area is calculated with the mass transfer (Eq. (5)), it is clear that the change in $a$ will
be less significant than the change in $k_L$. Because of the inverse relationship between $k_L$ and $a$, the response of the product $k_L a$ is also less notable than that of $k_L$ alone.

The sensitivity of the processed values to the inlet hydroxide concentration should not be of the utmost concern. The caustic soda feed tank was well mixed both prior to and during the experimental runs and it is therefore reasonable to assume a constant hydroxide feed concentration. Furthermore, liquid feed samples were analysed by titration with a reproducibility of 0.2 percent. Since the value of the temperature could be measured with an accuracy of well within one degree Celsius, inaccuracies in the temperature values is also not a main area of concern. However, the effect of variations in the liquid flow rate is quite significant, since it is not inconceivable that these variations exceeded one percent during the experimental runs. The main contribution to the uncertainty in the calculated values of the mass transfer parameters is due to the uncertainty in the value of the outlet hydroxide concentration. When one batch of feed solution was used to evaluate the reproducibility of the outlet hydroxide concentration, the concentrations of two product samples, taken at similar operational settings, differed by less than 1.5 percent. This difference is attributed to minor fluctuations in the gas and liquid flow rates. However, the difference in the outlet hydroxide concentrations of two experimental runs, performed on different days, but at the same operating conditions, was usually between 10 and 20 percent. The reason for this large variations is that the batches of reactor feed solution were not of constant quality. Although the demineralised water (used for the experiments) contained very low quantities of ions, the concentrations of these ions varied over time. Furthermore, the demineralising column did not remove any of the organic contaminants in the water. Because of the large scale of the experiments, the dry sodium hydroxide used to make up the feed solution was not of a high and constant quality. Consequently, ionic and organic contaminants were introduced to the feed solution via both the demineralised water and the dry sodium hydroxide reagent. These foreign substances have a dramatic effect on the absorption process in the reactor, even when present in minute quantities. For instance, many ions have a catalytic effect on the chemical reaction between carbon dioxide gas and hydroxide ions, while certain organic substances act as surfactants. These surfactants concentrate at the boundaries between the liquid and gas phases, so that, even if present in very low concentrations, the hydrodynamic behaviour of the liquid near the phase interface is changed considerably. Interfacial area production and the rate of mass transfer are very much affected by this. In view of the above, it
DISCUSSION

To determine the extent to which micro-cracking occurs within the particles, a Scanning Electron Microscope (SEM) was used to obtain qualitative visual data. (See Figure 6). SEM images obtained at a magnification of 32500X indicate only a small visible crack and no other visible signs of micro-cracking on the particle surfaces were observed. However, these images do not discount the possible effects of attrition and size reduction which would lead to an increase in particle surface area amenable to leaching, and therefore an increase in recovery.

Fig. 5 A typical leaching result obtained for refractory ores.

Fig. 6 Single particle magnified 12000X. A small crack at the bottom of the particle gives little evidence that micro-cracking can be a contributor to increased recovery.
The results of an experiment to determine whether size reduction of the particles occur when subjected to a jet of water in the reactor are shown in Figure 7. The increase in the cumulative mass of particles, passing through a certain size fraction has only a slight increase of between 1% and 3% over that of untreated ore. Particle size reduction inside the reactor is thus minimal.

![Graph showing cumulative mass percent vs. equivalent spherical diameter.

Fig. 7 The increase in the cumulative mass of particles, passing through a certain size fraction (only a slight increase of between 1% and 3% over that of untreated ore).

Sitek et al. [12] point to the fact that the observed increased leaching kinetics are probably due to the intensive mixing rather than micro-cracking, since much higher jet velocities would be required for cracking to occur. Experiments in waterjet cutting show that particles disintegrate upon passing through a mixing chamber. However, in this investigation, pressures are limited to between 30 and 40 MPa, which would restrict comminution action to abrasion.

Other reasons for an increase in leaching kinetics could be attributed to the impinging stream reaction taking place within the reactor which reduces the external resistance to diffusion by (1) increasing the relative velocity between the particles and the continuous phase, which is also associated with an increase of the inter-phase friction (2) reducing the dimensions of the particles, which promotes reduction of the laminar sub-layer thickness formed near the surface (3) uniform distribution of the dispersed particles in the continuous phase and maintaining small distances between them, again promoting reduction of the laminar sub-layer and (4) exerting additional effects on the particles, such as inertia or centrifugal forces, which might promote reduction in the thickness of the fluid layer near the solid surface.

**SUMMARY AND CONCLUSIONS**

This paper investigates the application of jet reaction technology to the leaching of refractory ores. Two slurry streams and a single cyanide stream are impinged under high pressure (30 MPa) in order to improve the recovery kinetics (mass transfer) in gold leaching. Results show that recovery is improved by up to 10% for non-refractory ores. Little improvement in the case of the refractory ore indicates that micro-cracking may not be occurring, a fact which is supported in the literature [12]. Rather, increased mass transfer due to the relatively high pressures and particle abrasion (size reduction) are proposed as being the main reasons for improved recoveries. The advantages of jet leaching are related to the ability to improve recovery in ores as well as decreasing cyanidation times by up to 90% in some cases.
Effect of jet reactors on leaching of gold

REFERENCES


NOTATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>pressure [bar]</td>
</tr>
<tr>
<td>Q</td>
<td>volumetric flow rate [l/min]</td>
</tr>
<tr>
<td>R</td>
<td>recovery</td>
</tr>
<tr>
<td>t</td>
<td>time [min]</td>
</tr>
<tr>
<td>V</td>
<td>velocity [m/s]</td>
</tr>
</tbody>
</table>

Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>diameter [inches]</td>
</tr>
<tr>
<td>θ</td>
<td>spray angle [degrees]</td>
</tr>
</tbody>
</table>
THE DEVELOPMENT OF HIGH INTENSITY GAS–LIQUID JET REACTORS

F. G. BOTES*, L. LORENZEN† and J. S. J. VAN DEVENTER‡

Department of Chemical Engineering, University of Stellenbosch, Private Bag X1, Matieland, 7602, Stellenbosch, South Africa

(Received 13 May 1997; In final form 23 July 1998)

A novel type of gas–liquid contactor was researched and developed to enhance phase mixing. These high velocity impinging stream reactors are characterised by small reactor volumes supplied with nozzles, which are directed towards each other. The gas and liquid feed streams are jetted through the nozzles into the reactor volume, resulting in a highly turbulent mixture of the phases. Under these enhanced mixing conditions, mass transfer rates are increased dramatically. A mechanism for bubble formation and breakup in gas–liquid jet reactors, operated in the bubble mode, is proposed and a design philosophy of such reactors is also formulated.

Keywords: Mass transfer; jet reactors; impinging stream reactors; gas–liquid; high intensity turbulent

1. INTRODUCTION

The kinetics of a heterogeneous chemical reaction are not only governed by the intrinsic reaction rate, but also by the rate of mass transfer between the phases. If the rate of mass transfer is comparable to, or smaller than the intrinsic reaction rate, the chemical reaction as a whole is slowed down by mass transfer. An improved contact of the phases would increase the rate of mass transfer and thus also the rate of chemical reaction for such reactions.

*Present Address: Sasoltech R&D, Sasolburg, 9570, South Africa.
† Corresponding author. Tel.: +27 (21) 808 4485. Fax: +27 (21) 808 2095.
‡ Present Address: Department of Chemical Engineering, The University of Melbourne, Parkville, Vic. 3052, Australia.
Phase contact is of vital importance for all mass transfer operations in process engineering. These include gas absorption, liquid–liquid extraction, distillation, as well as chemical reactions where reagents are in different phases. In view of this importance, it was decided to contact liquid and gas phases in a jet reactor in an attempt to establish improved contact between fluid phases. Jet reactors are characterised by small reactor volumes and short residence times, and are therefore an intensification of chemical reactors. All reagent streams are introduced to the reactor through nozzles operating at medium pressures (preferably not higher than 5 bar), thus impinging on one another. Since all reagent streams are entering the reactor at high speed, there is no stagnant phase in the jet reactor. This results in an intense turbulent mixing of the phases in a fairly small volume and consequently improves mass transfer. The geometry of the reactor mixing chamber, as well as the location of the nozzles in the chamber, was regarded to be the most important factors to consider in the development of such reactors. Consequently, these aspects were investigated during the experimental research of high intensity jet reactors.

2. EXISTING GAS–LIQUID CONTACTING DEVICES

A survey of the literature revealed that a vast number of jet-type reactors have been investigated by previous researchers. These different types of jet reactors have been discussed by Botes (1996) and will only be reviewed very briefly in this paper.

Mechanically agitated reactors have gas entering through orifices or gas spargers into a liquid phase (Charpentier, 1981). Mechanical mixers stir the liquid to break up bubbles and to promote mass transfer. Some mixing vessels do not have mechanical agitators, but are supplied with nozzles for the purpose of agitation. A characteristic of such vessels is that one of the phases enters the tank through a small orifice or a specially designed nozzle. This phase is thus injected into a virtually stagnant phase. In many cases the resultant gas or liquid jet is a free jet, since it does not impinge on another stream or a fixed surface. If a gas is injected into a liquid, this type of vessel can be viewed as a jet stirred reactor where mechanical agitation has been replaced by jet agitation. In other cases a liquid is sprayed into a stagnant gas atmosphere like, for instance, spray towers (Charpentier, 1981). The aim here is to produce fine liquid droplets (a large interfacial area), but not much turbulence is induced in the liquid phase (Atay, 1987). Submerged-jet and
plunging-jet reactors, as well as ejector reactors, are examples of attempts to improve jet stirred reactors (Charpentier, 1981; Burgess, 1972 and 1973).

All the jet mixed tank reactors discussed above have one common aspect: one phase is injected into another, stagnant phase. The phases impact upon one another at low momentum. This means that inertial forces are small in comparison to viscous forces, resulting in poor turbulence. Consequently the values of the mass transfer coefficient ($k_L$) and the interfacial area ($a$), are low. Furthermore, areas away from the nozzle exit are poorly stirred. This promotes bubble coalescence, which increases the mean bubble size in the reactor.

Jet loop reactors have been widely discussed in the literature. Some of the more recent articles are by Dirix (1990), Padmavathi (1993), Tebel (1989) and Velan (1991). There is some impingement effect present in jet loop reactors, since the feed is injected into a cross-flowing fluid stream. Because there exists a strong flow pattern in the bulk of the fluid throughout the reactor volume, bubble coalescence is limited and a large interfacial area is sustained. The “impinging-stream loop reactor” was conceived as a further attempt to increase turbulence in jet-type reactors (Gaddis, 1992). In this type of jet loop reactor, a high intensity impingement zone is created by the two feed streams which meet one another head-on. It was found that, at high specific power inputs, the impinging effect provided the main contribution to the mixing process. The high efficiency of this “impinging-stream loop reactor” in comparison to normal loop reactors was also evident.

In the past decade, a group of researchers have published a series of articles on a newly developed impinging stream jet absorber (Tamir, 1985 and 1986 and Herskowits, 1987, 1988 and 1990). This absorber was the only mixing device found in the literature to use opposing jets to spray, feed streams into one another, thereby creating finely dispersed phases with high levels of turbulence. It performed outstandingly when compared to traditional phase contacting devices.

The discussion on existing gas-liquid contacting devices has demonstrated how mixing devices have been developed towards a type of phase contacting device where intense turbulent mixing is increasingly used to enhance interfacial area production and mass transfer. It has also been proven that the impinging effect of two streams, contacting at high relative velocities, has a substantial enhancement effect on mass transfer. In view of the above, it was decided to investigate the further intensification of jet reactors. This would be achieved by injecting fluid feed streams into a small reactor volume at higher flow velocities than is obtained in existing mixing
devices. The focus of this investigation would be on reactors operated in the "bubble mode" (i.e., reactors in which the gas phase exists as bubbles in a continuous liquid phase) as opposed to reactors operated in the "spray mode" (i.e., reactors in which liquid droplets are formed in a continuous gas phase).

3. EXPERIMENTAL

The absorption of carbon dioxide into a sodium hydroxide solution,

\[ \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]  

was considered as a suitable chemical system for the experimental investigation. For the above reaction, the resistance to mass transfer is almost completely in the liquid phase, which makes it ideal for the investigation of "bubble mode" reactors.

Many common ions have a catalytic effect on the above reaction and their presence is therefore undesirable. In addition to this, certain foreign substances can act as surfactants that concentrate at the gas-liquid interface. Even when present in minute quantities, surfactants can have an overwhelming effect on bubble behaviour and interfacial area production in the reactor. In view of the above, chemical reagents used during the experimental investigation had to be as pure as possible. Inert materials, such as stainless steel and certain plastics, were used for the construction of the experimental setup to minimise the amount of corrosion product introduced to the chemical system. A schematic diagram of the experimental setup is shown in Figure 1.

The liquid feed mixing tank \{1\} had a capacity of approximately 210 litres and was equipped with a mechanical stirrer. Demineralised water, with a conductivity of less than 2 µmhos, was used to fill the tank to the desired level. Caustic soda, with a purity of 98.5% (the main impurities being carbonate, iron and chloride ions), was added to the water. The tank was thoroughly mixed until all the caustic soda had dissolved. Then the liquid feed pump \{2\} was started and the mixing of the tank continued for about 15 minutes under full pump recycle to ensure a homogeneous feed concentration. It was desirable to use caustic soda of a higher purity, considering the catalytic effect of certain ions on the chemical reaction between carbon dioxide and sodium hydroxide. However, due to the large scale of the operation, this was not practical. Using sodium hydroxide of a higher purity
would have escalated reagent costs tremendously, because two to three kilograms of caustic soda were used for every experimental run.

The carbon dioxide feed cylinder \(5\) supplied the 99% pure carbon dioxide gas used in the absorption experiments. The gas is stored under high pressure in the liquid form in the cylinder. When the feed valve is opened, liquid \(\text{CO}_2\) in the cylinder changes to gas and expands as it flows through the expansion valve. This consecutive boiling and gas expansion causes the gas to cool down dramatically. Therefore, the gas was heated as it flowed through a copper coil submerged in a constant temperature water bath \(6\). The gas feed temperature was measured with a thermocouple \(7\) and was maintained between 24°C and 27°C. The gas feed temperature was not a varied parameter during the experimental investigation; it was merely measured to ensure that it remained at a constant value.

The first step in the experiment start-up was to set the gas feed at the desired pressure setting. The gas pressure was measured with a pressure gauge \(8\). Since the gas nozzles had been calibrated previously with a wet gas flow meter for gas flow rates at different pressures and constant temperature, no gas rotometer was installed in the gas line of the experimental setup. After the gas flow rate was set, the valve feeding liquid to the reactor \(9\) was opened. A liquid rotometer \(3\) and a liquid pressure gauge \(4\) measured the liquid flow rate and feed pressure, respectively. Inside the reactor, the liquid was contacted with the carbon dioxide gas and the product stream left the reactor as a two-phase mixture.
As the two-phase mixture left the reactor, it immediately entered the phase separator. The separator was of simple construction. It consisted of a cylindrical tube, approximately 70 mm in diameter, supplied with a baffle as shown. The gas–liquid mixture was sprayed against the baffle and separated into two phases. As the reactor outlet was merely 6 mm in diameter, the separator diameter could be viewed as very large in comparison with the reactor outlet. Thus, the separator allowed quick and complete phase separation. It is also reasonable to assume that the extent of reaction taking place in the tranquil environment of the separator is negligible in comparison with the extent of reaction taking place in the intensely mixed, highly turbulent reactor. A liquid sample was drawn for analysis at the liquid sampling point. As the liquid flowed towards the outlet, its temperature was measured with a thermometer. An excess of barium chloride was added to the liquid sample and after the barium carbonate precipitate had settled down, the concentration of hydroxide ions in the sample was determined by means of titration with an analytical hydrochloric acid solution.

It is desirable to use nozzles manufactured from an inert material to limit the amount of foreign ions in the reactor. However, availability of nozzles proved to be a major limiting factor in choosing the most appropriate nozzles for the experimental program. Consequently, Delevan HB2 nozzles were used to inject the gas into the reactor. Although they were manufactured from brass, they were the only nozzles with the desired pressure-flow rate relationship that were readily available. Delevan HC10 nozzles were used as liquid nozzles. These were also from brass, but they had stainless steel inlays so that the corrosive liquid did not make contact with the brass as it flowed through the nozzle. The HB2 and HC10 nozzles were of the hollow cone spray geometry with spray angles of 70°. For the final experiments, the HB2 nozzles were used again for gas injection. Delevan BF1 nozzles replaced the HC10’s as the liquid nozzles, since they consisted entirely of stainless steel. The BF1 nozzles provided a solid cone spray with a spray angle of 60°.

4. THE PRELIMINARY INVESTIGATION

A number of different reactors were initially tested as a preliminary investigation into the effects of reactor geometry and feed flow rates on the absorption efficiency in jet reactors. Only the most significant of these preliminary reactors are shown in Figure 2. The opposing jets reactor
(Fig. 2(a)) was manufactured by drilling two 12 mm diameter holes perpendicular through one another. The resultant reactor volume was almost cubical and four nozzles (two gas and two liquid nozzles) were fitted in a vertical plane opposing one another. The nozzles could be fitted so that similar phase nozzles faced one another (hereafter referred to as the GG-configuration) or so that dissimilar phase nozzles faced one another (hereafter referred to as the GL-configuration). The outlet of the reactor was a tube (5 mm in diameter and 60 mm long) which ran along the horizontal axis, right through the middle of the reactor volume. The spherical reactor (Fig. 2(b)) was also fitted with two gas and two liquid nozzles. These nozzles were all fitted at an angle of 45° to the main axis as shown in the schematic diagram. The outlet tube of the reactor was on the opposite side of the sphere and had the same dimensions as the tube used for the opposing jets reactor. The hemispherical reactor (Fig. 2(c)) was exactly the same as the spherical reactor, with the exception that the sphere had been halved as shown in the diagram. The respective volumes of the different reactors are indicated on their schematic representation in Figure 2.

For the preliminary investigation, all experimental runs were performed with the same sodium hydroxide feed concentration. Different reactors and operating conditions were compared on the basis of the percentage of the hydroxide ions that reacted with the gas. The quantification of the absorption efficiency in terms of the percentage of reacted hydroxide is

![Diagram of reactors](https://scholar.sun.ac.za)
was decided to perform the two experimental runs (of which the data were needed to calculate the mass transfer parameters) consecutively on the same day. This ensured that the quality of the demineralised water did not differ considerably for the two runs.

It has been explained extensively by Botes (1996) why highly accurate values for the mass transfer parameters could not be obtained. To sum up, there is an uncertainty in the hydroxide concentration of each product sample taken during the absorption experiments, because of unknown, varying quantities of foreign substances in the reactor feed solution. The results of these experiments were then processed by means of a function (Eq. (2)) which, firstly, is only an approximation and, secondly, greatly amplifies variations in the input parameters. There is also an uncertainty in the values of certain quantities, such as diffusivities and reaction rate constants, used during the processing of the results. In view of the above, it is clear that there is a great uncertainty in the determined values of the mass transfer parameters and the results are expected to be only vaguely reproducible. For reasons explained previously, higher reproducibility is expected with respect to \( a \) and \( k_{La} \) than with respect to \( k_L \) alone. It should be noted that the uncertainty of the final results is not a consequence of a poor experimental technique. Mass transfer operations are notorious for their sensitivity to contaminants and the inability to produce highly reproducible results.

7. DISCUSSION OF THE FINAL RESULTS

The ranges of operating conditions of the final experiments are presented in Table I. In Table II, the performance of the newly developed jet reactors for the specified range of operation is compared to the performance of other gas–liquid mixing devices (Charpentier, 1981 and Herskowits, 1990). The values of \( k_{La} \) for the new jet reactors are more than an order of magnitude higher than that of any of the other fluid contacting devices. Even considering the fact that there were some uncertainty in the values of the final results, the improvement over other devices is so vast that the superior performance of the new reactors has been proven.

<table>
<thead>
<tr>
<th>TABLE I Range of operating conditions of final experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH inlet concentration, mol/l</td>
</tr>
<tr>
<td>Gas inlet pressure, kPa</td>
</tr>
<tr>
<td>Gas flow rate, l/min</td>
</tr>
<tr>
<td>Liquid inlet pressure, kPa</td>
</tr>
<tr>
<td>Liquid flow rate, l/min</td>
</tr>
</tbody>
</table>
The development of gas-liquid reactors

**TABLE II Comparison of the mass transfer parameter intervals of different gas-liquid contacting devices**

<table>
<thead>
<tr>
<th>Type of gas-liquid contactor</th>
<th>$k_L$ $(m/s \times 10^4)$</th>
<th>$a$ $(m^2/m^3)$</th>
<th>$k_La$ $(s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed columns:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>countercurrent</td>
<td>0.4 - 2.0</td>
<td>10 - 350</td>
<td>0.0004 - 0.07</td>
</tr>
<tr>
<td>concurrent</td>
<td>0.4 - 6.0</td>
<td>10 - 170</td>
<td>0.0004 - 1.02</td>
</tr>
<tr>
<td>Plate columns:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bubble caps</td>
<td>1.0 - 5.0</td>
<td>100 - 400</td>
<td>0.01 - 0.20</td>
</tr>
<tr>
<td>sieve plates</td>
<td>1.0 - 20.0</td>
<td>100 - 200</td>
<td>0.01 - 0.40</td>
</tr>
<tr>
<td>Bubble columns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0 - 4.0</td>
<td>50 - 600</td>
<td>0.005 - 0.24</td>
</tr>
<tr>
<td>Packed bubble columns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0 - 4.0</td>
<td>50 - 300</td>
<td>0.005 - 0.12</td>
</tr>
<tr>
<td>Tube reactors:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>horizontal/coiled</td>
<td>1.0 - 10.0</td>
<td>50 - 700</td>
<td>0.005 - 0.70</td>
</tr>
<tr>
<td>vertical</td>
<td>2.0 - 5.0</td>
<td>100 - 2000</td>
<td>0.02 - 1.00</td>
</tr>
<tr>
<td>Spray columns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7 - 1.5</td>
<td>10 - 100</td>
<td>0.0007 - 0.015</td>
</tr>
<tr>
<td>Mechanically agitated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bubble reactors</td>
<td>0.3 - 4.0</td>
<td>100 - 2000</td>
<td>0.003 - 0.30</td>
</tr>
<tr>
<td>Submerged and plunging</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>jet reactors</td>
<td>0.15 - 0.5</td>
<td>20 - 120</td>
<td>0.0003 - 0.006</td>
</tr>
<tr>
<td>Hydrocyclones</td>
<td>10.0 - 30.0</td>
<td>20 - 50</td>
<td>0.02 - 0.15</td>
</tr>
<tr>
<td>Venturi scrubbers</td>
<td>5.0 - 10.0</td>
<td>160 - 250</td>
<td>0.08 - 0.25</td>
</tr>
<tr>
<td>Impinging jet absorber</td>
<td>2.9 - 6.6</td>
<td>90 - 2050</td>
<td>0.025 - 1.22</td>
</tr>
<tr>
<td>(Herskowits, 1990)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newly developed jet reactors</td>
<td>2.6 - 22.2</td>
<td>1500 - 9000</td>
<td>1.00 - 14.20</td>
</tr>
</tbody>
</table>

The experimental values of the mass transfer coefficient ($k_L$) were so scattered that no definite trends could be detected in the results. The reason is that the uncertainty in the determined values is greater than, or comparable to, the variation of $k_L$ with the operating conditions; thus, the dependency of $k_L$ on the flow conditions is concealed by the scatter in the data. Since the range of the determined values was not too wide for any of the three final reactors, it would be fair to assume that, for a given reactor, the value of $k_L$ was fairly constant over the whole range of operating conditions. It is therefore concluded that $k_L$ is not heavily dependent on either the liquid or the gas flow rate.

The results of the final experiments will be presented in graphical form by plotting the mass transfer parameters $a$ and $k_La$ against the gas and liquid flow conditions (Figs. 8 to 10). Five groups of points are presented on a graph and each of these groups corresponds to a certain liquid flow rate. The liquid flow rate increases from a rotameter value of 14 through to 22, by increments of two. Within each of the five groups, there are five points which represent the five different gas pressures: 140, 180, 220, 260 and 300 kPa. The volumetric liquid and gas flow rates that correspond to the rotameter values and gas pressures, respectively, are presented in Tables III and IV. The results of three different experimental runs are displayed together so that
each graph contains three sets of data. This enables the evaluation of the reproducibility of the results.

7.1. The Triangular Reactor and the Kite Shaped Reactor

The experimental values of the interfacial area (a) and the combined mass transfer coefficient (k_La) are displayed in Figures 8(a) and (b), for the case of the triangular reactor, and in Figures 9(a) and (b), for the case of the kite
shaped reactor. As expected, the uncertainty in these values is much less than that in the values of $k_L$ alone. Therefore the graphs are quite smooth. Even though the results were not highly reproducible with respect to specific values, it was highly reproducible with respect to certain trends. If Figures 8(a) and 9(a) are compared and the small degree of scatter in the data is disregarded, it can be seen that the interfacial areas of the two reactors exhibit very similar trends. Even though the interfacial area increased slightly as the inlet gas pressure was raised, this parameter was not heavily
FIGURE 10(a) Interfacial area ($a$) of square reactor (last set of data only).

FIGURE 10(b) Combined mass transfer coefficient ($k_L a$) of square reactor (last set of data only).

TABLE III Calibration of liquid flow rate

<table>
<thead>
<tr>
<th>Rotameter value</th>
<th>Liquid flow rate (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1.06</td>
</tr>
<tr>
<td>16</td>
<td>1.21</td>
</tr>
<tr>
<td>18</td>
<td>1.36</td>
</tr>
<tr>
<td>20</td>
<td>1.52</td>
</tr>
<tr>
<td>22</td>
<td>1.68</td>
</tr>
</tbody>
</table>
dependent on the inlet gas pressure. The interfacial area also increased with an increase in the liquid flow rate, but its value was more sensitive to changes in the liquid flow rate than to changes in the gas flow rate. It is very important to note that the gradients of the interfacial area curves of the two reactors seem to be exactly the same, but that the value of $a$ is constantly higher for the case of the kite shaped reactor than for the triangular reactor. The experimental $k_La$-values of the two reactors exhibit the same trends as the $a$-values (consider Figs. 8(b) and 9(b)). The value of $k_La$ increased with increasing gas and liquid flow rates, but was more dependent on the magnitude of the liquid flow rate. Again, the gradients of the two sets of curves were the same, with the values of the kite shaped reactor constantly higher than that of the triangular reactor.

The similarity between the results of the two reactors suggests that the mechanisms of bubble formation and breakup in the two reactors are the same. The proposed mechanism for these processes is as follows. The spray from each liquid nozzle causes a forceful, directed flow pattern past the gas nozzles. This liquid flow shears off small bubbles from the entering gas stream at the gas nozzle’s orifice and transports the bubbles to the bulk of the reactor. Since the kinetic energy of the entering liquid streams must be dissipated by the liquid, intense small scale turbulence is created in the liquid phase. This random turbulence is also distributed through the reactor by the macro flow patterns. Interactions between the small scale turbulence and the bubbles in the bulk of the reactor cause bubble breakup; thus the interfacial area for mass transfer is increased. The proposed mechanism for interfacial area production in the jet reactors can explain the observed trends in the results. If the inlet gas pressure (and therefore also the gas flow rate) were raised, the gas holdup inside the reactor would increase; thus there might be more bubbles, and therefore a larger interfacial area, in the reactor. In addition to this, the liquid holdup would decrease. Since the rate at which kinetic energy is introduced to the reactor stays constant, while the mass of

<table>
<thead>
<tr>
<th>Gas inlet pressure (kPa)</th>
<th>Gas flow rate (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>9.56</td>
</tr>
<tr>
<td>180</td>
<td>11.43</td>
</tr>
<tr>
<td>220</td>
<td>12.90</td>
</tr>
<tr>
<td>260</td>
<td>13.91</td>
</tr>
<tr>
<td>300</td>
<td>15.91</td>
</tr>
</tbody>
</table>

The development of gas-liquid reactors

Table IV Calibration of gas flow rate
liquid inside the reactor decreases, the rate of energy dissipation per unit mass of liquid is higher. Consequently, more turbulence is created in the liquid phase, so that more bubbles are ruptured, and a larger interfacial area is created. Therefore, the values of $a$ and $k_L a$ would increase slightly as the gas pressure is raised. An increase in the liquid flow rate not only means that the specific energy of the entering liquid is higher (since the flow velocity is higher), but also that the rate of liquid entering the reactor is higher. Consequently, the rate at which energy enters the reactor and is dissipated by the liquid, is much higher. Therefore, the degree of turbulence in the reactor is increased considerably, so that bubble breakup is promoted; hence the heavy dependency of $a$ and $k_L a$ on the liquid flow rate.

The superior performance of the kite shaped reactor over the triangular reactor is explained in terms of the suggested mechanism, as follows: The angle of impingement between the gas and liquid streams in the kite shaped reactor is close to the optimum. The liquid nozzles are directed slightly toward their corresponding gas nozzles and small gas bubbles are sheared off quite effectively. However, the liquid stream impacts the gas stream and the reactor wall at an angle, so that it is reflected; thus the force of the liquid flow, needed to distribute the random turbulence throughout the whole reactor, is sustained. Conversely, for the case of the triangular reactor, the periphery of the liquid spray cone meets the gas stream at an angle of almost 90°, because the liquid nozzles have a spray angle of 60°. Same as previously, small bubbles are sheared off the gas stream, but the liquid stream is not reflected very efficiently. High levels of small scale turbulence will be created in the vicinity of the gas nozzles. Nevertheless, in the absence of a forceful macro flow pattern, this turbulence will be confined to certain regions of the reactor. Thus, effectively, only a fraction of the triangular reactor’s volume is used for mass transfer. This is the reason that, while the two reactors behave almost identically, the kite shaped reactor always performs better than the triangular reactor.

7.2. The Square Reactor

Figures 10(a) and (b) portray the experimental values of the interfacial area and the combined mass transfer coefficient, respectively. There is more scatter in these data than in the corresponding data of the other two reactors. Especially this set of data, and also some of the other sets, clearly shows that $a$ and $k_L a$ are extremely sensitive to changes in the gas flow rate, but seems to be almost independent of the liquid flow rate. The reason for the scatter in the data is now evident. During the course of the experiments,
there would have been greater fluctuations in the gas flow rate than in the liquid flow rate, because the gas flow rate was set according to a pressure gauge (which is not as accurate a rotameter). Since the gas flow rate has been different for the two consecutive experimental runs (needed to calculate the mass transfer parameters), results that are heavily dependent on the gas flow rate would be more scattered than otherwise. This explains the high reliability of the results obtained for the triangular and kite shaped reactors as opposed to the scattered data of the square reactor.

The reason for the difference in behaviour between the square reactor and the other two reactors can be explained in terms of the mechanism of bubble formation. In the square reactor, the liquid nozzles are not directed at the gas nozzles, and the liquid spray flows past the gas nozzles. The momentum of the gas stream is much less than that of the liquid stream, because of the difference in density between the two phases. As a result, the gas stream does not penetrate effectively into the liquid stream. Since the liquid spray does not impact on any surface before reaching the gas stream, no random turbulence and vortices are created to aid in the process of drawing bubbles into the liquid stream. Even though the high velocity liquid flow ensures high levels of turbulence in the bulk of the reactor, there is a deficiency of gas bubbles and the overall rate of mass transfer is low. Dead regions are also created in the reactor by lumps of gas that build up in the vicinity of the gas nozzles. However, as the gas pressure is increased, the gas stream penetrates further into the liquid stream. Consequently, more gas bubbles are taken up in the liquid stream and transported to the highly turbulent regions of the reactor (where mass transfer mostly takes place). Therefore, the performance of the square reactor is greatly enhanced by raising the inlet gas pressure.

8. CONCLUSIONS

The efficiency of high intensity jet reactors was proven beyond doubt. The value of the combined mass transfer coefficient ($k_L\alpha$) was an order of magnitude higher for the new jet reactors than for any other gas-liquid contacting device. By using specially designed nozzles or by further optimisation of the nozzle arrangement, the high impact reactors may be improved even further.

It is concluded that the angle of impingement between the gas and liquid streams is the most important aspect to influence the behaviour and
efficiency of the jet reactors. It was explained that for the case of the square reactor, liquid is sprayed past the gas nozzles, so that a high velocity liquid flow is sustained. This ensures high levels of turbulence in the reactor, but gas bubbles are not effectively drawn into the fast flowing liquid stream. As a result, there is a deficiency of gas bubbles in the bulk of the reactor, and the overall rate of mass transfer is low. In the case of triangular reactor, the liquid sprays are directed too much towards the gas nozzles. Even though gas bubbles are taken up effectively by the liquid stream, the force of the liquid stream is destroyed by the head-on impact with the reactor wall. Consequently, the turbulence is not well distributed through the whole reactor, so that dead regions exist in the reactor. The kite shaped reactor is a highly effective combination of the other two reactors. The liquid sprays are directed slightly towards the gas nozzles, which ensures that gas bubbles are taken up effectively by the liquid streams. However, the liquid streams impact the wall at an angle, so that it is reflected. Thus, the turbulence is transported to the bulk of the reactor, where it enhances bubble breakup and mass transfer.

With the insight gained from the experimental program, a new design philosophy of gas—liquid jet reactors, operated in the bubble mode, can now be formulated. Liquid sprays must not impact a wall or one another directly. Even though this nozzle arrangement will create high levels of random turbulence, the gas phase (with much lower density and momentum than the liquid phase) will not penetrate the liquid effectively and the deficiency of gas in the highly turbulent liquid regions will lead to poor mass transfer. Each liquid spray must be slightly directed towards a gas nozzle so that gas bubbles are sheared off by the liquid, rather than trying to force the low momentum gas stream into the liquid stream. After the liquid stream had collected and carried away the gas bubbles, it must collide with another liquid stream or the reactor wall to create high levels of small scale turbulence in the bulk of the reactor to promote bubble breakup. The reactor geometry must support a homogeneous distribution of turbulence throughout the reactor. Plug flow regions must be avoided, since phase separation will occur, resulting in dead reactor regions. Within this design philosophy, a number of different reactor geometries and nozzle configurations can still be tested to further enhance the efficiency of jet reactors.

It would be highly desirable to validate the proposed mechanism of bubble formation and breakup in the new jet reactors. Thencefore, a model, based on this mechanism, has been developed from fundamental principles to predict the interfacial area in the jet reactors. This will be the topic of a further publication.
THE DEVELOPMENT OF GAS–LIQUID REACTORS

NOMENCLATURE

\( a \) \hspace{1cm} \text{Interfacial area per unit volume of reactor, } m^2/m^3

\( C_A \) \hspace{1cm} \text{Concentration of dissolved gas } A \text{ at interface, in equilibrium with gas at interface, mol/l}

\( G_{AO} \) \hspace{1cm} \text{Concentration of dissolved gas } A \text{ in bulk of liquid, mol/l}

\( G_{BO} \) \hspace{1cm} \text{Concentration of dissolved reagent } B \text{ in bulk of liquid, mol/l}

\( D_A \) \hspace{1cm} \text{Diffusivity of dissolved gas } A \text{ in liquid phase, } m^2/s

\( E \) \hspace{1cm} \text{Enhancement factor}

\( E_1, E_2 \) \hspace{1cm} \text{Enhancement factors of the two experimental runs performed at the same operating conditions}

\( E_i \) \hspace{1cm} \text{Enhancement factor for instantaneous chemical reaction}

\( k_2 \) \hspace{1cm} \text{Second order reaction rate constant, l/mol·s}

\( k_L \) \hspace{1cm} \text{Liquid film mass transfer coefficient, m/s}

\( \dot{n} \) \hspace{1cm} \text{Absorption rate per unit volume of reactor, mol/l·s}

References


Section 14  Publications on Diagnostic Leaching
THE IDENTIFICATION OF REFRACTORINESS IN GOLD ORES
BY THE SELECTIVE DESTRUCTION OF MINERALS

L. LORENZEN and J.S.J. VAN DEVENTER

Department of Metallurgical Engineering, University of Stellenbosch,
Stellenbosch, 7600, South Africa
(Received 23 February 1993; accepted 9 April 1993)

ABSTRACT

With the increasingly lower grades of ore mined, the introduction of backfill mining, and the reduction of profit margins, it has become imperative to increase the efficiency of gold dissolution. Diagnostic leaching (selective decomposition of refractory minerals associated with gold) tests conducted on a large number of composite residue samples, indicated that a large portion of the gold in the residue was leachable (up to 60%). About half of this leachable gold was dissolved by a quick cyanide wash, indicating that it was precipitated gold. A significant portion of the non-leachable gold in the residue was coated with various films, of which iron oxide was the major one. These films varied in nature from oxides, sulphates, carbonates and cyanide complexes. The complexes can be destroyed, depending on the nature of the film by interstage dilute acid and/or cyanide washes in an agitated vessel. The major cyanide consumers in the residue streams were found to be copper, nickel and soluble sulphides.

The reality of an ultimate residue (thus only gold enclosed in fine quartz remains), is within the reach of most of the major gold producing mines, as at least 50% of the gold in the residue could be recovered at little additional cost. It is suggested that residue values at many gold plants are unsatisfactorily high due to the complex nature of the ore and because plant personnel do not utilize all available knowledge on gold dissolution.

Keywords
Mineralogy; ultimate residue; gold; leaching; cyanide; diagnostic leaching

INTRODUCTION

In most South African ores more than 97% of the gold is dissolved in a cyanide medium after a residence time of about 16 to 24 hours in Pachuca tanks. This high percentage may be the reason why so little research has been done into the mechanism and kinetics of the leaching process. With the increasingly lower grades of ore mined, the introduction of backfill mining, and the reduction of profit margins, it has become imperative to increase the efficiency of gold dissolution. If the loss of gold to the tailings could be reduced by 50%, a decrease in residence time would also be a more attractive proposition. This change in emphasis may be the reason for the renewed interest in the mechanism and kinetics of gold dissolution.

The first step in the design of a process to treat a possible economic gold residue should be an examination of the mineralogy of the ore in the residue. Factors affecting the extraction of gold are in many cases of a mineralogical nature. Knowledge of the mineralogy of the ore or metallurgical product to be treated, if appropriately combined with the mineralogical testwork, may improve gold recoveries. These factors affecting gold recoveries include:
the gold-bearing minerals,
- their grain size and, particularly where the grain size is very fine (10 microns in diameter and less),
- their host minerals and
- the association these form with the gold-bearing minerals [1].

Usually the first question by the metallurgist is, "To what size do I need to grind the ore to liberate the gold?". If more accurate mineralogical data were available, the first question might be, "With which minerals is the gold associated and how will this affect the extraction route I use?".

Diagnostic leaching was developed by the Anglo American Research Laboratories [2-5] to answer the above question and in doing so opened up the field of mineralogical analysis to the metallurgist. With diagnostic leaching, the metallurgist or scientist is able to get a much clearer view of which minerals the gold is associated with. When a mineralogist looks at the deportment of gold in an ore, he is usually looking for an element which is present in parts per million, so that errors in sampling are multiplied dramatically. Diagnostic leaching offers a cheap, simple, practical alternative. In order to determine with which minerals the desired precious metal is associated, a specific mineral is first eliminated using a selective oxidative leach, and cyanidation is used to extract the precious metal (in this case gold) liberated by the destruction of this mineral. The precious metal extracted can be measured in solution to give a fairly accurate record of the amount of the precious metal associated with that mineral. Furthermore, the residue from this first stage can be subjected to another selective acid leach, and the process repeated. Interstage dilute acid and cyanide washes can also be used to destroy surface deposits. The procedure can be varied to suit the mineralogy of the matrix material. At the end of this diagnostic leach the metallurgist is left with a complete record of the deportment of the precious metal. He can now use this information to design a metallurgical flowsheet to treat the ore.

Diagnostic leaching is thus an analytical tool which can be used by the metallurgist not only to examine new ores, but also to look at problems occurring at existing plants. The procedure is not only limited to ores and residues but in fact can deal with any type of intermediary product that occurs on a plant [6].

Ideal crushing and milling occurs when rocks are broken along grain boundaries. Up until now no selective method of achieving this ideal has been obtained. The conventional techniques break rocks irrespective of mineralogy and confuse the furtherance of the ideals of obtaining an ultimate residue. In this paper one of the diagnostic leaching steps, the nitric acid leach, was used for the decomposition of ROM (run of mine) ore from two plants. This was followed by a cyanidation step to determine the amount of gold that could be liberated from the various minerals in the ore, excluding the silicates. The gold that remains in the silicates would thus be the ultimate residue. Plant residue samples from the ROM ore plants chosen above were then taken to determine the refractoriness of the residues, using the technique of diagnostic leaching and the interpretation of results.

**EXPERIMENTAL**

The concept of diagnostic leaching, as already mentioned, is very simple. The least stable mineral present in the matrix of the sample is first solubilised in aqueous acid medium. The residue is filtered, washed (water/dilute acid), cyanided to extract the gold liberated and washed with a dilute cyanide solution. The process is repeated with a more oxidative acid leach until all the non-refractory re-cyanided gold is leached by the cyanide to give an accurate record of the amount of gold associated with the various minerals. An overlap of the extent of leaching does occur [4] but is generally limited to 90% of the required mineral and 10% of the next most stable mineral. The various stages of acid pre-treatment and the minerals it will most likely destroy are presented in Figure 1 and Table 1.

Two ROM samples (particle size approximately 5 to 10cm in diameter) were obtained from Western Deep Levels (WDL) carbon leader and Durban Deep (DD) main reef in South Africa respectively. The samples were each cut in half and the experimental programme followed are depicted in Figure 2. The cyanidation
of the rock was achieved by its suspension in a magnetically stirred cyanide solution. The nitric acid leach was carried out at 80°C on a hotplate in a fume cupboard. The seven day cyanidation was carried out in the traditional rolling bottles. The mineral composition of each sample is presented in Table 2 and the mineralized portion of the surface of the cut samples was photographed under a stereomicroscope and presented in Figures 3 and 4.

<table>
<thead>
<tr>
<th>Cyanide Wash - Precipitated Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide Leach - Free or Leachable Gold</td>
</tr>
<tr>
<td>HCl/Cyanidation - Gold associated with pyrrhotite, calcite, ferrites, etc</td>
</tr>
<tr>
<td>H₂SO₄/Cyanidation - Gold associated with labile copper sulphides, labile pyrite, base metal sulphides, uraninite, etc</td>
</tr>
<tr>
<td>HNO₃/Cyanidation - Gold associated with pyrite, arsenopyrite, marcasite</td>
</tr>
<tr>
<td>Interstage Acid Washes - Surface coatings</td>
</tr>
<tr>
<td>Acetonitrile Elution - Gold adsorbed on carbon, kerogen, coal.</td>
</tr>
</tbody>
</table>

Fig. 1 Typical diagnostic leach procedure for the deportment of gold

Plant residues from the two plants, Western Deep Levels and Durban Deep were obtained. The samples were subjected to a diagnostic leaching procedure to determine the deportment of the gold in the two residues. This was compared with the results obtained from the dissolution of the ROM samples from the two plants to determine the ultimate residue for each ore sample.

RESULTS AND DISCUSSION

ROM Samples from Western Deep Levels and Durban Deep Mines

From the mineral composition of the two samples depicted in Table 2, it is evident that Western Deep Levels has abundant chlorite and Durban Deep very little or basically none. Durban Deep has abundant chloritoid and Western Deep Levels a minor amount, whereas Western Deep Levels has major pyrite and in Durban Deep it is fairly abundant. According to the literature [7], chloritoid is soluble in sulphuric acid, and chlorite in all strong acids. Therefore, in addition to gold enclosed in quartz, which is not amenable to HNO₃/cyanide leaching, gold in chloritoid would also be shielded, provided H₂SO₄ is not formed from the reaction of pyrite and nitric acid. It was thus decided to leach the washed solids (after 7 day cyanidation) for 48 hours with H₂SO₄ at 80°C, followed by cyanidation.
TABLE 1 Selective pre-treatment leach stages and the minerals destroyed

<table>
<thead>
<tr>
<th>Pre-treatment stage</th>
<th>Minerals likely to be destroyed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NaCN washes</td>
<td>Precipitated gold</td>
</tr>
<tr>
<td>2. NaCN</td>
<td>Gold</td>
</tr>
<tr>
<td>3. HCl</td>
<td>Pyrrhotite, Calcite, Ferrrites, Dolomite, Galena, Haematite, Goethite, Calcium carbonate</td>
</tr>
<tr>
<td>4. H₂SO₄</td>
<td>Uraninite, Sphalerite, Labile Copper Sulphides, Labile Base Metal Sulphides, Labile Pyrite</td>
</tr>
<tr>
<td>5. HNO₃</td>
<td>Pyrite, Arsenopyrite, Marcasite</td>
</tr>
<tr>
<td>6. Na₂CO₃</td>
<td>Gypsum and Arsenates</td>
</tr>
<tr>
<td>7. FeCl₃</td>
<td>Sphalerite, Galena, Labile Sulphides, Tetrahedrite</td>
</tr>
<tr>
<td>8. Oxalic Acid Washes</td>
<td>Oxide Coatings</td>
</tr>
<tr>
<td>9. HF</td>
<td>Silicates</td>
</tr>
<tr>
<td>10. Acetonitrile elution</td>
<td>Gold adsorbed on Carbon, Kerogen, Coal</td>
</tr>
</tbody>
</table>

Note: All the above-mentioned pre-treatment stages can be varied according to the matrix of the material. Temperature, potential, concentration, leaching time, etc. All play a major role in the selection of the desired pre-treatment stage.

* ROM ore

24 hour cyanidation

4 weeks concentrated nitric acid leach with fresh solution each week. Solutions were analysed for gold

Solids washed with water and size distribution determined

7 day cyanidation of the various size fractions

48 hour sulphuric acid leach. Solutions were analysed for gold

24 hour cyanidation of the solids

Solids washed and analysed mineralogically. Each size fraction assayed for gold.

* Samples of rocks were assayed and photographed

Fig.2 ROM ore experimental programme.
TABLE 2 Mineral Composition of the WDL and DD ROM samples

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>WDL</th>
<th>DD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>Predominant</td>
<td>Predominant</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Abundant</td>
<td>None</td>
</tr>
<tr>
<td>Chloritoid</td>
<td>Minor</td>
<td>Abundant</td>
</tr>
<tr>
<td>Mica</td>
<td>Minor</td>
<td>None</td>
</tr>
<tr>
<td>Pyrite</td>
<td>Major</td>
<td>Abundant</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Minor</td>
<td>Abundant</td>
</tr>
</tbody>
</table>

Predominant (>50 %); major (>15 %); abundant (>5 %); minor (<5 %)

Fig.3 Mineralized portion of the WDL ROM rock surface

Treatment of the two rock samples indicated that 1.3 % to 2.4 % of the gold content was leachable with direct cyanidation (see Figures 5 and 6). The fumes from the nitric acid leach of the rocks indicated that the reaction was nearing completion after 10 to 24 days. The nitric acid leach residue was washed with water, filtered and cyanided for 7 days. The sample was thereafter leached with sulphuric acid for 48 hours before final cyanidation. The results are presented in Figures 5 and 6.

The cyanidation of the nitric acid leached ore indicated that 85.3 % of the gold was liberated at WDL (gold head grade of 34.17 g/t) and 78.9 % at DD (gold head grade 8.98 g/t). The size distribution after nitric acid leaching shows that:

- 36 % > 5 mm for WDL (34.17 g/t)
- 51 % > 5 mm for DD (8.98 g/t)
From results in Figures 5 and 6 it is evident that another 9.5% of gold in the case of WDL and 16.8% in the case of DD were liberated by the subsequent sulphuric acid leach/cyanidation. Thus, approximately 94.5% of the gold in WDL ROM ore and 95.6% of the gold in DD ROM ore can be liberated by means of selective dissolution of minerals. The residual gold grade in the silica was found:

- to increase with decreasing silica particle size for each sample, and
- to be proportional to the rock head grade for all the silica particle size fractions.
These results indicated that 5.5% of the gold in the WDL ore sample and 4.4% of the gold in the DD ore sample are associated with silicates and thus not amenable to conventional extraction techniques. For comparison, the gold grades of the leached screen fractions and the minus 150 mesh unleached quartz-rich (2.85 SG Float) fractions are presented in Table 3. The results clearly indicated that if gold enclosed in quartz was the only mode of gold in the residues, the coarsest fractions would have the highest grades. The grades of all the screen fractions, other than WDL -4 +8 mesh, are higher than their respective 2.85 SG Float fractions, which confirms a mode(s) of gold other than enclosure in quartz. Re-cyanidation of the residue samples from the ROM ore (Figures 7 and 8) yielded at least 2.5% and 1.7% extra gold from WDL and DD respectively. A significant proportion of the "non-leachable" gold in the residue was coated with various films, of which sulphates and cyanide complexes were the major ones. This confirms the results obtained in Table 3 that other modes of gold other than enclosure in silicates are present in the final residue of the ROM ore samples.

**TABLE 3 Gold grades of the WDL and DD screen fractions**

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>WDL Gold grade (g/t)</th>
<th>DD Gold grade (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+4 -8 mesh</td>
<td>2.68</td>
<td>1.81</td>
</tr>
<tr>
<td>-8 +20 mesh</td>
<td>4.43</td>
<td>1.95</td>
</tr>
<tr>
<td>-20 +48 mesh</td>
<td>8.08</td>
<td>2.42</td>
</tr>
<tr>
<td>-48 +150 mesh</td>
<td>9.76</td>
<td>1.76</td>
</tr>
<tr>
<td>2.85 SG Float</td>
<td>4.08</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Fig. 6 Deposition of gold in the DD ROM ore sample
Residue Samples from Western Deep Levels and Durban Deep Plants

The reality of an ultimate residue (thus only gold enclosed in fine quartz remains), is within the reach of most of the major gold producing mines, if at least 50% of the gold in the residue could be recovered at little additional cost. Plant residue samples from WDL and DD Plants were obtained and re-cyanided to
determine how much gold can still be extracted. The leaching of the composite plant residue samples yielded at least 0.1 g/t at WDL and 0.08 g/t at DD, extra gold which is as present lost. This is in the region of 46 to 55% of the gold present in the composite plant residue samples. About half of this leachable gold (0.05 g/t) was dissolved by a quick cyanide wash, indicating that it was precipitated gold.

A significant proportion of the (directly) non-leachable gold in the residue was coated with various films, of which oxides, sulphates and cyanide complexes were the major ones. The complexes can be destroyed, depending on the nature of the film, by interstage dilute acid and/or cyanide washes in an agitated vessel. The major cyanide consumers in the residue streams were found to be copper, nickel and soluble sulphides. The destruction of sulphides and the oxidation of other gangue constituents result in a reduction of the split leach effect (extra gold solubilised on cyanidation of a sample which has already been cyanided and thoroughly washed).

This testwork on plant residues confirms the diagnostic leaching results obtained from the ROM ore samples that mode(s) other than gold enclosed in silicates or quartz are present in residue samples and that the gold not enclosed can be extracted by conventional cyanidation (with or without an acid/cyanide wash step).

Diagnostic leaching as an analytical tool for plant problems

Diagnostic leaching can also be used as the first step in the investigation of a plant that is experiencing problems. A flotation plant in the Free State was experiencing the problem of an increasing feed head grade to the plant while the recovery was decreasing. Feed to the plant, flotation concentrate and tails were analysed using diagnostic leaching to determine the deportment of gold. The results indicated that the decrease in recovery was not a metallurgical problem at the plant but due to a change in the deportment of gold in the feed to the flotation plant. The efficiency of gold flotation recovery from the sulphide fraction is very high, but only 50% of the cyanidable gold was floated. This was probably due to the fact that about 85% of the cyanidable gold in the feed was present as precipitated gold, (as mentioned before), and therefore not amenable to flotation. In fact, the flotation recovery of cyanidable gold was relatively high and indicated that the gold must have precipitated preferentially on sulphides. However, this was not likely since the surface of the sulphides would be reducing. Increased gold recovery at this Free State flotation plant would only be possible by cyanidation of the flotation tailings where it would be possible to extract up to 50% of the gold. This analysis and various others were so successful that diagnostic leaching is currently being used routinely for various flotation plants throughout South Africa to analyse problems.

Increasing the selectivity of a diagnostic leach

Until recently the selectivity of the various diagnostic leaches had only been estimated and not quantified. This, however, had never affected the validity of the conclusions drawn. In an attempt to examine how selective an oxidising acid pre-treatment is, a sulphide concentrate was used and subjected to a series of sulphuric acid leaches at various Eh values, controlled by the addition of hydrogen peroxide. Lorenzen [8] explained this selective leaching of base metal sulphides in sulphuric acid in more detail. The conclusions drawn from this testwork are:

- Pyrite is leached above 400 mV (vs SCE), based on the sulphide and iron extractions. About 35% of the pyrite has been leached at 600 mV and the reaction appears to stop. More than 99% of the pyrite is however leached using nitric acid as oxidant.

- There is a steep increase in gold extraction when increasing the acid pre-treatment potential from 300 to 400 mV. Above 400 mV there is no significant increase in gold extraction, and therefore 400 mV appears to be the optimum potential for liberating gold from sulphide concentrates containing base metal sulphides in an oxidising sulphate medium at 80°C. Below 300 mV basically all the uranium is leached and therefore also the gold associated with uranium.
No significant increase in gold extraction occurs between 400 and 600 mV. This suggests that passivation of the gold by sulphides is not the main reason, but rather the fact that pyrite is actually barren. If this is the case, then the steep increase in gold extraction between 300 and 400 mV is due to gold released by oxidation of the of base metal sulphides. About 70% of the base metal sulphides and roughly 10% of the pyrite were leached when the potential was increased from 300 to 400 mV. This corresponds to a step increase in the locked gold extraction of about 20%. As the potential increases to 600 mV a further 25% of the pyrite and roughly 15% of the base metals are leached and yet there is no further increase in gold extraction.

If a shrinking-core model of the sulphide particles being leached is envisaged, then the first 10% of the particles leached was really only a small surface layer ("the icing on the cake") i.e. the decrease in radius varies with the cube root of the volume or mass leached (for a 100 micrometer particle, 10% of the mass equals 1 micrometer thickness). This indicates that the gold associated with the pyrite was exposed on the surface but was passivated when initially leached by cyanide. It is only made available for cyanidation after oxidation of the sulphide surface.

Base metal sulphides should be leached in oxidising sulphuric acid conditions and yet there is no significant increase in base metal extractions until the labile pyrite begins to dissolve. When the labile pyrite extraction levels off, then generally, the base metal extraction levels off which suggests that the base metals are either associated with the pyrite or that the base metal sulphides themselves are partially locked in pyrite. This would then have to be confirmed by a mineralogical analysis.

Ferric oxidation in a sulphate medium was also used in an attempt to eliminate arsenopyrite which was believed to contain most of the gold present in a European flotation concentrate sample. The leach was unselective in leaching arsenopyrite and pyrite. Gold extraction by cyanidation after this pre-treatment was poor. It is possible that passivation of the surface of the sulphides by the formation of sulphur, a traditional problem in leaching base metals from their sulphides, was responsible. The leach was therefore repeated, but interstage washing with carbon disulphide was used to remove the sulphur formed. The results showed that almost total extraction of gold was possible after this treatment, with total destruction of sulphides. The implication of this work is that plant scale oxidation of refractory sulphides such as pyrite and copper sulphides is possible as a viable alternative to roasting.

This interstage washing led to the development of interstage cyanide and acid washes to destroy cyanide and ion complexes. Lorenzen and Van Deventer [9] described this phenomenon in detail. Oxalic acid washes can also be used to destroy oxide coatings on the liberated gold surfaces after acid pre-treatment leaches.

CONCLUSIONS

From the results presented in this paper it is possible to explain the leaching behaviour of gold from ROM ore and composite plant residues from the Western Deep Levels Gold Mine and Durban Deep Gold Mine. Modes of gold other than those enclosed in fine quartz are present in ROM and composite plant residue samples. These modes include for example precipitated gold and gold in cyanide complexes.

The reality of an ultimate residue (thus only gold enclosed in fine quartz remains), is within reach of most of the major producing gold mines, as at least 50% of the gold in the residue could be recovered at little additional cost, if any. It is suggested that residue values at many gold plants are unsatisfactorily high due to the complex nature of the ore and because plant personnel do not utilize all available knowledge on gold dissolution.

The technique can cope with any plant problem caused by (i) change in operation, (ii) change in the mineralogy and/or gold deportment in the feed or (iii) a combination of the above mentioned. In can also deal with new ore deposits, refractory minerals, i.e. calcines, clinker, sulphide concentrates, etc. The
Refractoriness in gold ores

The method is flexible and depends on the sample to be analysed. The data obtained from a modest amount of testwork enable the derivation of possible process routes for treatment of the ore-body/refractory minerals for gold recovery. The routes chosen depend on such factors as the economics of the project, location of the ore-body/refractory minerals and relative amount of the latter.

REFERENCES


The interrelationship between mineral liberation and leaching behaviour

L. Lorenzen, J.S.J. van Deventer
Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch, 7600, South Africa
(Received 2 March 1993; accepted after revision 21 October 1993)

Abstract

The liberation characteristics of any ore are intimately related to the mineralogical texture. In this paper, leaching experimental results were used with the liberation model of King to predict the liberation of gold from complex ores. Diagnostic leaching results were used with the liberation model, as the results from a diagnostic leaching procedure explain the deportment of gold in the various minerals in a complex ore. The free or leachable gold in an ore obtained from such an experiment would be similar to the gold liberated by crushing and/or milling. The leachable gold in each size fraction of an ore can be determined by diagnostic leaching, before and after milling. Thus, it would be very useful if the leachable (liberated) gold in a specific unmilled ore can be used to predict leachable (liberated) gold in the milled ore of that specific ore. If this can be achieved, then the leachable gold in each size fraction of the unmilled and milled ore can be predicted by the model.

An explicit solution to King’s liberation model was modified in order to predict the leachable gold in different size fractions on the basis of data gathered for the unmilled ore. In this model, $\mu_m$ is the mean linear intercept length for gold in the ore, and the term $A \cdot \exp(1/D)$ indicates the fraction of leachable gold which cannot be attributed directly to liberation:

$$L_g(D) = \frac{2\mu_m}{D^2}[\mu_m - (\mu_m + D)\exp(-D/\mu_m)] + [A \cdot \exp(1/D)]$$

It was found that this model gives reasonable predictions of the leachable gold for milled ore when the leachable gold in the unmilled ore is known.

1. Introduction

The liberation characteristics of any ore are intimately related to the mineralogical texture. A major problem (King, 1982) is the quantification of the relationship between texture and liberation. In 1972, Amstutz and Giger presented a
brief review of the classical quantitative work and anticipated a new era of rapid expansion of quantitative work that was then starting. Rapid developments in quantitative textural analysis were encouraged by the emergence of a new generation of automatic image analysis systems capable of analysing large numbers of thin polished sections.

Grinding is used to liberate minerals prior to further upgrading by subsequent ore dressing operations. It is the interaction between the comminution and textural properties of an ore that determines the efficiency of the liberation process and thus determines the technological limitations on the efficiency of separation in any ore dressing process. The efficiency of the concentrating procedure is very much dependent on the degree of liberation of the valuable minerals that is achieved, and the ore must be sufficiently finely ground to permit the production of a concentrate of sufficiently high grade to be satisfactory for smelting or other finishing operations. However, overgrinding must be avoided because this is expensive and can have a deleterious effect on mineral recovery in operations such as flotation. The choice of fineness of grind is consequently an important decision in the operation of mineral processing plants.

Quantitative models for the grinding operation on the one hand, and for concentrating operations such as flotation on the other, are now very well developed and are finding increasing use in the design and simulation of plants. Although comminution models have received much attention, the development of models for liberation (King, 1979) has lagged far behind. It is important to rectify this, since in mineral processing plants, ores are ground to liberate minerals and not to produce fine powders. It is the degree of liberation and not the particle size distribution that is an important property of the product from a milling circuit.

It was decided to use the liberation model developed by King (1975, 1979) in this study due to its relative simplicity. After the numerical integration of his proposed model equation, King observed that an explicit solution could be obtained with only one parameter, the mean intercept length in unbroken rock, \( \bar{L}_m \).

In the King model, the fractional degree of liberation \( L_m(D) \) of mineral m for a particle size \( D \), is given by:

\[
L_m(D) = 1 - \frac{1}{\mu_m} \int_0^{D_m} \{1 - N(\delta/D)\}\{1 - F_m(\delta)\} d\delta
\]  

(1)
where
\[ \mu_m = \text{mean linear intercept length of mineral in ore (\mu m)} \]
\[ N(\delta/D) = \text{fraction of linear intercept lengths less than or equal to } \delta \text{ for particles of size } D \]
\[ F_m(\delta) = \text{fraction of linear intercept lengths less than or equal to } \delta \text{ in the ore} \]
\[ D_u = \text{upper size screen interval (\mu m)} \]
\[ D = \text{geometric mean of screen interval (\mu m)} \]

To solve Eq. (1) without numerical integration requires a relationship between \( F_m(\delta) \) and \( \delta \), and \( N(\delta/D) \) and \( \delta \). Relationships suggested by King are:

\[ F_m(\delta) = 1 - \exp(-\delta/D) \] (2)

and

\[ N(\delta/D) = \delta^2/D^2 \] (3)

the latter being derived by Underwood (1979) for spherical particles. Finlayson (1980) suggested from analysis of his data:

\[ N(\delta/D) = 1 - (1 - \delta/\sqrt{2 \cdot D_u}) \exp(-R^2\delta/\sqrt{2 \cdot D_u}) \] (4)

where \( R=\text{ratio of upper to lower size of screen interval.} \)

By inspection, Eq. (4) gives a good fit to the data although, curiously for \( \delta > \sqrt{2 \cdot D_u} \), \( N(\delta/D) \) becomes greater than 1, which is impossible (Finch and Petruk, 1984). Also based on the \( N(\delta/D) \) data of King, the authors suggested the following:

\[ N(\delta/D) = 1 - \exp(-k\delta/D) \] (5)

where \( k \) is a constant of about 2. With \( k=2 \), Eq. (5) gives a good fit as Eq. (4) to King’s data. By inspection, \( k \) is in the range \( 2 \pm 0.4 \) (i.e. 20%) (Finch and Petruk, 1984).

Eq. (2) can be combined with Eq. (3) and integrated. With \( F_m(\delta) = 1 - \exp(-\delta/\mu_m) \), \( N(\delta/D) = \delta^2/D^2 \) and assuming \( D=D_u \), Eq. (1) can be written as follows:

\[ L_m(D) = 1 - \frac{1}{\mu_m} \int_0^{D_u} (1 - \delta^2/D^2) \exp(-\delta/\mu_m) \, d\delta \]

\[ = \exp(-D/\mu_m) + \frac{1}{D^2\mu_m} \int_0^{D_u} \delta^2 \exp(-\delta/\mu_m) \, d\delta \]

The second term on the right hand side can be written as:

\[ \int_0^{D} \delta^2 \exp(-\delta/\mu_m) \, d\delta = -\mu_m D^2 \exp(-D/\mu_m) - 2\mu_m^2 D \exp(-D/\mu_m) \]

\[ - 2\mu_m^3 \exp(-D/\mu_m) + 2\mu_m^3 \]

\[ L_m(D) = 2\mu_m/D^2 [\mu_m - (\mu_m + D) \exp(-D/\mu_m)] \] (6)
Another form of Eq. (6) derived by Finlayson (1980) is:

\[ L_m(D) = 1 - D/(2\mu_m + D) \left[ 1 - \exp\left\{ -\left(2\mu_m + D/\mu_m\right) \right\} \right] \]  

(7)

Eqs. (6) and (7) are particularly convenient. In all cases there is only one unknown, \( \mu_m \).

2. Testing the King liberation model on diagnostic leaching results

As mentioned before, the first step in the design of a process to treat a possible economic precious metal deposit should be an examination of the mineralogy of the ore. Diagnostic leaching (Lorenzen and Tumilty, 1992) was designed to open up the field of mineralogical analysis to the metallurgist. In order to determine with which minerals the desired precious metal is associated, a specific mineral is first eliminated using a selective oxidative leach, and cyanidation is used to extract the precious metal liberated by the destruction of this mineral. The precious metal extraction can be measured in solution to give a fairly accurate record of the amount of the precious metal associated with that mineral. Furthermore, the residue from this first step can be subjected to another selective acid leach, and the process repeated. The procedure can be varied to suit the mineralogy of the matrix material. At the end of a diagnostic leach procedure, the metallurgist is left with a complete record of the deportment of the precious metal.

Knowledge of the mineralogy of the ore to be treated, if appropriately combined with the mineralogical testwork, may improve gold recoveries. These factors affecting gold recoveries include:

- gold-bearing minerals,
- their grain size and particularly where the grain size is small,
- their host minerals, and
- the association these form with the gold bearing minerals.

For all the liberation models as mentioned in the introduction, the first question by the metallurgist usually is, “To what size do I need to grind the ore to liberate the gold?” In this section, liberation (leaching) experimental results were used with the liberation model of King to predict the liberation of gold from a complex ore. Diagnostic leaching results can thus be used with liberation models, as the results from a diagnostic leaching procedure explain the deportment of gold in the various minerals in a complex ore. The free or leachable gold in an ore obtained from such an experiment would be similar to the gold liberated by crushing and/or milling. The leachable gold in each size fraction of an ore can be determined with diagnostic leaching, before and after milling. It would be very useful if the leachable (liberated) gold in a specific unmilled ore can be used to predict leachable (liberated) gold in the milled ore of that specific ore. If this can be achieved, then the leachable gold in each size fraction of the unmilled and milled ore can also be predicted by the model.
King’s model as described was tested on experimental results, and the results predicted by the model for milled and unmilled ore were compared to the experimental results. Diagnostic leaching results from three different ores were used: i.e. unmilled FSG, WDL and Harties ore as well as milled (to 70%–75 µm) ore of these ore bodies. The gold deportment in each particle size fraction for FSG, WDL and Harties is presented in Tables 1 to 6. The overall gold deportment in the three ores at various average size fractions were also determined and are presented in Tables 7 to 11. The leachable gold was plotted against particle size for each ore (milled and unmilled), and the results are presented in Figs. 1, 2 and 3.

As mentioned before, King’s model was used as basis in this study. The mean linear intercept length of the mineral in the ore ($\mu_m$), as well as $F_m(\delta)$ and $N(\delta/D)$, are not known. Also, it is not possible to determine any distribution of intercept lengths in gold ores using SEM. Information on the ores available in this

Table 1
Gold deportment vs. size fraction (FSG unmilled ore)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
<th>Head grade (g/t)</th>
<th>Free$^a$ Au (%)</th>
<th>Au in BMS$^b$ (%)</th>
<th>Au in pyrite (%)</th>
<th>Au in silicates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>80.1</td>
<td>4.38</td>
<td>23.0</td>
<td>35.5</td>
<td>31.0</td>
<td>10.5</td>
</tr>
<tr>
<td>-300+150</td>
<td>11.8</td>
<td>10.63</td>
<td>24.6</td>
<td>36.8</td>
<td>28.5</td>
<td>10.1</td>
</tr>
<tr>
<td>-150+106</td>
<td>2.1</td>
<td>8.63</td>
<td>23.8</td>
<td>33.5</td>
<td>25.3</td>
<td>17.4</td>
</tr>
<tr>
<td>-106+75</td>
<td>0.9</td>
<td>15.75</td>
<td>31.2</td>
<td>31.9</td>
<td>24.4</td>
<td>12.5</td>
</tr>
<tr>
<td>-75+45</td>
<td>1.5</td>
<td>18.81</td>
<td>34.5</td>
<td>31.1</td>
<td>21.7</td>
<td>12.3</td>
</tr>
<tr>
<td>-45</td>
<td>3.6</td>
<td>14.35</td>
<td>30.4</td>
<td>34.8</td>
<td>31.7</td>
<td>3.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>5.88</td>
<td>25.2</td>
<td>35.3</td>
<td>29.4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

$^a$Free gold = leachable gold.
$^b$BMS = base metal sulphides.

Table 2
Gold deportment vs. size fraction (FSG 70%–75 µm)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
<th>Head grade (g/t)</th>
<th>Free$^a$ Au (%)</th>
<th>Au in BMS$^b$ (%)</th>
<th>Au in pyrite (%)</th>
<th>Au in silicates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>0.6</td>
<td>2.91</td>
<td>18.1</td>
<td>42.7</td>
<td>34.1</td>
<td>5.1</td>
</tr>
<tr>
<td>-300+150</td>
<td>6.8</td>
<td>3.03</td>
<td>18.2</td>
<td>40.6</td>
<td>32.9</td>
<td>8.3</td>
</tr>
<tr>
<td>-150+106</td>
<td>12.1</td>
<td>3.50</td>
<td>25.6</td>
<td>36.1</td>
<td>31.8</td>
<td>8.1</td>
</tr>
<tr>
<td>-106+75</td>
<td>10.5</td>
<td>5.20</td>
<td>46.0</td>
<td>20.0</td>
<td>22.1</td>
<td>11.1</td>
</tr>
<tr>
<td>-75+45</td>
<td>9.7</td>
<td>6.23</td>
<td>55.1</td>
<td>18.6</td>
<td>20.5</td>
<td>5.8</td>
</tr>
<tr>
<td>-45</td>
<td>60.3</td>
<td>6.20</td>
<td>54.2</td>
<td>20.6</td>
<td>23.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>5.52</td>
<td>47.4</td>
<td>23.8</td>
<td>24.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$^a$Free gold = leachable gold.
$^b$BMS = base metal sulphides.
Table 3
Gold deportment vs. size fraction (WDL unmilled ore)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
<th>Head grade (%)</th>
<th>Free* Au (%)</th>
<th>Au in BMS b (%)</th>
<th>Au in pyrite (%)</th>
<th>Au in silicates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>78.0</td>
<td>2.98</td>
<td>7.4</td>
<td>30.5</td>
<td>47.0</td>
<td>15.1</td>
</tr>
<tr>
<td>-300 +150</td>
<td>11.7</td>
<td>5.96</td>
<td>7.9</td>
<td>30.0</td>
<td>46.1</td>
<td>16.0</td>
</tr>
<tr>
<td>-150 +106</td>
<td>4.4</td>
<td>6.21</td>
<td>8.4</td>
<td>30.6</td>
<td>43.6</td>
<td>17.4</td>
</tr>
<tr>
<td>-106 +75</td>
<td>1.0</td>
<td>6.70</td>
<td>10.1</td>
<td>27.2</td>
<td>45.2</td>
<td>17.5</td>
</tr>
<tr>
<td>-75 +45</td>
<td>0.8</td>
<td>9.87</td>
<td>12.1</td>
<td>30.5</td>
<td>42.0</td>
<td>15.4</td>
</tr>
<tr>
<td>-45</td>
<td>4.1</td>
<td>8.29</td>
<td>11.8</td>
<td>25.8</td>
<td>44.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>3.78</td>
<td>8.3</td>
<td>29.9</td>
<td>46.1</td>
<td>15.7</td>
</tr>
</tbody>
</table>

aFree gold = leachable gold.
bBMS = base metal sulphides.

Table 4
Gold deportment vs. size fraction (WDL 70% – 75 µm)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
<th>Head grade (g/t)</th>
<th>Free* Au (%)</th>
<th>Au in BMS b (%)</th>
<th>Au in pyrite (%)</th>
<th>Au in silicates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>1.2</td>
<td>1.85</td>
<td>5.9</td>
<td>39.5</td>
<td>49.2</td>
<td>5.4</td>
</tr>
<tr>
<td>-300 +150</td>
<td>5.3</td>
<td>2.20</td>
<td>6.8</td>
<td>34.6</td>
<td>53.6</td>
<td>5.0</td>
</tr>
<tr>
<td>-150 +106</td>
<td>12.8</td>
<td>2.60</td>
<td>11.2</td>
<td>33.1</td>
<td>49.6</td>
<td>6.2</td>
</tr>
<tr>
<td>-106 +75</td>
<td>9.7</td>
<td>3.41</td>
<td>18.5</td>
<td>32.3</td>
<td>43.1</td>
<td>6.2</td>
</tr>
<tr>
<td>-75 +45</td>
<td>9.1</td>
<td>4.70</td>
<td>21.3</td>
<td>29.6</td>
<td>39.8</td>
<td>9.4</td>
</tr>
<tr>
<td>-45</td>
<td>61.9</td>
<td>4.30</td>
<td>22.8</td>
<td>29.3</td>
<td>40.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>3.86</td>
<td>20.2</td>
<td>30.1</td>
<td>42.1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

aFree gold = leachable gold.
bBMS = base metal sulphides.

study is the leachable gold in each size fraction as well as the overall leachable gold in the total ore at various stages of milling (and unmilled ore).

Eq. (6) was fitted against experimental data obtained from the leaching of gold from each size fraction in the types of unmilled ore mentioned, and was found to entirely underestimate the amount of free leachable gold in each particle size fraction.

A modified version of Eq. (6) which gives a reasonable prediction of the experimental results is presented in Figs. 4, 5 and 6 as well as in Eq. (8) below:

\[ L_g(D) = \frac{2\mu_m}{D^2} \left[ \mu_m - (\mu_m + D) \exp \left( -\frac{D}{\mu_m} \right) \right] + \left[ A \cdot \exp \left( \frac{1}{D} \right) \right] \tag{8} \]

where:
\[ L_g(D) \] = fraction of leachable gold for particle size \( D \),

\[ \mu_m \] = characteristic leaching rate parameter.
\[ \mu_m = \frac{1}{2\tau} \]
\[ A = \text{empirical constant for the specific ore}, \]
\[ \{A\exp(1/D)\} = \text{fraction of leachable gold for particle size (D) not related to liberation}, \]
\[ D = \text{geometric mean of the screen interval (\(\mu m\))}, \]
\[ \mu_m = \text{mean linear intercept length of gold in the ore (\(\mu m\))}. \]

No provision is made in Eq. (6) for the amount of leachable gold in the various particle size fractions that is not related to the liberation of gold due to comminution. In each particle size fraction there is a certain amount of gold available to cyanide (gold in fractures and pores, etc.) which is not accounted for by the liberation model of King (Eq. 6). The second term in Eq. (8) was thus added to Eq. (6) to compensate for the fraction of leachable gold for each particle size which cannot be attributed directly to liberation. This implies that a certain fraction of gold in the ore is leachable even for coarse lumps of unmilled ore, such as being practised in some heap leaching operations. The empirical constant for a specific ore, \(A\) and the mean linear intercept length of the gold in the ore, \(\mu_m\), were

**Table 5**
Leachable gold vs. size fraction (Harties unmilled ore)

<table>
<thead>
<tr>
<th>Size fraction ((\mu m))</th>
<th>Mass (%)</th>
<th>Head grade Au (g/t)</th>
<th>Free* Gold (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>72.5</td>
<td>11.5</td>
<td>40.9</td>
</tr>
<tr>
<td>-300+150</td>
<td>13.3</td>
<td>14.1</td>
<td>51.2</td>
</tr>
<tr>
<td>-150+106</td>
<td>6.0</td>
<td>12.8</td>
<td>55.4</td>
</tr>
<tr>
<td>-106+75</td>
<td>1.8</td>
<td>14.9</td>
<td>65.6</td>
</tr>
<tr>
<td>-75+45</td>
<td>2.8</td>
<td>18.1</td>
<td>73.1</td>
</tr>
<tr>
<td>-45</td>
<td>3.8</td>
<td>16.9</td>
<td>69.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>12.4</td>
<td>45.7</td>
</tr>
</tbody>
</table>

*Free gold = leachable gold.

**Table 6**
Leachable gold vs. size fraction (Harties 70% – 75 \(\mu m\))

<table>
<thead>
<tr>
<th>Size fraction ((\mu m))</th>
<th>Mass (%)</th>
<th>Head grade Au (g/t)</th>
<th>Free* Gold (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>1.0</td>
<td>8.5</td>
<td>25.6</td>
</tr>
<tr>
<td>-300+150</td>
<td>7.2</td>
<td>10.6</td>
<td>26.5</td>
</tr>
<tr>
<td>-150+106</td>
<td>12.1</td>
<td>10.7</td>
<td>32.8</td>
</tr>
<tr>
<td>-106+75</td>
<td>8.6</td>
<td>11.8</td>
<td>54.6</td>
</tr>
<tr>
<td>-75+45</td>
<td>11.8</td>
<td>13.3</td>
<td>75.8</td>
</tr>
<tr>
<td>-45</td>
<td>58.3</td>
<td>12.8</td>
<td>77.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>12.23</td>
<td>67.4</td>
</tr>
</tbody>
</table>

*Free gold = leachable gold.
Table 7
Gold deportment vs. particle size (FSG)

<table>
<thead>
<tr>
<th>Deposition of gold</th>
<th>Unmilled (%)</th>
<th>70%—150 µm (%)</th>
<th>70%—75 µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachable gold (experimental)</td>
<td>25</td>
<td>28</td>
<td>47</td>
</tr>
<tr>
<td>Leachable gold (model prediction)</td>
<td>21</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>Gold in base metal sulphides</td>
<td>35</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td>Gold in pyrite</td>
<td>29</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>Gold in silicates</td>
<td>11</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 8
Mass distribution of FSG ORE (70%—150 µm)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>12.8</td>
</tr>
<tr>
<td>−300+150</td>
<td>16.5</td>
</tr>
<tr>
<td>−150+106</td>
<td>24.5</td>
</tr>
<tr>
<td>−106+75</td>
<td>23.3</td>
</tr>
<tr>
<td>−75+45</td>
<td>12.3</td>
</tr>
<tr>
<td>−45</td>
<td>10.6</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 9
Gold deportment vs. particle size (WDL)

<table>
<thead>
<tr>
<th>Deposition of gold</th>
<th>Unmilled (%)</th>
<th>70%—150 µm (%)</th>
<th>70%—75 µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachable gold (experimental)</td>
<td>8</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>Leachable gold (model prediction)</td>
<td>7</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>Gold in base metal sulphides</td>
<td>30</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>Gold in pyrite</td>
<td>46</td>
<td>44</td>
<td>42</td>
</tr>
<tr>
<td>Gold in silicates</td>
<td>16</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

estimated for each of the unmilled ores (WDL, FSG and Harties) using Eq. (8). The results are presented in Table 12. \( \mu_m \) was found to be 8.5 µm for WDL ore, 17 µm for FSG ore and 38 µm for Harties ore. There was also a corresponding increase in the value of A with an increase in \( \mu_m \), which is probably related to the size of the gold particles in each particle size fraction. The larger the gold particles in an ore, the more exposed such gold will probably be to leaching, even without further liberation. The second term in Eq. (8) increases with a decrease in particle size fraction, which agrees with the experimental results obtained for the various ores tested.
Table 10
Mass distribution of WDL ORE (70% - 150 µm)

<table>
<thead>
<tr>
<th>Size fraction (µm)</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+300</td>
<td>18.7</td>
</tr>
<tr>
<td>-300+150</td>
<td>9.8</td>
</tr>
<tr>
<td>-150+106</td>
<td>20.4</td>
</tr>
<tr>
<td>-106+75</td>
<td>14.6</td>
</tr>
<tr>
<td>-75+45</td>
<td>15.5</td>
</tr>
<tr>
<td>-45</td>
<td>21.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Table 11
Gold deportment vs. particle size (Harties)

<table>
<thead>
<tr>
<th>Deporment of gold</th>
<th>Unmilled (%)</th>
<th>70% - 75 µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachable gold (experimental)</td>
<td>45.7</td>
<td>67.4</td>
</tr>
<tr>
<td>Leachable gold (model prediction)</td>
<td>44.1</td>
<td>65.4</td>
</tr>
<tr>
<td>Gold in base metal sulphides</td>
<td>8.3</td>
<td>7.7</td>
</tr>
<tr>
<td>Gold in pyrite</td>
<td>8.3</td>
<td>4.9</td>
</tr>
<tr>
<td>Gold in silicates</td>
<td>37.7</td>
<td>20.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Fig. 1. Leachable gold as a function of particle size (FSG) experimental.
A general decrease in $L_g(D)$ with increasing particle size, as expected, is evident from Figs. 4 to 6 for the unmilled ore. The solid lines on the graphs show the liberation predicted by Eq. (8) (with $\mu_m$ and $A$ estimated by Eq. 8). The correct trend is predicted in all three cases and the model as described in Eq. (8) gives reasonable predictions to about 50 $\mu$m, whereafter it slightly overpredicts.

The ore (FSG, WDL and Harties) was milled down to 70%–75 $\mu$m and the
samples were screened into particle size fractions. A diagnostic leaching procedure was performed on each size fraction (except Harties where only the leachable gold was determined). The results are presented in Tables 1 to 11 as well as in Figs. 7, 8 and 9.
Eq. (8) was then used to estimate the gold liberated \( L_g(D) \) for each particle size. The mean linear intercept lengths of the gold in the milled ore as well as the empirical constants were kept constant for the specific ore \( (\mu_m \text{ and } A \text{ as estimated from Eq. 8}) \). The predictions are shown by the solid lines in Figs. 7, 8 and 9.

The modified King's model for ores (Eqs. 8) as shown in Figs. 4 to 9 gives reasonable predictions. For the present data the predicted \( L_g(D) \) and \( \mu_m \) using Eq. (8) tend to slightly underestimate for particle size fractions smaller than 125 \( \mu m \) and slightly overestimate for particle size fractions larger than 125 \( \mu m \). The overall leachable gold for different fineness of grind for each of the ores is presented in Tables 7 to 11. From the results it can be seen that the model slightly underpredicts the leachable gold in the ore for all fineness of grind. It must be taken into account that the mineralogy of the ore was not taken into account in the model predictions, although this was shown by Lorenzen and Van Deventer (1992) to have a pronounced effect. Nevertheless, the model gives reasonable predictions of the leachable gold fraction for milled ore when the leachable gold in the unmilled ore is known. It must be taken into account that this is only a
preliminary model and that some refinement is still needed before it can be used accurately for predicting leachable gold. However, there are currently no models available for the prediction of leachable gold as a function of particle size.
Fig. 9. Leachable gold as a function of particle size for milled Harties ore with application of Eqs. (8).

Nevertheless, the model predicts that high leachable gold values will require a grinding size of 70% - 75 μm for FSG and Harties ores, and a grinding size of 70% - 50 μm for WDL ore. This agrees with liberation data and grinding studies on the various ores (Lorenzen and Francis, 1987).

3. Conclusions

An explicit solution to King’s liberation model was modified in order to predict leachable gold ($L_g(D)$) in different size fractions ($D$) on the basis of data gathered for the unmilled ore. In this model, $\mu_m$ is the mean linear intercept length for gold in the ore, and term $A \cdot \exp(1/D)$ indicates fraction of leachable gold which cannot be attributed directly to liberation:

$$L_g(D) = 2\mu_m/D^2[\mu_m - (\mu_m + D)\exp(-D/\mu_m)] + [A \cdot \exp(1/D)]$$

It was found that this model gives reasonable predictions of the leachable gold for three different types of ore. Although this model can still be improved substantially, it is a first attempt to relate diagnostic leaching results to liberation theory.

References


NEURAL NET ANALYSIS OF THE LIBERATION OF GOLD USING DIAGNOSTIC LEACHING DATA

G.J. ANNANDALE, L. LORENZEN, J.S.J. VAN DEVENTER and C. ALDRICH

Department of Chemical Engineering, University of Stellenbosch, Stellenbosch, 7600, South Africa
(Received 22 June 1995; accepted 28 September 1995)

ABSTRACT

The interrelationship between mineral liberation and leaching behaviour of a gold ore is ill defined, mainly due to the complexity of both leaching and mineral liberation. A better understanding of this relationship could result in lower operating costs on gold extraction plants, since an increase in the efficiency of gold dissolution and a decrease in costs related to the crushing and grinding operations could be expected. In this investigation artificial neural nets were used to analyse diagnostic leaching data of gold ores obtained from South African gold mines. A self-organising neural net with a Kohonen layer was used to generate order-preserving topological maps of the characteristics of both the unmilled and milled ores. The arrangement and shapes of these clusters could then be used to develop simple neural net models which were capable of predicting the degree of liberation more accurately than previously proposed models. Moreover, the neural net models were also capable of providing direct estimates of the reliability of their predictions by comparing new inputs with the data in their training bases.

Keywords
Gold ores; liberation; modelling; neural networks; ore mineralogy

INTRODUCTION

Comminution processes such as crushing, milling and grinding are used to liberate minerals prior to upgrading by subsequent ore-dressing and consequently play an important role in the overall profitability of mineral processing operations. Since high-grade concentrates can have a considerable impact on downstream processing, the choice of fineness of grind is an important decision, especially also in view of the high cost of grinding operations.

Models that can be used for the quantitative estimation of mineral liberation or the leachability of an ore as a function of particle size and the mineralogy of the ore will be of great practical use, such as in the design and simulation of plants, especially when combined with other quantitative models for concentrating operations, such as in flotation [1].

Presented at Minerals Engineering '95, St. Ives, Cornwall, England, June 1995
Perhaps the greatest drawback of present liberation models lies in the tedium associated with the determination of the model parameters, such as intercept lengths, the particle size at which the liberation reaches a particular level, the diameter of the gold particles, etc., in order to predict the liberation of the valuable mineral (gold). Although some progress has been made with regard to these difficulties, for example by making use of diagnostic leaching to determine the mineralogy of gold ores [2,3], these advances have not been sufficient to date. Moreover, owing to the limited use of available data, process engineers cannot always draw valid conclusions with regard to liberation processes and in certain cases this can lead to severe impairment of their ability to adjust operations to changing circumstances.

It is for this reason that other approaches to the modelling and analysis of liberation are increasingly being considered, either in lieu of fundamental or semi-empirical methods, or more often to supplement existing representations of these processes. Some of the novel techniques being considered are based on the use of artificial neural nets, which are flexible, can handle large sets of data and have the ability to learn complex and non-linear relationships which can include noisy or incomplete information. In this investigation it is shown that neural nets can be used either by themselves or in conjunction with other modelling approaches to assist in understanding the relationship between mineral liberation and leaching behaviour as fully as possible.

ARTIFICIAL NEURAL NETWORKS

Neural network technology has initially evolved from studies of the mammalian cerebral cortex. These systems essentially consist of collections of interconnected computational nodes, and their characteristics are derived from the collective behaviour of these nodes, also known as artificial neurons, neurodes, processing elements or processing units [4,5].

Back propagation neural nets

In back propagation neural networks (BPNN), which are presently used in most applications, the processing nodes are usually divided into disjoint subsets or layers, in which all the nodes have similar computational characteristics.

A distinction is made between input, hidden and output layers depending on their relation to the information environment of the net. The nodes in a particular layer are linked to other nodes in successive layers by means of artificial synapses or weighted connections (adjustable numeric values), as shown in Figure 1.

![Figure 1: Generic structure of a back propagation neural net](https://scholar.sun.ac.za)
Back propagation neural nets learn by repeatedly attempting to match sets of input data to corresponding sets of output data or target values. Learning occurs by means of algorithms usually designed to minimise the mean square error between the desired and the actual output of the net through incremental modification of the weight matrix of the net [6]. In back propagation neural nets information is propagated back through the net during the learning process, in order to update the weights, which constitute a distributed representation of the features of the process. The net eventually constructs an internal representation of the relationship between the inputs and the outputs presented to it. More formally, the training process can be described as follows.

A randomised set of weights is initially used to represent the first pattern presented to the net. The weighted summed inputs to the i'th node are first determined (see Figure 2)

\[ u_i(t) = \sum w_{ij} z_j(t) - \theta_i \]  

(1)

where \( u_i(t) \) is the potential of the i'th node at time or iteration t, \( w_{ij} \) is the weight associated with the connection between nodes i and j, \( z_j(t) \) is the output of the j'th node connected to the i'th node and \( \theta_i \) is a bias connected to the node. The potential of the node is then transformed, i.e.

\[ z_i(t+1) = \phi_i[u_i(t)] \]  

(2)

The transfer function \( \phi_i[^*] \) could assume a linear, step, sigmoidal or some other form, with a domain typically much smaller than that of the potential of the process unit, such as [0;1] or [-1;1], for example. Sigmoidal functions of the form \( \phi[u] = 1/[1 + e^{-u}] \) are used widely, since they are continuous, easily differentiable (\( \phi'[u] = \phi[u][1 - \phi[u]] \)), increases monotonically and approaches a fixed value as the magnitude of the input becomes large.

![Fig.2 Typical node of a back propagation neural net](image)

The principle behind one of the most widely used back propagation training algorithms, the generalised \( \delta \)-rule [6], is applied as follows. After initialisation of the weight matrix of the net, the nodes in the net are activated in a forward pass, the computed output of the net is compared with the desired or target output values and an error signal is generated. An error gradient \( \delta_{0,i} \) is then calculated for each node in the output layer, i.e.

\[ \delta_{0,i} = z'_{0,i} (t_{0,i} - z_{0,i}) \]  

(3)

where \( t_{0,i} \) is the target value associated with the output of the i'th node in the output layer, \( z_{0,i} \) and \( z'_{0,i} \) the derivative of \( z_{0,i} \) with respect to the potential of the node.

The error gradient for the hidden layers is based on the weighted sum of the errors in the previous (output) layer k.
By applying this procedure recursively until the input layer is reached, errors are propagated back through the net. The weight matrix of the net is subsequently updated as follows

$$w_{ij}(t+1) = w_{ij}(t) + \Delta w_{ij}(t)$$  \hspace{1cm} (5)

where

$$\Delta w_{ij}(t) = -\tau \cdot \delta_i z_i(t)$$  \hspace{1cm} (6)

and where $\tau$ is a learning rate parameter which defines the step size during gradient descent search. Convergence can sometimes be improved by the inclusion of a momentum term, which takes the effect of previous weight changes $\Delta w_{ij}(t-1)$ into account, that is

$$\Delta w_{ij}(t) = -\tau \cdot \delta_i z_i + \alpha \Delta w_{ij}(t-1)$$  \hspace{1cm} (7)

Self-organising neural nets

Self-organising neural nets [7] are valuable tools for the visualisation of complex or clustered process data and can be used to create two-dimensional topological order-preserving feature maps of the data, as was among others demonstrated by Aldrich et al. [8] and Laine et al. [9] in the field of mineral processing. Such a net learns without supervision and typically consists of an input layer that is fully connected to a two-dimensional Kohonen layer, as shown in Figure 3. Each process element in the Kohonen layer measures the Euclidean distance of its weights to the input values fed to the layer and competes with its neighbours for assignment of a particular exemplar.

Suppose the input data consist of N-dimensional vectors of the form $x = \{x_1, x_2, x_3, .. x_N\}$, then each Kohonen element will have N weight values, that can be denoted by $w_i = \{w_{i1}, w_{i2}, w_{i3}, .. w_{iN}\}$. The Euclidean distance, $D_i = \|x - w_i\|$, between the input vectors and the weights of the net is then computed for each of the Kohonen elements and the winner is determined by the minimum Euclidean distance.
The weights of the element with the smallest Euclidean distance, as well as its neighbouring elements are subsequently adjusted in order to move the weights closer to the input vector, that is

$$w_{ij,\text{new}} = w_{ij,\text{old}} + \beta(x_j - w_{ij,\text{old}})$$

(8)

where $\beta$ is an appropriate learning coefficient that is time-dependent (decreases with time, typically starting at 0.4 and decreasing to 0.1 or lower).

The adjustment of the weights of the elements in the immediate vicinity of the element with the smallest Euclidean distance is important in the preservation of the order of the input space and amounts to an order preserving projection of the input space onto the two-dimensional Kohonen layer. Back propagation and Kohonen neural nets were used in a complementary way to analyse and model the data discussed below.

**EXPERIMENTAL DATA**

Nine different ores obtained from South African gold mines were used in the experiments, viz. ores from the Beatrix, St. Helena, Western Deep Levels (WDL), Free State Geduld (FSG), Unisel, Harmony, Kinross, Leslie and Barberton mines. All the ores, except the refractory Barberton ore, were fed directly to autogenous mills. The Barberton ore was crushed to −2000 mm before milling. The deportment of gold in the different ores was determined by diagnostic leaching and can be summarised as follows.

**Beatrix gold ore**

The Beatrix reef is situated in the Orange Free State gold fields with an average head grade of 6 g/ton (1994). From mineralogical analyses reported by the mine, gold occurs in four main forms in the Beatrix reef, namely as free gold, gold associated with quartz and other silicates, gold associated with pyrite and gold associated with carbonaceous materials.

About 70% of the gold in the Beatrix reef occurs as free gold interstitially dispersed in the quartz. Gold grains observed in studies varied in size from $210 \times 75$ square $\mu$m to $5 \times 2$ square $\mu$m, with a median size of $38 \times 14$ square $\mu$m. Gold locked-up in quartz and other silicates, such as chlorite, comprised 10% of the Beatrix gold and the median size of these grains was $32 \times 10$ square $\mu$m. On the other hand, gold associated with pyrite comprised roughly 5% of the total gold in the ore. These grains (with a median size of $15 \times 6$ square $\mu$m) are generally smaller than the free gold grains and those associated with silicates. The remaining 15% of the gold had a median size of $8 \times 3$ square $\mu$m and was associated with hydrocarbons in the ore.

**St. Helena and Unisel gold ores**

The St. Helena gold ore is mined from the Basal reef with an average head grade of 4 to 5 g/ton. Two-thirds of the Unisel gold ore derive from the Basal reef and one-third from the Leader reef. The average head grade is approximately 5.5 g/ton. Only the gold mineralisation of the Basal reef was available (report from St. Helena) and thus only a general description of the St. Helena gold ore can be given. Gold occurred as free gold, gold attached to pyrite, gold included in pyrite and gold associated with carbonaceous matter. An estimated 50% of all the gold occurred as free gold grains. The sizes of hackly (sharp angular) gold grains varied considerably, ranging from a few millimetres in diameter down to a few microns.

Approximately 10% of the gold occurred as gold attached to pyrite grains, usually pyritic grains which also occluded gold. It was found to be completely extractable by cyanidation. Gold included in the pyrites was estimated to comprise approximately 35% of the total gold. The average diameter of these gold grains was approximately 10 $\mu$m. The estimated recoverability by cyanidation of these gold grains with a size greater than 20 $\mu$m is 80%; a size smaller than 20 $\mu$m but larger than 5 $\mu$m is 50% and a
size smaller than 5 μm is approximately 10%. An estimated 5–10% of the gold was associated with hydrocarbons. These gold grains were extremely small, averaging roughly 2 μm in diameter.

**Kinross and Leslie gold ore**

The Kinross and Leslie gold mines are situated in the eastern and western parts of the Evander gold field, respectively. Due to their extreme locations relative to each other and to the other gold fields, their gold mineralogies differ significantly, with an average head grade of 7 g/ton (1994) for the Kinross gold ore and 5–6 g/ton (1994) for the Leslie gold ore.

In contrast to the other ores which were milled to 70% −75 μm, the Leslie gold ore was milled to 90% −75 μm due to the large occurrence of shale in this region which tends to interfere with the extraction of gold by cyanidation.

**Barberton gold ore**

The Barberton gold mine is situated in the Barberton region in the eastern Transvaal and owing to the presence of large amounts of pyrite and arsenopyrite in the gold ore, the extraction of gold by means of the normal cyanidation procedure is unsuccessful. The gold from this refractory ore is therefore recovered by means of bacterial leaching.

**Western Deep Level, Free State Geduld and Harmony gold ores**

The Western Deep Level (WDL) gold mine is situated on the West Wits Line; while Free State Geduld (FSG) and Harmony gold mines are situated in the Free State gold fields. These ores were previously investigated by Lorenzen [10] and since the same experimental procedures were followed, his data could be included with those pertaining to the above-mentioned ores.

Since the ores contained a lot of moisture, ore samples had to be wet-screened (washed) to retrieve all the fine material from the coarser lumps. Ore samples were first screened into three size intervals, namely a +6700 μm, +1500−6700 μm and a −1500 μm fraction.

The −1500 μm fraction (residue from the first wet screening), was further classified into six additional fractions, viz. a +300−1500, +150−300, +106−150, +75−106, +53−75 and a −53 μm fraction. The −53 μm fraction was filtered in a pressure filter to remove the excess water and the filter cake was dried with the other particle size fractions. The dry particle size fractions were then screened and dried on a vibrating sieve shaker (Fritsch Analysette type 03.502) for a period of 45 minutes.

These eight particle size fractions represent the unmilled ore. A representative sample was subsequently taken from the unmilled sample. The −53 μm up to the +1500−6700 μm fraction was split with a rotary sample splitter (Hi-Vi vibratory equipment from Eriez magnetics, model 15A) and the +6700 μm was split randomly by hand. This representative sample, about one eighth of the unmilled sample, was used for further processing, namely crushing and milling.

The +1500−6700 μm and the +6700 μm particle size fractions were then crushed, first by a jaw crusher and then by a cone crusher, to −1500 μm. This crushed sample was screened using the same technique as mentioned above. The size fractions −53 μm up to the +150−300 μm fraction represent crushed samples.

The size fractions −53 μm up to the +300−1500 μm of the representative sample taken from the unmilled sample, combined with the +300−1500 fraction from the crushers, were fed to a laboratory ball mill with iron balls of different sizes, to produce the milled sample of 70% −75 μm. This milled sample was also screened into the above-mentioned size fractions.
After pretreatment of the ores, diagnostic leaching \([3,10]\) was performed once on each of the particle size fractions \((-53 \mu m; +53-75 \mu m; +75-106 \mu m; +106-150 \mu m; +150-300 \mu m; +300\mu m)\) of the unmilled and milled samples of each ore and on the crushed samples of some ores. The results are shown in Figures 4–12.

![Graph showing Au dissolution for different particle sizes and treatments](image)

**Fig. 4** Occurrence of free gold in Kinross ore

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>CRUSHED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>36.49</td>
<td>36.77</td>
<td>84.91</td>
</tr>
<tr>
<td>BMS</td>
<td>13.31</td>
<td>13.42</td>
<td>3.64</td>
</tr>
<tr>
<td>PYRITE</td>
<td>6.93</td>
<td>7.84</td>
<td>3.84</td>
</tr>
<tr>
<td>SILICATES</td>
<td>38.87</td>
<td>38.33</td>
<td>5.24</td>
</tr>
<tr>
<td>CARBON</td>
<td>4.4</td>
<td>4.4</td>
<td>2.38</td>
</tr>
</tbody>
</table>

![Graph showing Au dissolution for different particle sizes and treatments](image)

**Fig. 5** Occurrence of free gold in Leslie ore

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>32.08</td>
<td>75.82</td>
</tr>
<tr>
<td>BMS</td>
<td>8.25</td>
<td>5.08</td>
</tr>
<tr>
<td>PYRITE</td>
<td>11.02</td>
<td>3.23</td>
</tr>
<tr>
<td>SILICATES</td>
<td>46.03</td>
<td>13.83</td>
</tr>
<tr>
<td>CARBON</td>
<td>2.62</td>
<td>2.04</td>
</tr>
</tbody>
</table>
Fig. 6 Occurrence of free gold in Unisel ore

Fig. 7 Occurrence of free gold in FSG ore
Neural net analysis of the liberation of gold

Au DISSOLUTION (%)

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>8.3</td>
<td>20.2</td>
</tr>
<tr>
<td>BMS</td>
<td>29.9</td>
<td>30.1</td>
</tr>
<tr>
<td>PYRITE</td>
<td>46.1</td>
<td>42.1</td>
</tr>
<tr>
<td>SILICATES</td>
<td>15.7</td>
<td>7.5</td>
</tr>
</tbody>
</table>

UNMILLED
MILLED

Fig. 8 Occurrence of free gold in WDL ore

Au DISSOLUTION (%)

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>7.36</td>
<td>25.9</td>
</tr>
<tr>
<td>BMS</td>
<td>14.51</td>
<td>28.96</td>
</tr>
<tr>
<td>PYRITE</td>
<td>65.65</td>
<td>40.24</td>
</tr>
<tr>
<td>SILICATES</td>
<td>4.45</td>
<td>1.2</td>
</tr>
<tr>
<td>CARBON</td>
<td>8.04</td>
<td>3.7</td>
</tr>
</tbody>
</table>

UNMILLED
MILLED

Fig. 9 Occurrence of free gold in Barberton ore
### Fig. 10 Occurrence of free gold in Beatrix ore

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>17.4</td>
<td>64.05</td>
</tr>
<tr>
<td>BMS</td>
<td>10.22</td>
<td>8.03</td>
</tr>
<tr>
<td>PYRITE</td>
<td>9.93</td>
<td>8.58</td>
</tr>
<tr>
<td>SILICATES</td>
<td>55.3</td>
<td>11.45</td>
</tr>
<tr>
<td>CARBON</td>
<td>7.14</td>
<td>7.89</td>
</tr>
</tbody>
</table>

### Fig. 11 Occurrence of free gold in St Helena ore

<table>
<thead>
<tr>
<th></th>
<th>UNMILLED</th>
<th>CRUSHED</th>
<th>MILLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FREE Au</td>
<td>23.21</td>
<td>17.42</td>
<td>68.76</td>
</tr>
<tr>
<td>BMS</td>
<td>6.31</td>
<td>6.4</td>
<td>9.97</td>
</tr>
<tr>
<td>PYRITE</td>
<td>6.44</td>
<td>6.61</td>
<td>7.36</td>
</tr>
<tr>
<td>SILICATES</td>
<td>53.72</td>
<td>58.41</td>
<td>8.04</td>
</tr>
<tr>
<td>CARBON</td>
<td>10.31</td>
<td>11.13</td>
<td>5.88</td>
</tr>
</tbody>
</table>
Neural net analysis of the liberation of gold

**Fig. 12** Occurrence of free gold in Harmony ore

**DATA ANALYSIS AND MODELLING**

The percentage gold deportment in the various milled and unmilled ore minerals ($Au_p$, $Au_s$, $Au_b$, $Au_c$) and the percentage of free gold ($Au_o$) in each of the particle size fractions, the head grade ($G$), as well as the mass distribution ($m$) were projected to a two-dimensional topological map with a self-organising neural net. The seven variables, i.e. $x = \{Au_p, Au_s, Au_b, Au_c, Au_o, G, m\}$ were used as inputs to the net, which consisted of an input layer with 7 nodes (corresponding to each of the inputs), a two-dimensional 10x10 Kohonen layer and a two-node output layer which provided x- and y-coordinates derived from the two-dimensional Kohonen layer via interpolation. The net was trained and after convergence maps of the unmilled (Figure 13) and milled ore samples (Figure 14) were generated.

**Fig. 13** Topological feature map of unmilled gold ores
Cluster analysis

The centres of gravity \( c_j(X_j, Y_j) \) of each ore \( j (j = 1, 2, \ldots, 9) \) on the topological maps shown in Figures 13 and 14, as well as the distance \( D_{ijk} \) of the \( i \)’th data point in ore \( k \) from each of the centres of gravity \( c_j \) were calculated in order to quantify the clustering of the various attributes pertaining to specific ores, where \( D_{ijk} \) indicates the distance of the \( i \)’th point in cluster (ore) \( k \) from the centre of gravity (COG) of cluster (ore) \( j \) (if \( j = k \) then the centre of gravity is also associated with the points in cluster \( k \), otherwise not). The centres of gravity and distances were calculated as follows:

\[
c_j(X_j, Y_j) = (\Sigma_i x_{ij} / n; \Sigma_i y_{ij} / n) \tag{9}
\]

\[
D_{ijk} = [(x_{ik} - X_j)^2 + (y_{ik} - Y_j)^2]^{1/2} \tag{10}
\]

where \( x_{ik} \) is the x-coordinate of the \( i \)’th data point from the \( k \)’th ore, \( y_{ik} \) the y-coordinate of the \( i \)’th data point from the \( k \)’th ore, and \( X_j \) and \( Y_j \) the x- and y-coordinate of the centre of gravity of the \( j \)’th ore respectively. For comparative purposes the Euclidean distances \( D_{ijk} \) were normalised, i.e. \( d_{ik} = (D_{ijk} - D_{ijk,\min}) / (D_{ijk,\max} - D_{ijk,\min}) \), so that \( 0 \leq d_{ik} \leq 1 \).

If the ore data are perfectly clustered, all distances \( d_{ik} \) \( (j = k) \) can be expected to be smaller than the distances \( d_{ik} \) \( (j \neq k) \). The degree of clustering, which is a measure of the sharpness of the separation, can be constructed by sorting all \( d_{ik} \) values for each ore \( j \) from small to large. Nine ranking lists, one for each ore, will thus be constructed. The measure of dispersion \( M_j \) is then calculated as \( M_j = \Sigma_{ik} m_{ik} \), where \( m_{ik} \) is the ranking order of \( d_{ik} \) if \( j \neq k \), and 0 otherwise. The lower the value of \( M_j \), the sharper the definition of the clusters. The dispersion \( M_j \) is now normalised and also subtracted from one to enable generalised comparisons between ores. That is \( M'_j = -1 + 2 (M_j - M_j,\min) / (M_j,\max - M_j,\min) \) where \( M'_j \) is the normalised dispersion, \( M_j,\min \) is the best degree of clustering possible for the system, and \( M_j,\max \) is the worst degree of clustering possible for the system. Due to the subtraction from one, an absolute value of unity for \( M'_j \) is thus an indication of perfect clustering, while an absolute value tending to zero indicates perfect dispersion or random mapping of the various ore members.
The centres of gravity and the normalised measure of dispersion are presented in Tables 1 and 2 for the unmilled and milled ores respectively. The normalised Euclidean distances \( d_j^k = (D_{ij}^k - D_{ij}^{k,min}) / (D_{ij}^{k,max} - D_{ij}^{k,min}) \) between the centres of gravity of the unmilled and milled ores are tabulated in Table 3. From these data the measure of clustering for the unmilled Kinross, Beatrix, St. Helena and Barberton gold ores is about the same (\( M_j^' = 0.7 \)), as well as for the unmilled Harmony and Unisel gold ores (\( M_j^' = 0.92 \)), although the ores are mapped to different areas on the topological feature map.

**TABLE 1** The measure of clustering and centres of gravity for each unmilled ore

<table>
<thead>
<tr>
<th>Ores</th>
<th>Measure of clustering</th>
<th>COG: x-coordinate</th>
<th>COG: y-coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinross</td>
<td>0.719</td>
<td>0.291</td>
<td>0.538</td>
</tr>
<tr>
<td>Leslie</td>
<td>0.608</td>
<td>0.269</td>
<td>0.490</td>
</tr>
<tr>
<td>Beatrix</td>
<td>0.698</td>
<td>0.437</td>
<td>0.470</td>
</tr>
<tr>
<td>Harmony</td>
<td>0.920</td>
<td>-0.128</td>
<td>0.863</td>
</tr>
<tr>
<td>St. Helena</td>
<td>0.705</td>
<td>-0.166</td>
<td>0.480</td>
</tr>
<tr>
<td>Unisel</td>
<td>0.913</td>
<td>-0.163</td>
<td>0.285</td>
</tr>
<tr>
<td>Barberton</td>
<td>0.712</td>
<td>-0.177</td>
<td>-0.862</td>
</tr>
<tr>
<td>WDL</td>
<td>1.000</td>
<td>0.476</td>
<td>-0.823</td>
</tr>
<tr>
<td>FSG</td>
<td>1.000</td>
<td>-0.204</td>
<td>-0.709</td>
</tr>
</tbody>
</table>

**TABLE 2** The measure of clustering and centres of gravity for each milled ore

<table>
<thead>
<tr>
<th>Ores</th>
<th>Measure of clustering</th>
<th>COG: x-coordinate</th>
<th>COG: y-coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinross</td>
<td>0.851</td>
<td>-0.604</td>
<td>0.145</td>
</tr>
<tr>
<td>Leslie</td>
<td>0.375</td>
<td>-0.177</td>
<td>0.104</td>
</tr>
<tr>
<td>Beatrix</td>
<td>0.795</td>
<td>-0.168</td>
<td>0.486</td>
</tr>
<tr>
<td>Harmony</td>
<td>0.623</td>
<td>-0.581</td>
<td>-0.304</td>
</tr>
<tr>
<td>St. Helena</td>
<td>0.840</td>
<td>0.390</td>
<td>0.527</td>
</tr>
<tr>
<td>Unisel</td>
<td>0.566</td>
<td>0.191</td>
<td>0.091</td>
</tr>
<tr>
<td>Barberton</td>
<td>0.892</td>
<td>0.315</td>
<td>-0.618</td>
</tr>
<tr>
<td>WDL</td>
<td>1.000</td>
<td>0.380</td>
<td>-0.806</td>
</tr>
<tr>
<td>FSG</td>
<td>0.910</td>
<td>0.788</td>
<td>-0.472</td>
</tr>
</tbody>
</table>
TABLE 3 The Euclidean distances between the centres of gravity
of the unmilled and milled ores

<table>
<thead>
<tr>
<th>Ores</th>
<th>Euclidean distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinross</td>
<td>0.604</td>
</tr>
<tr>
<td>Leslie</td>
<td>0.242</td>
</tr>
<tr>
<td>Beatrix</td>
<td>0.384</td>
</tr>
<tr>
<td>Harmony</td>
<td>0.588</td>
</tr>
<tr>
<td>St. Helena</td>
<td>0.255</td>
</tr>
<tr>
<td>Unisel</td>
<td>0.183</td>
</tr>
<tr>
<td>Barberton</td>
<td>0.465</td>
</tr>
<tr>
<td>WDL</td>
<td>0.404</td>
</tr>
<tr>
<td>FSG</td>
<td>0.097</td>
</tr>
</tbody>
</table>

It can also be seen from Table 1 and Figure 13 that although the measure of clustering of the Kinross and Leslie gold ores differs with approximately 10%, these areas are mapped to fairly similar regions on the feature map. This is in accord with the fact that both ores originate from the same area, namely the Evander Gold Field. The same applies to the St. Helena and Unisel gold ores, with the variation in $M'_{ij}$ about 20%, but also projected to similar regions on the feature map. This can be expected, since the Unisel and St. Helena gold ores are very similar as explained before.

It is noticeable that the shapes and location of the clusters of the milled Kinross and Leslie gold ores differ markedly from their unmilled counterparts. This is in contrast from what was found in the unmilled ores where the centres of gravity of these ores were close to each other. This shift in relative positions on the map is well illustrated by the normalised Euclidean distances (Table 3) between the unmilled and milled Kinross and Leslie ores which are 0.604 and 0.241 respectively, showing that these ores behave differently when milled. This conclusion is also valid for the St. Helena and Unisel gold ores as shown in Tables 1, 2 and 3.

From Figure 14 and Table 2 the measure of clustering for the milled Kinross, Beatrix, St. Helena and Barberton is again more or less the same ($M'_{ij} = 0.85$). However, it is again evident from the centres of gravity (Table 2) that the ores exhibit different characteristics, mainly due to their different origins.

The unmilled as well as the milled WDL and FSG gold ores are located in similar regions on the feature maps and it is evident from Figures 13 and 14 and Tables 1 and 2 that they are mineralogically quite different from the non-refractory ores such as Kinross, Leslie, etc. The Barberton gold ore differs substantially from the other ores as well, as indicated by the feature maps in Figures 13 and 14 and the data in Tables 1 and 2. Despite these differences, the normalised Euclidean distances between the centres of gravity of the unmilled and milled WDL and Barberton ores are more or less the same (0.46 and 0.40 respectively), indicating some resemblance in the way the ores liberate gold when comminuted.
NEURAL NET MODELLING OF DIAGNOSTIC LEACHING RESULTS

The compact characterisation derived from the SOM feature maps in Figures 13 and 14 can consequently be used to model the liberation of gold during comminution of the ores. This is accomplished by linking the feature maps to a simple back propagation neural net, as indicated in Figure 15 and effectively amounted to the assumption that similar ores (i.e. ores projected to the same area of the SOM map) would also be similar with regard to the liberation of gold during comminution.

![Diagram of neural net model of gold liberation](image)

**Fig. 15** Neural net model of gold liberation, consisting of a sigmoidal back propagation neural net with a Kohonen hidden layer

A hold-out method was used by training the net on the data \{x, y, Au_0^{unmilled} | Au_0^{milled}\} of eight of the nine ores at a time and testing it against the ore data not used for training the net. Note that the free gold in the unmilled ore is presented to the net explicitly, as well as implicitly being one of the attributes originally projected to the Kohonen feature map. The net consisted of an input layer with three nodes (for the x- and y-coordinates of the Kohonen feature map, as well as for the free gold in the unmilled ore), and an output layer with a single node for prediction of the free gold in the milled ore. This 4-parameter (weights) single layer neural net model was able to predict the data with an average absolute error of less than 15%. This compared very favourably with previous models, such as the one proposed by Annandale [11] based on the particle size fractions of the ores, and which effectively contains seven parameters.

\[
\text{Au}_{\text{Liberated}}^{\text{Leachable}} = 100 - (a_1 + a_2) + b_1\sqrt{d} + b_2\ln d + e^{a_3 + b_4} + e^{a_5 + b_6}
\]  

(11)

The Lorenzen model could predict the total amount of liberated gold with an absolute average error of 19%. The SOM mapping effectively reduces the attributes (particle sizes) used by the Lorenzen model to a more compact set of features which provides a more powerful basis for the prediction of leachable gold, as shown in Figure 16, where the predictions of Eq (11) are compared with those of the neural net.
Moreover, by making use of the Kohonen feature maps of the ores it was possible to construct corresponding error maps to estimate the reliability of predictions pertaining to the liberation of gold, as shown in Figure 17. On this map areas occupied by clusters used to train the back propagation neural net represent zones where estimates of the free gold in the comminuted ore are deemed highly reliable. Areas bordering the zones occupied by these reference clusters are deemed to be moderately reliable, while areas far from any reference clusters are considered to be unreliable. Demarcation of...
Neural net analysis of the liberation of gold

the areas is accomplished by making use of the test data which were also used to validate the performance of the back propagation net. This meant that there were eight reference clusters on the error map at any given time, and since these clusters constituted the training data base of the net, predictions of the liberated gold were also relatively accurate in these areas. At any given time the test cluster was consequently used to demarcate the different zones surrounding the reference clusters. If the net could estimate the amount of free gold associated with the test case relatively accurately, the area occupied by the test cluster was also considered reliable. Areas that could not be tested were considered to be unreliable.

DISCUSSION AND CONCLUSIONS

Although mineral liberation is discussed thoroughly in the literature by various researchers [12-15], it remains a complicated problem. Moreover, only a few investigations have been conducted to date [2,11] in order to understand the interrelationship between mineral liberation and leaching behaviour. In this investigation it was shown that neural nets can be used to assist in the understanding of this relationship.

With only 54 exemplars of the liberation of gold available, other attempts to model the liberation behaviour proved to be less successful. For example, attempting to model the liberation of gold as a function of the characteristics of the unmilled ores, i.e. $Au_{\text{lib}} = f(Au_0, Au_s, Au_p, Au_c, d_1, d_2, .. d_6, G, m_{\text{unmil}}$ with a neural net (or other empirical methods) is impractical, owing to the large number of parameters which have to be estimated with relatively few data. It is well-known that dimensionality is a critical component in the complexity of a problem [16] and by preprocessing or compressing the data with a Kohonen feature map the dimensionality is reduced sufficiently to facilitate modelling of the process.

Despite moderate success regarding the interpretation of a sparse set of data, clearly more information is required in order to develop a better understanding of the liberation behaviour of gold ores. Although the data could be compressed effectively with a Kohonen net, some information is inevitably lost in the process, which could lead to unacceptable distortions in subsequent representations of liberation. Provided that sufficient data are available, it should be possible not only to accurately predict the leachable gold, but also the deportment of gold in the various minerals in a milled ore when the deportment of gold in the unmilled ore is known.

REFERENCES


NOMENCLATURE

\( a_i \) model parameters

\( b_i \) mass percentage of free gold in ores

\( c_i(X_j, Y_j) \) mass percentage free gold in base metal sulphides in ores

\( d \) mass percentage free gold in carbonaceous material in ores

\( x_i \) mass percentage free gold in pyrites in ores

\( b_i \) mass percentage free gold in sulphides in ores

\( D_{ij} \) model parameters

\( d \) centre of gravity of the j'th ore of a Kohonen feature map

\( d_i \) particle size

\( D_{ij,k} \) Euclidean distance between vectors

\( d_i \) particle size of the i'th fraction

\( d_{ij,k} \) normalised Euclidean distance between two vectors in a set

\( D_{ij,k} \) the Euclidean distance of the i'th point in cluster (ore) k from the centre of gravity of cluster (ore) j

\( D_{ij,k,max} \) maximum Euclidean distance between two vectors in a set

\( D_{ij,k,min} \) minimum Euclidean distance between two vectors in a set

\( G \) head grade of an ore

\( m \) mass distribution of the constituents of an ore

\( M_j \) normalised measure of the dispersion of a cluster (values close to zero indicate random dispersion, while absolute values tending to unity indicate sharp clustering)

\( M_j \) measure of dispersion of a cluster

\( M_{j,k} \) ranking order of the i'th exemplar of the k'th ore

\( M_{j,max} \) maximum measure of dispersion of a cluster

\( M_{j,min} \) minimum measure of dispersion of a cluster

\( t \) time or iteration step

\( t_{0,i} \) target value associated with the i'th node in the output layer of a neural net

\( u_i(t) \) potential of the i'th node in a neural net at time t

\( w_{ij}(t) \) weight associated with the connection between the i'th and j'th nodes in a neural net at time t

\( w_{ij,new} \) updated value of weight connecting the i'th and j'th nodes in a neural net

\( w_{ij,old} \) value of weight connecting the i'th and j'th nodes in a neural net prior to updating

\( \Delta w_{ij} \) change in the value of weight

\( x \) vector of independent or input variables

\( X_j \) abscissa of the centre of gravity of the j'th ore of a Kohonen feature map

\( x_i \) i'th independent or input variables

\( Y_j \) abscissa of the centre of gravity of the j'th ore of a Kohonen feature map

\( z_j(t) \) output of the j'th node in a neural net at time t
**Greek letters**

\( \alpha \) parameter accounting for the effect of previous weight changes during training

\( \beta \) time-dependent learning coefficient

\( \delta_{h,i} \) error gradient associated with the output of the \( i \)'th node in a hidden layer of a neural net

\( \delta_{o,i} \) error gradient associated with the output of the \( i \)'th node in the output layer of a neural net

\( \theta_{i} \) bias of the \( i \)'th node in a neural net

\( \phi_{i}( \cdot ) \) transfer function of the \( i \)'th node in a neural net

\( \tau \) learning rate parameter.
The Mineralogical Identification of Refractory Gold Ores by Means of the Selective Decomposition of Minerals

L LORENZEN1 AND J S J VAN DEVENTER1

ABSTRACT

The first step in the design of a process to treat a possible economic precious metal deposit should be an examination of the mineralogy of the ore. Using this and other initial tests, the extractive metallurgist can design a process to treat the ore. In the field of precious metal metallurgy, little emphasis is placed on the mineralogical information available to the metallurgist. The information is of far more use to the geologist and the mining engineer. Diagnostic leaching was designed to open up the field of mineralogical analysis to the metallurgist.

When a mineralogist looks at the department of gold in an ore, he is usually looking for an element which is present in parts per million, so that errors in sampling are multiplied dramatically. Diagnostic leaching offers a cheap, simple, practical alternative. In order to determine with which minerals the desired precious metal is associated, a specific mineral is first eliminated using a selective oxidative leach, and cyanidation is used to extract the precious metal (in this case gold and silver) liberated by the destruction of this mineral. The precious metal extracted can be measured in solution to give a fairly accurate record of the amount of the precious metal associated with that mineral. Furthermore, the residue from this first stage can be subjected to another selective acid leach, and the process repeated. The procedure can be varied to suit the mineralogy of the matrix material. At the end of this diagnostic leach the metallurgist is left with a complete record of the deposit of the precious metal. He can now use this information to design a metallurgical flowsheet to treat the ore.

Diagnostic leaching is thus an analytical tool which can be used by the metallurgist not only to examine new ores, but also to look at problems occurring at existing plants. The procedure is not only limited to ores and residues but in fact can deal with any type of intermediary product that occurs in a plant. The information gained from analyzing an intermediary product can give a useful indication of how well a unit process is working, e.g. flotation, roasting, etc.

INTRODUCTION

The first step in the design of a process to treat a possible economic gold deposit should be an examination of the mineralogy of the ore. Factors affecting the extraction of gold are of a mineralogical nature. Knowledge of the mineralogy of the ore or metallurgical product to be treated, combined with the mineralogical testwork, may improve gold recovery. Usually the first question by the metallurgist is, 'To what size do I need to grind the ore to liberate the gold?'. If more accurate mineralogical data were available, the first question might be, 'Which minerals is the gold associated with and how will this affect the extraction route I use?'.

Diagnostic leaching was developed by the Anglo American Research Laboratories (Lorenzen, et al, 1986 and Lorenzen and Tumilty, 1992) to answer the above question and in doing so opened-up the field of mineralogical analysis to the metallurgist.

With diagnostic leaching, the metallurgist or scientist is able to get a much clearer view of which minerals the gold is associated with. Diagnostic leaching combines sequential selective oxidative leaches of an ore, concentrate, intermediary or stream with stage cyanidation. The process is varied according to the mineralogy of the matrix material and aims to destroy selectively the minerals associated with gold. Interstage dilute acid and cyanide washes can also be used to destroy surface deposits. At the end of the diagnostic leach the metallurgist is left with a complete record of the deposition of gold. He can now use this information to formulate a metallurgical flowsheet to treat the deposit.

In this paper various case studies were chosen to explain the technique of diagnostic leaching and the interpretation of results.

EXPERIMENTAL

The concept of diagnostic leaching, as already mentioned, is very simple. The least stable mineral present in the matrix of the sample is first solubilised in aqueous acid media. The residue is filtered, washed (water/dilute acid), cyanided to extract the gold liberated and washed with a dilute cyanide solution. The process is repeated with a more oxidative acid leach until all the non-refractory re-cyanidied gold is leached by the cyanide to give an accurate record of the amount of gold associated with the various minerals. An overlap of the extent of leaching does occur (Tumilty, et al, 1987) but is generally limited to 90 per cent of the required mineral and ten per cent of the next most stable mineral. The various stages of acid pre-treatment and the minerals it will most likely destroy are presented in Table 1.

<table>
<thead>
<tr>
<th>Pre treatment stage</th>
<th>Minerals likely to be destroyed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NaCN washes</td>
<td>Precipitated gold</td>
</tr>
<tr>
<td>2. NaCN</td>
<td>Gold</td>
</tr>
<tr>
<td>3. HCl</td>
<td>Pyrrhotite, Calcite, Ferites,</td>
</tr>
<tr>
<td>4. H2SO4</td>
<td>Dolomite, Galena, Haematite,</td>
</tr>
<tr>
<td>5. HNO3</td>
<td>Goethite, Calcite carbonate</td>
</tr>
<tr>
<td>6. Na2CO3</td>
<td>Copper Sulphides, Labile Base</td>
</tr>
<tr>
<td>7. FeCl3</td>
<td>Metal Sulphides, Labile Pyrite</td>
</tr>
<tr>
<td>8. Oxalic Acid Washes</td>
<td>Sphalerite, Galena, Labile</td>
</tr>
<tr>
<td>9. HF</td>
<td>Sulphides, Tetrahedrite</td>
</tr>
<tr>
<td>10. Aconitine elution</td>
<td>Oxide Coatings</td>
</tr>
</tbody>
</table>

Various examples of South African ores were chosen to explain the concept.

1. Department of Metallurgical Engineering, University of Stellenbosch, Stellenbosch 7600, South Africa.
Cyanidation plant feeds

The first samples to be examined with the diagnostic leaching technique were cyanidation plant feeds from various mines in South Africa. The ore has already been ground to gold ‘liberation’ size (usually 70 per cent minus 74 micrometers) and most plants achieve gold extractions in the region of 95 per cent. The samples were split into representative portions from the head and each ore (sample) subjected to different leach conditions. The first was subjected to a cyanidation treatment under fairly aggressive leaching conditions to ascertain the amount of free, cyanidable gold in the sample. The second was subjected to a strong sulphuric acid leach under oxidising conditions to destroy uraninite, the less refractory base metal sulphides and pyrrhotite. The third sample was leached with concentrated nitric acid to destroy all the minerals present in the Witwatersrand ore other than silicates and kerogen. Cyanidation after the acid treatment of the second and third samples gave a measure of the gold associated with the minerals destroyed.

From this testwork it was found that at the grind used at most of the plants, about 70 per cent minus 74 micrometers, gold is almost totally liberated from silicates. Extractions after nitric acid pre-treatment were typically in the order of 98 to 99 per cent. This has a marked effect on the processing of gold ores in South Africa. If gold is liberated from silicates at the current grind practised by plants, then maybe the grind could be coarsened and sulphides treated separately to liberate gold more economically. In all cases there was an increase in the amount of gold liberated after the sulphuric acid leach. Sulphuric acid leaching is currently used on some plants to leach uranium from ores, but in this application, as long as the increase in gold extraction was sufficient to cover costs, it could be used as a pre-treatment step for the recovery of gold. On some of the samples, a hydrochloric acid pre-treatment was used to destroy pyrrhotite and base metal sulphides. Thus the difference in extraction of gold after sulphide removal was drastically increased (see Figure 2). This is due to the partial combination of three effects:

1. the total liberation of gold occluded in sulphides,
2. the elimination of sulphide minerals (precluding the formation of soluble sulphides which compete to react with cyanide and oxygen), and
3. the elimination of the galvanic passivation effect that sulphides have on the dissolution of gold (Lorenzen and Van Deventer, 1992). Density separation of the residue indicated that the majority of gold in the residue (East Rand ore) after sulphide destruction is associated with quartz and pyrophyllite, and only a very small portion is associated with kerogen.

Gold liberated from silicates

If a process to treat gold in sulphides separately was used, then it would be necessary to find the minimum grind necessary to liberate gold from silicates. Primary cyclone overflow, ie primary ball mill product, was used from two plants and subjected to a series of grindings from the original size down to cyanidation plant feed size. Diagnostic leaching was performed on each ground sample. From the results it was observed (see Figure 1) that one plant’s minimum grind required was 80 per cent minus 100 micrometers and the other 60 per cent minus 74 micrometers. This is substantially coarser than grinds currently employed at the existing plants, and the implication is that separate treatment of sulphides, savings could be made in milling capital and operating costs.

FUG sulphide concentrates

One way of treating sulphides separately for gold recovery would be to have a process in the form:

\[ F - U - G - R - G \text{ or } U - G - F - R - G \]

where \( F \) = flotation, \( U \) = uranium ore, \( G \) = gold cyanidation and \( R \) = roasting. Float tailings would be treated by gold cyanidation (Tumilty and Schmidt, 1987). The advantage of this circuit would be that a small proportion of the mass could be subjected to a far more intensive treatment to recover a greater amount of gold than at present. Milling costs could be reduced as the initial grind would not have to be as fine as current grinds. The objective of the grind would not be to liberate gold from sulphides but to produce an optimum size for flotation.

Flotation concentrates of ROM ore were subjected to diagnostic leaching to determine the possible gold recovery. The final residues after sulphide destruction were very low, and when combined with the residue values obtained from cyanidation of the flotation tailings, indicated that lower overall residues were obtainable by this treatment route as compared to the conventional circuit (Tumilty and Schmidt, 1987). Density separation of the residue indicated that the majority of gold in the residue (East Rand ore) after sulphide destruction is associated with quartz and pyrophyllite, and only a very small portion is associated with kerogen.

Cyanidation kinetics after sulphide removal

Two samples of cyanidation plant feed were leached with cyanide before and after nitric acid pre-treatment to examine the dissolution kinetics. The rate of dissolution after sulphide removal was drastically increased (see Figure 2). This is due to a possible combination of three effects:

1. the total liberation of gold occluded in sulphides,
2. the elimination of sulphide minerals (precluding the formation of soluble sulphides which compete to react with cyanide and oxygen), and
3. the elimination of the galvanic passivation effect that sulphides have on the dissolution of gold (Lorenzen and Van Deventer, Hydrometallurgy, 1992).

When the sulphides were destroyed, the extraction kinetics approached the theoretical minimum time for gold dissolution in cyanide solution.

Nitric acid was never considered as a plant reagent due to the inherent high cost of manufacture. If a cheaper hydrometallurgical route was available to remove sulphides then there could be a benefit in terms of subsequent cyanide leach time and consumption. However this selective leach proved to be an adequate tool for evaluating the amount of gold available in sulphide minerals.
also some present in the pyrrhotite and several base metal sulphides. Sulphide concentrates from several plants were analysed by diagnostic leaching to examine the deportment of the refractory gold (the gold which was unleached in the cyanide circuit). Two extra steps were incorporated to examine the deportment of gold. The first was a hydrochloric acid leach (Table 1, point 3) at ambient temperatures to destroy pyrrhotite only. This was used ahead of any other oxidative leaches as it is the mildest. The other was an elution with acetonitrile (Table 1, point 10) at the end of the series of leaches to quantify the proportion of gold which was adsorbed on carbon, eg kerogen, carbon or coal. Acetonitrile was used as eluant as sodium cyanide elution appeared to be ineffective.

Due to the wider variation in the gold content of samples split from the bulk sample which occurs when sampling sulphide concentrates rather than ores, it was decided to make the leaches sequential rather than in parallel. In this way the gold dissolved into cyanide solution gave a direct measure of the gold extracted from the solids after each acid treatment and can be compared to the final residue obtained to give a fairly accurate percentage extraction. With sequential leaches a calculated head was used rather than an assayed head. This method was found to be more realistic and was used in all subsequent diagnostic leaches.

In all the samples treated from the East Rand, West Rand and Free State, a substantial amount of free gold was present. The older tailing dams that were treated on the East Rand contained about 70 per cent free gold, and the newer ones in the Western Transvaal and Free State about 40 to 60 per cent free gold (see Figure 3). This free gold could be present as:

1. soluble loss associated with filtering the pulp after cyanidation, and
2. sulphides that have oxidised and exposed the gold that had previously not been amenable to cyanidation.

The gold lost in solution with the pulp would presumably precipitate as a cyanide salt in the dam. Sample of the Free State and East Rand dam material were both subjected to quick cyanide washes to try and dissolve any precipitated gold present. The results indicated that although the East Rand dam material had the highest amount of free gold present, the Free State dam material had the greatest proportion of precipitated gold (50 per cent of the free gold - Free State and 28 per cent of the free gold - East Rand). The validity of the precipitated gold diagnostic leach (Table 1, point 1) was verified by performing the leach without oxygen, which gave similar results. The results indicated that the...
increased cyanidable gold available in the East Rand dam material was due to the presence of a greater amount of metallic gold, which had presumably come from the oxidation of sulphides.

On the East Rand the majority of the locked gold was associated with labile base metal sulphides. The residue after a strongly oxidising sulphuric acid leach is low: 83 per cent of associated gold is increased in this leach which suggests that the base metals are finely distributed in the haematite. In this case, chlorine was used as lixiviant for gold instead of cyanide. About 50 per cent of the base metals were extracted in this leach which suggests that the base metals are finely distributed in the haematite.

Sulphides other than pyrophyllite were leached with a two stage hydrofluoric acid leach. This highly aggressive and dangerous leach was successful, but took a long time and solutions were too corrosive for base metal analysis. This leach is no longer considered practical in terms of information gained by using it in the analysis of gold bearing ores. Acetonitrile elution was used to determine the deportment of gold adsorbed on carbon.

The results of the work conducted on two calcine products showed that the majority of the refractory gold was associated with the base metal minerals (sulphides and ferrites) and haematite (see Figure 4). The proportions of refractory gold were similar to those associated with base metal sulphides and pyrite in the sulphide concentrates from which the calcine was obtained. One conclusion that can be made if the roasting was preceded by a strong oxidizing acid leach to destroy base metals, is that it would be possible to decrease the gold locked in calcine. This hypothesis was tested by treating an East Rand sulphide concentrate using several routes including acid leach followed by roasting. Using the latter route increased the overall extraction of gold from 89 per cent to 96 per cent. A test using a cyanidation step before roasting (acid leach - cyanidation - roasting) increased the final recovery to 94 per cent, indicating that gold locked up by ferrites and haematite was responsible for about 50 per cent of the refractory gold. There was a significant proportion of gold (ca 20 per cent) locked in gypsum and arsenates and this gold could possibly be removed by the addition of soda ash to the quench tank after roasting. In the sample of sulphide concentrate from the Free State, the majority of the refractory gold was associated with pyrite. In this case the majority of this gold could be liberated by roasting as a strong, oxidising acid leach prior to roasting, which yields only a one to two per cent increase in gold extraction. Thus, it is evident that diagnostic leaching can be used to determine the deportment of the refractory gold in calcine, thus integrating the fields of applied mineralogy and process design.

**Calcinates**

Calcination, one of the most popular processes by which gold is recovered from refractory sulphides, only renders about 60 per cent of the refractory gold amenable to subsequent cyanidation. Calcine products were investigated by diagnostic leaching to examine the deportment of this refractory gold. The techniques previously used on ores and sulphide concentrates were of little use and new techniques had to be derived.

Gypsum and arsenates were leached using sodium carbonate. Calcium carbonate that formed was leached with dilute hydrochloric acid solution. Although conditions were not optimised, the leach seemed fairly selective. Residual sulphides including pyrite were destroyed using an ambient temperature chlorination at a high oxidation potential. This leach, however, destroyed less than ten per cent of the sulphides present and it was probably due to sulphides occluded by ferrites and haematite.

Ferrites were leached using a high temperature dilute HCl leach. Ferrites formed at the interface of pyrite and base metal sulphides. Iron has a higher affinity for oxygen than other base metal sulphides and, therefore, the base metals tended to be starved of oxygen during the roasting process. At the interface, iron diffused into the base metal sulphides and a layer of ferrites was formed. Unreacted base metal sulphide minerals were encapsulated inside this layer and possibly free gold too.

**Diagnostic leaching as an analatycal tool for plant problems**

Diagnostic leaching can also be used as the first step in the investigation of a plant that is experiencing problems. A flotation plant in the Free State was experiencing the problem of an
Increasing feed head grade to the plant while the recovery was decreasing. Feed to the plant, flotation concentrate and tails were analysed using diagnostic leaching to determine the deportment of gold. The results indicated that the decrease in recovery was not a metallurgical problem at the plant but due to a change in the deportment of gold in the feed to the flotation plant. The efficiency of gold flotation recovery from the sulphide fraction is very high, but only 50 per cent of the cyanidable gold was floated. This was probably due to the fact that about 85 per cent of the cyanidable gold in the feed was present as precipitated gold, (as mentioned before), and therefore not amenable to flotation. In fact, the flotation recovery of cyanidable gold was relatively high and indicated that the gold must have precipitated preferentially on sulphides. However, this was not likely since the surface of the sulphides would be reducing. Increased gold recovery at this Free State flotation plant would only be possible by cyanidation of the flotation tailings where it would be possible to extract up to 50 per cent of the gold. This analysis and various others were so successful that diagnostic leaching is currently being used routinely for various flotation plants throughout South Africa to analyse problems.

Increasing the selectivity of a diagnostic leach

Until recently the selectivity of the various diagnostic leaches had only been estimated and not quantified. This, however, had never affected the validity of the conclusions drawn. In an attempt to examine how selective an oxidising acid pre-treatment is, a sulphide concentrate was used and subjected to a series of sulphuric acid leaches at various Eh values, controlled by the addition of hydrogen peroxide. Lorenzen (1992) explained this selective leaching of base metal sulphides in sulphuric acid in more detail. The conclusions drawn from this testwork are:

- Pyrite is leached above 400 mV (vs SCE), based on the sulphide and iron extractions. About 35 per cent of the pyrite has been leached at 600 mV and the reaction appears to stop. More than 99 per cent of the pyrite is however leached using nitric acid as oxidant.

- There is a steep increase in gold extraction when increasing the acid pre-treatment potential from 300 to 400 mV. Above 400 mV there is no significant increase in gold extraction, and therefore 400 mV appears to be the optimum potential for liberating gold from sulphide concentrates containing base metal sulphides in an oxidising sulphate medium at 80°C. Below 300 mV basically all the uranium is leached and therefore also the gold associated with uranium.

- No significant increase in gold extraction occurs between 400 and 600 mV. This suggests that passivation of the gold by sulphides is not the main reason, but rather the fact that pyrite is actually barren. If this is the case, then the steep increase in gold extraction between 300 and 400 mV is due to gold released by oxidation of the base metal sulphides. About 70 per cent of the base metal sulphides and roughly ten per cent of the pyrite were leached when the potential was increased from 300 to 400 mV. This corresponds to a step increase in the locked gold extraction of about 20 per cent. As the potential increases to 600 mV a further 25 per cent of the pyrite and roughly 15 per cent of the base metals are leached and yet there is no further increase in gold extraction.

- If a shrinking-core model of the sulphide particles being leached is envisaged, then the first ten per cent of the particles leached was really only a small surface layer ("the icing on the cake") the decrease in radius varies with the cube root of the volume or mass leached (for a 100 micrometer particle, ten per cent of the mass equals one micrometer thickness). This indicates that the gold associated with the pyrite was exposed on the surface but was passivated when initially leached by cyanide. It is only made available for cyanidation after oxidation of the sulphide surface.

- Base metal sulphides should be leached in oxidising sulphuric acid conditions and yet there is no significant increase in base metal extractions until the labile pyrite begins to dissolve. When the labile pyrite extraction levels off, then generally, the base metal extraction levels off which suggests that the base metals are either associated with the pyrite or that the base metal sulphides themselves are partially locked in pyrite. This would then have to be confirmed by a mineralogical analysis.

Ferric oxidation in a sulphate medium was also used in an attempt to eliminate arsenopyrite which was believed to contain most of the gold present in an European flotation concentrate sample. The leach was unselective in leaching arsenopyrite and pyrite. Gold extraction by cyanidation after this pre-treatment was poor. It is possible that passivation of the surface of the sulphides by the formation of sulphur, a traditional problem in leaching base metals from their sulphides, was responsible. The leach was therefore repeated, but interstage washing with carbon disulphide was removed to use the sulphur formed. The results showed that almost total extraction of gold was possible after this treatment, with total destruction of sulphides. The implication of this work is that plant scale oxidation of refractory sulphides such as pyrite and copper sulphides is possible as a viable alternative to roasting.

This interstage washing led to the development of interstage cyanide and acid washes to destroy cyanide and iron complexes. Lorenzen and Van Deventer (1992) described this phenomenon in detail. Oxalic acid washes can also be used to destroy oxide coatings on the liberated gold surfaces after acid pre-treatment leaches.

CONCLUSIONS

From the above mentioned it is evident that diagnostic leaching is a useful tool for the metallurgist, chemist or scientist to evaluate and determine the gold deportment in refractory gold ores. He can use this information to design metallurgical flowsheets, solve problems occurring at an existing plant and/or evaluate the effect of selectivity of various reagents on a plant.

The case studies have shown clearly that the technique can cope with any plant problem caused by:

1. change in operation,
2. change in the mineralogy and/or gold deportment in the feed or
3. a combination of the above mentioned. In can also deal with new ore deposits, refractory minerals, calcines, clinker, sulphide concentrates, etc. The method is flexible and depends on the sample to be analysed. The data obtained from a modest amount of testwork enable the derivation of possible process routes for treatment of the ore-body/refractory minerals for gold recovery. The routes chosen depend on such factors as the economics of the project, location of the ore-body/refractory minerals and relative amount of the latter.

The technique can thus be used in the laboratory by reagent manufacturers and distributors, plant personnel and researchers. New types and suites of leaches and washes can still be devised for the study of different ores and concentrates.

REFERENCES


INTERNATIONAL CONGRESS ON APPLIED MINERALOGY

ICAM'93

MINERALOGY IN THE SERVICE OF MANKIND

PROGRAMME AND ABSTRACTS

The liberation of any ore are intimately related to the mineralogical texture. Grinding is used to liberate minerals prior to further upgrading by subsequent ore dressing operations. It is the interaction between the comminution and textural properties of an ore that determines the efficiency of the liberation process and thus determines the technological limitations on the efficiency of separation in any ore dressing process. The efficiency of the concentrating procedure is very much dependent on the degree of liberation of the valuable minerals that is achieved, and the ore must be sufficiently finely ground to permit the production of a concentrate of sufficiently high grade to be satisfactory for various finishing operations.

In this paper, leaching experimental results were used with the liberation model of King to predict the liberation of gold from complex ores. Diagnostic leaching results were used with the liberation model, as the results from a diagnostic leaching procedure explain the deportment of gold in the various minerals in a complex ore. The free or leachable gold in an ore obtained from such an experiment would be similar to the gold liberated by crushing and/or milling. The leachable gold in each size fraction of an ore can be determined by diagnostic leaching, before and after milling. Thus, it would be very useful if the leachable (liberated) gold in a specific unmilled ore can be used to predict leachable (liberated) gold in the milled ore of that specific ore. If this can be achieved, then the leachable gold in each size fraction of the unmilled and milled ore can be predicted by the model.

An explicit solution to King's liberation model was modified in order to predict the leachable gold in different size fractions on the basis of data gathered for the unmilled ore. In this model, \( J_m \) is the mean linear intercept length for gold in the ore, and the term \( A \cdot \exp(1/D) \) indicates the fraction of leachable gold which cannot be attributed directly to liberation:

\[
L_m(D) = \frac{2 \mu_m^2}{D} \left[ (\mu_m + D) \exp(-D/\mu_m) + [(A \cdot \exp(1/D))] \right]
\]

It was found that this model gives reasonable predictions of the leachable gold for milled ore when the leachable gold in the unmilled ore is known.

THE KING LIBERATION MODEL

King \(^{1,2}\) developed and tested a model of liberation. To solve it, it required two intercept length distributions, that of the mineral in unbroken rock and in size fractions, followed by numerical integration. King observed that an explicit solution could be calibrated with a single parameter, the mean intercept length in the unbroken rock, \( \mu_m \). In the King model, the fractional degree of liberation \( (L_m(D)) \) of mineral \( m \) for a particle size \( D \), is given by:

\[
L_m(D) = 1 - D/(2\mu_m + D)(1 - \exp(-2\mu_m + D/\mu_m))
\]

TESTING THE KING LIBERATION MODEL ON DIAGNOSTIC LEACHING RESULTS

As mentioned before, the first step in the design of a process to treat a possible economic precious metal deposit should be an examination of the mineralogy of the ore. Diagnostic leaching was designed to open up the field of mineralogical analysis to the metallurgist. In order to determine with which minerals the desired precious metal is associated, a specific
mineral is first eliminated using a selective oxidative leach, and cyanidation is used to extract the precious metal liberated by the destruction of this mineral. The precious metal extraction can be measured in solution to give a fairly accurate record of the amount of the precious metal associated with that mineral. Furthermore, the residue from this first step can be subjected to another selective acid leach, and the process repeated. The procedure can be varied to suit the mineralogy of the matrix material. At the end of a diagnostic leach procedure, the metallurgist is left with a complete record of the deportment of the precious metal.

King's model as described was tested on experimental results, and the results predicted by the model for milled and unmilled ore were compared to the experimental results. Diagnostic leaching results from two different ores were used: i.e. unmilled FSG and Harties ore as well as milled (to 70% - 75 μm) ore of these ore bodies. The mean linear intercept length of the mineral in the ore (μm) is not known. Also, it is not possible to determine any distribution of intercept lengths in gold ores using SEM. Information on the ores available in this study is the leachable gold in each size fraction as well as the overall leachable gold in the total ore at various stages of milling (and unmilled ore). Equation (1) was fitted against experimental data obtained from the leaching of gold from each size fraction in the unmilled ore of two ore bodies mentioned, and was found to entirely underestimate the amount of free leachable gold in each particle size fraction. A modified version of equation (1) which gives a reasonable prediction of the experimental results is presented in Figures 1 and 2 as well as equation (2) below:

$$L(D) = 2 \mu_m / D^2 \left[ \mu_m - (\mu_m + D) \exp(-D/\mu_m) + [A \exp(1/D)] \right]$$

where:

- $L(D)$ = fraction of leachable gold for particle size (D)
- $[A \exp(1/D)]$ = fraction of leachable gold for particle size (D) not related to liberation,
- $A$ = empirical constant for the specific ore
- $D$ = geometric mean of the screen interval (μm)
- $\mu_m$ = mean linear intercept length of gold in the ore (μm)

No provision is made in equation (1) for the amount of leachable gold in the various particle size fractions that is not related to the liberation of gold due to comminution. In each particle size fraction there is a certain amount of gold available to cyanidation (gold in fractures and pores, etc) which is not accounted for by the liberation model of King (equation 1). The second term in equation (2) was thus added to equation (1) to compensate for the fraction of leachable gold for each particle size which cannot be attributed directly to liberation. This implies that a certain fraction of gold in the ore is leachable even for coarse lumps of unmilled ore, such as being practised in some heap leaching operations. The empirical constant for a specific ore, A and the mean linear intercept length of the gold in the ore, $\mu_m$ were estimated for each of the unmilled ores (FSG and Harties) using equation (2). The results are presented in Table 1. $\mu_m$ was found to be 17 μm for FSG ore and 38 μm for Harties ore. There was also a corresponding increase in the value of A with an increase in $\mu_m$ which is probably related to the size of the gold particles in each particle size fraction. The larger the gold particles in an ore, the more exposed such gold will probably be to leaching, even without further liberation. The second term in equation (2) increases with a decrease in particle size fraction, which agrees with the experimental results obtained for the various ores tested.
A general decrease in $L_g (D)$ with increasing particle size, as expected, is evident from Figures 1 and 2 for the unmilled ore. The solid lines on the graphs show the liberation predicted by equation (2) (with $\mu_m$ and $A$ estimated by equation (2). The correct trend is predicted in both cases and the model as described in equation (2) gives reasonable predictions to about 50 $\mu$m, whereafter it slightly overpredicts.

The ore (FSG and Harties) was milled down to 70% - 75 $\mu$m and the samples were screened into particle size fractions. A diagnostic leaching procedure was performed on each size fraction. The results are presented in Figures 3 and 4.

Equation (2) was then used to estimate the gold liberated ($L_g (D)$ for each particle size. The mean linear intercept lengths of the gold in the milled ore as well as the empirical constants were kept constant for the specific ore ($\mu_m$ and $A$ as estimated from equation 2). The predictions are shown by the solid lines in Figures 3 and 4.

The modified King's model for ores (equations 2) as shown in Figures 1 to 4 gives reasonable predictions. For the present data the predicted $L_g (D)$ and $\mu_m$ using equation (2) tend to slightly underestimate for particle size fractions smaller than 125 $\mu$m and slightly overestimate for particle size fractions larger than 125 $\mu$m. It must be taken into account that the mineralogy of the ore was not taken into account in the model predictions, although this was shown in previous chapters to have a pronounced effect. Nevertheless, the model gives reasonable predictions of the leachable gold fraction for milled ore when the leachable gold in the unmilled ore is known. It must be taken into account that this is only a preliminary model and that some refinement is still needed before it can be used accurately for predicting leachable gold. However, there are currently no models available for the prediction of leachable gold as a function of particle size.

Nevertheless, the model predicts that high leachable gold values will require a grinding size of 70% - 75 $\mu$m for FSG and Harties ores. This agrees with liberation data and grinding studies on the various ores [3].

### TABLE 1: ESTIMATES OF $\mu_m$

<table>
<thead>
<tr>
<th>ORE</th>
<th>A</th>
<th>$\mu_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSG</td>
<td>0.172</td>
<td>17</td>
</tr>
<tr>
<td>Harties</td>
<td>0.231</td>
<td>38</td>
</tr>
</tbody>
</table>

### REFERENCES


FIGURE 1: Leachable gold as a function of particle size for unmilled FSG ore with application of Equation (2).

FIGURE 2: Leachable gold as a function of particle size for unmilled Harties ore with application of Equation (2).

FIGURE 3: Leachable gold as a function of particle size for milled FSG ore with application of Equation (2).

FIGURE 4: Leachable gold as a function of particle size for milled Harties ore with application of Equation (2).