

# **CONTRIBUTIONS TO AN IMPROVED UNDERSTANDING OF THE FLOTATION PROCESS**

**BY**

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## 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 generally as the originator of the work unless otherwise explicitly stated. Where it is claimed that the primary intellectual origin of such work is not duly recognized the author withdraws his rights. 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.

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**C T O'Connor**

31 August 2005

The author wishes to dedicate this thesis to his wife, Nanette, in appreciation for her continuous support in this endeavour .

He also wishes to thank his promoter, Professor Leon Lorenzen, for his support and advice in the submission of this dissertation.

## ABSTRACT

This dissertation covers research carried out over the past 25 years in the area of flotation. Flotation is one of the most widely used processes in the beneficiation of minerals. The process is characterized by a number of important sub-processes each with their own set of critical variables. These include:

- The pulp phase which is influenced by variables such as pH, Eh, the nature of the chemical reagents used, the chemical state of the surface of the ore particles, etc.
- The reactor in which the process occurs, viz. the flotation cell, which is influenced by factors such as aspect ratio, degree of agitation, mechanical design criteria, energy input, aeration processes, etc.
- The froth phase which is arguably the heart of the process and probably the least well understood but which is influenced by factors such as size and shape of the solid particles in the froth, the nature of the surfactant used, the aeration rate, the water recovery rate, the froth depth, etc.

Research carried out over this period has focused on all three of these sub-processes in different ways. The research has aimed ultimately at developing a better understanding of the effect of various parameters on case sub-process and then integrating this understanding with that of the other sub-processes with the aim of improving our overall understanding of the overall flotation process.

The chemistry of the flotation process is a function of the extent to which various reagents are able to improve the recovery of the desired mineral while depressing the recovery of the undesirable gangue minerals. The research has focused generally on the recovery of sulphide minerals. The minerals studied have changed over the years depending on the industrial interest at any given time. Hence in the early 1980s the focus was on pyrite which was recovered with a view to producing sulphuric acid for downstream leaching processes. Later, with the increased interest in the recovery of platinum group minerals (PGM), the focus changed to PGM-bearing sulphides. In all these cases however the common need is to develop the

proper chemical environment which will facilitate the optimal use of chemical reagents. This requires a fundamental understanding of the solid-liquid-gas phase interactions in the pulp phase. Factors such as the pH of the pulp, which causes the surface charge of the particles to change while at the same time influencing the nature of the various metal (Cu, Ca, etc) hydroxy species formed in the aqueous phase, Eh which influences the nature of the chemical reactions occurring, the surface oxidation state of the mineral particles, are but some examples of such parameters. For example, the pH – Eh effect on the surface chemistry is of critical importance. Methods used in such studies have included adsorption studies, the use of instrumental techniques such as ToF-SIMS, EDAX, zeta potential measurements, etc. An important class of reagent is depressants which are both synthetic and modified natural polysaccharides or polyacrylamides. This dissertation will also describe how other separate research by the author involving the understanding of an important class of aluminosilicates, viz. zeolites, has contributed serendipitously to this aspect of flotation research.

Flotation cells have increased in size by at least an order of magnitude over the past 20 years and this has resulted in the need to develop a better understanding of the hydrodynamic characteristics of these cells. The need to ensure that an appropriate amount of energy is transferred to the contents of the cell so as to ensure that there is sufficient agitation to keep all solids suspended as well as to create properly sized bubbles has opened up an important area of research. The dissertation will present details of research carried out using both small scale cells, such as a Rushton Turbine, as well as the use of isotopic tracers to characterize both microturbulence as well as the macro-mixing characteristics of large industrial cells. The use of CFD by one of the author's colleagues has become an important methodology in this regard. In particular, in the early 1990s, column cells became very popular and the dissertation will describe research work that was carried out to model the residence time distribution properties of the solid and liquid phases in such cells.

It is generally accepted that one of the most complex challenges in flotation is the need to gain a better understanding of the froth phase. The dissertation will describe research carried out to model the froth phase and will also refer to work carried out by colleagues developing methods to analyze images of the froth surface with a view

to quantifying the behaviour of the froth and understanding the factors which most affect its characteristics. Ultimately, it may be possible to use these froth related parameters both to diagnose the efficiency of the overall process as well as to control it.

The author wishes to acknowledge that in all of the above research he has been closely assisted by many research colleagues, students, assistants and industrial collaborators whose contributions have been of critical importance. These contributions are indicated and recognized, hopefully without omission, where appropriate.

## OPSOMMING

Hierdie verhandeling doen verslag van navorsing oor die afgelope 25 jaar binne die area van flotasië. Flotasië is een van die mees gebruikte prosesse in die verwerking van minerale. Die proses word gekenmerk deur 'n aantal sub-prosesse, elkeen met hulle eie stel kritiese variabiliteite. Dit sluit in:

- \* Die pulffase wat beïnvloed word deur variabele soos pH, Eh, die aard van die chemiese reagente wat gebruik is, die chemiese laag van die oppervlak van die grondpartikels, ens.
- \* die reaktor waarbinne die proses voorkom, naamlik die flotasië-sel, word weer beïnvloed deur faktore soos die aspek-ratio, die graad van menging, meganiese ontwerp-maatstawwe, energie-inset, (aeration) prosesse, ens.
- \* Die skuim-fase wat hoogs waarskynlik die hart van die proses verteenwoordig en moontlik die minste verstaan word, word beïnvloed deur faktore soos die grootte en vorm van die soliede partikels in die skuim, die aard van die (surfactant) wat gebruik is, die standaard van die (aeration), die (recovery rate) van die water, die diepte van die skuim, ens.

Die navorsing tydens hierdie periode het op verskillende wyses gefokus op hierdie sub-prosesse. Die uiteindelijke doel van die navorsing was om 'n beter begrip te ontwikkel van die effek van verskeie parameters in 'n bepaalde sub-proses en om daarna hierdie begrip te integreer met die ander sub-prosesse met die verdere doel om die algehele begrip van die flotasië-proses te verruim.

Die chemiese werking van die flotasië-proses is 'n funksie van die moontlikhede waartoe die onderskeie reagente in staat is om die (recovery) van die gewenste mineraal te verbeter terwyl dit terselfdertyd die herstel van die ongewenste minerale onderdruk. Oor die algemeen het die navorsing gekonsentreer op die herstel van sulfiede minerale. Die bestudeerde minerale het oor die jare verander, afhangende van die industriële belangstelling. So was die fokus in die vroeë tagtiger-jare op piriet met die oog op die produksie van sulfiedsuur vir latere verblykingsprosesse. Later, tydens die toenemende belangstelling in die herstel van die platinum mineraalgroep, het die fokus oorgegaan na die PMG-draende sulfiedes. Die

algemene behoefte egter, in al hierdie gevalle, was steeds om 'n geskikte chemiese omgewing te ontwikkel waarin die optimale gebruik van die chemiese reagente gehuisves kon word. Dit vereis 'n grondige verstaan van die interaksies van die soliede, likiede, en gas-fases in die pulp-fase. Voorbeelde van sulke parameters is faktore soos die pH van die pulp wat oppervlak-veranderinge meebring by die partikels terwyl dit terselfdertyd die aard van die verskeie metaal (Cu, Ca, ens.) hidroxied spesies vorm tydens die vloeibare fase; Eh wat die aard van die chemiese reaksies beïnvloed, en die oppervlak-oksidasie van die minerale partikels. Ter voorbeeld, die effek van pH - Eh op oppervlak-chemie is van die hoogste belang. Die metodes wat gebruik is in studies van hierdie aard, sluit in adsorpsie studies, die gebruik van instrumentele tegnieke soos ToF-SIMS, EDAX, zeta potensiële meting, ens. 'n Belangrike kategorie van reagente is depressante wat sowel sintetiese as gemodifiseerde polisacchariede of poliacrylamiede is. Die verhandeling dien ook as beskrywing van verdere navorsing deur die outeur wat ondersteunend bygedra het tot hierdie aspek van flotasiënavorsing, bv. 'n begrip van die belangrike kategorie van aluminosilicate, naamlik zeoliete.

Oor die afgelope 20 jaar het flotasië-selle in verbysterende mate toegeneem in grootte en dit het gelei tot die noodsaak vir die ontwikkeling van 'n beter begrip van die hidrodinamiek karakteristieke van hierdie selle. Die nodigheid om seker te maak dat 'n gepaste hoeveelheid energie oorgedra word na die inhoud van die sel sodat voldoende weerstand ontwikkel om die soliede elemente uit te hou en ook om genoeg seepbelle van voldoende grootte te skep, skep 'n verdere terrein vir navorsing. Die verhandeling beskryf besonderhede oor die navorsing wat gedoen is deur middel van sowel klein-skaal selle soos 'n Rushton Turbine, as die gebruik van isotopiese verkenner om eensyds mikro-turbulensie en andersyds die makro-vermengende karakteristieke van groot industriële selle te bepaal. Die gebruik van CFD by 'n kollega van die skrywer het 'n belangrike deel van die metodologie geword. Veral in die vroeë 90-er jare het kolom-selle baie gewild geword en die verhandeling doen ook verslag van die navorsingswerk wat gedoen is om die (residence time distribution properties) van die soliede en likiede fases in elke sel te beskryf binne 'n model.

Dit word algemeen aanvaar dat een van die mees komplekse uitdagings binne die terrein van flotasiënavorsing daarom gaan om 'n beter begrip van die skuim-fase te ontwikkel. Die verhandeling beskryf ook navorsing wat die gemik is om die skuim-fase te modelleer en verwys na die werk van ander navorsers met betrekking tot metodes in die analise van



voorstellings van die skuim-oppervlak met die oog daarop dat dit gebruik kan word vir die kwantifisering van die gedragpatroon van die skuim en begrip van die faktore wat die karakteristieke daarvan bepaal. Uiteindelik mag dit daartoe lei dat hierdie skuim-verwante parameters gebruik sou kan word vir sowel die diagnose van die doeltreffendheid van die proses in die geheel as die maniere om dit te kontroleer.

Die skrywer wil graag erkenning gee aan al die kollegas, studente, assistente en medewerkers uit die industrie wie se bydraes van die allergrootste belang was. Hierdie bydraes word erken en aangetoon waar ter sake. Hopelik is daar geen weglatings nie.

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1. Mr. R C Dunne and Dr I J Corrans of the former National Institute of Metallurgy who assisted the author in beginning this research.
2. Professor J-P Franzidis, an early collaborator, who joined the author's group in 1983 and with whom the author continues to collaborate today. Professor Franzidis joined the JKMRC in 1998 but he and his research colleagues there continue to collaborate very closely with the author's MPRU at the University of Cape Town.
3. Professor J S J van Deventer, Professor L Lorenzen and their colleagues at the University of Stellenbosch with whom the author has had a very close collaboration for 25 years.
4. The author's colleagues in the MPRU especially:
  - Dr D A Deglon, Deputy Director of the MPRU, who leads the Cell Design and CFD Group
  - Dr D J Bradshaw, who leads the Reagent Chemistry and Froth Imaging Group
  - Mr. M C Harris, who leads the Flotation Simulation and Modeling Group as well as the MPRU's involvement in the P9 Project
  - Dr M Powell who leads the Comminution Group.
7. Messrs E W Randall, A M Barker and R Senekal each of whom made significant contributions in the design of much of the equipment used by the

author and his co-workers over the years and made many key measurements possible.

8. The author's research students and other collaborators for their inspiring and creative contributions towards this research. Special mention should be made of:

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## GLOSSARY OF TERMS

**MPRU**: The Mineral Processing Research Unit is based in the Department of Chemical Engineering at the University of Cape Town. Following the growth of the activity in the 1980s the University granted Unit status to the research group in the early 1990s. Today the MPRU consists of about 20 full-time research staff and usually about 30-40 post-graduate students. The MPRU is jointly led by the author and his colleagues Dr D A Deglon (Deputy Director; Cell Modeling) Dr D J Bradshaw (Reagent Chemistry) Mr M C Harris (Modeling and Simulation of Flotation Circuits) and Dr M A Powell (Comminution). It is expected that the Unit will be granted Centre status during 2006.

**JKMRC**: The Julius Kruttschnitt Mineral Research Centre at the University of Queensland. This world famous Centre invited the MPRU to collaborate with it in 1996 as a research provider for the Amira P9 Project. This remains an on-going and strengthening collaboration.

**P9 Project**: This Project established in 1962 at the JKMRC is managed by the Australian Mineral Industry Research Association (AMIRA) and provides pre-competitive joint venture research to about 35 companies world-wide. The primary research provider is the JKMRC and the MPRU is retained by the JKMRC as a subsidiary research provider.

## **FORMAT OF DISSERTATION**

- Chapters 1 and 2, respectively, provide the Introduction to the Dissertation and describe the body of research developed under the guidance and leadership of the author over the past 25 years.
- Chapter 3 lists the publications referred to in the Introduction and each of the Sections of Chapter 2. The numbering of publications is the same as that used in Appendix A.
- Appendix A lists all the publications relevant to this Dissertation in ascending numerical order. Copies of all these publications are presented in the same numerical order.

# INDEX

<b>Declaration</b>	i
<b>Abstract</b>	iii
<b>Acknowledgements</b>	ix
<b>Glossary of Terms</b>	xi
<b>Format of Dissertation</b>	xii
<b>1. Introduction</b>	<b>1</b>
<b>2. Background to Publications submitted</b>	<b>4</b>
2.1 The Role of Reagents in Flotation	4
2.2 Flotation of different ore types	7
2.3 Effect of Physical Parameters on the Flotation Process	10
2.4 Characterization of Flotation Cells	12
2.5 Modeling and Simulation Studies	13
2.6 Measurement Techniques	14
2.7 Serendipitous and Miscellaneous Contributions	15
<b>3. List of Publications included with this submission and referred to in Chapters 1 and 2</b>	<b>18</b>
3.1 Publications referred to in Chapter 1	19
3.2 Publications on the Role of Reagents in Flotation	20
3.3 Publications on the Flotation of different ore types	23
3.4 Publications on the Effect of Physical Parameters on the Flotation Process	25
3.5 Publications on the Characterization of Flotation Cells	27
3.6 Publications on the Modeling and Simulation Studies	29
3.7 Publications on the Measurement Techniques	31
3.8 Publications on the Serendipitous and Miscellaneous Contributions	33
<b>Appendix A</b> List of Publications included in this submission	<b>35</b>
<b>Appendix B</b> List of Masters and Doctoral Students supervised to date	<b>44</b>
<b>Appendix C</b> List of Publications not included with this submission	<b>48</b>

# 1. INTRODUCTION

In the late 1970s and early 1980s there were approximately 25 pyrite flotation plants operating in South Africa. These were mainly located in the gold mining areas of the then Orange Free State and the feed material was the gangue from the slimes dams which had emanated from the earlier workings in the 1950s and 1960s. The objective was to produce a concentrate for roasting and the ultimate production of sulphuric acid. The gold content of the feed from the slimes dams was approximately 0.5g/t and the recovery of gold was usually at best 50%, this gold production essentially covering the cost of the flotation operation. In late 1979 the author was invited simultaneously by the then NIM (National Institute for Metallurgy), now Mintek, and the Anglo-American Research Laboratories (AARL) to begin research on two aspects of pyrite flotation, viz. the effect of temperature on the flotation of pyrite [29, 42] and investigating the poor recovery of the high gold-bearing mineral thucolite (also known as kerogen) during the flotation of pyrite [4]. At that time there had been no experience in flotation in the Chemical Engineering Department at the University of Cape Town and only minimal research in the area of mineral processing, focusing mainly on water treatment, and so this was entering an entirely new research territory.

Regarding the effect of temperature, it had been long noticed that the recoveries of pyrite in the flotation plants in the Free State gold fields decreased considerably during the winter months. The outcome of this work [2; MSc. dissertation: A. de Sousa] showed clearly that the major effect of the lower temperatures was on the behaviour of the froth. However, it later transpired that an equivalent effect of the lower winter temperatures was on the behaviour of the thickeners. Regarding the loss of gold through the poor recovery of kerogen, which originated in the gold-rich carbon leader and often contained up to 1000g/t of gold, it had been hypothesized that, as a result of the use of guar depressants to reduce the recovery to the concentrate of the talcaceous gangue minerals, such as pyrophyllite, kerogen particles were being locked inside pyrophyllite aggregates and thus reporting to the tailings of the flotation plants. This project showed that by the careful use of appropriate inorganic dispersants, it was possible to increase the recovery of gold

without unduly affecting the grades of the concentrate [1; MSc. dissertation: A van Zyl].

A chemical engineering approach to flotation proved also at the same time to be beneficial. In process engineering, one of the most important factors influencing the kinetics of a process is temperature and thus this first project immediately prompted the importance of modeling the flotation process. It so happened that in 1980 the late Professor R Klimpel, who was a consultant to Dow in the United States and also a Professor at Penn State University, had just published his well-known Klimpel model and, during a visit to South Africa, the author had the opportunity to meet him and to discuss the use of his model in flotation. This also coincided with the early development of the use of PCs and so this gave us the early opportunity to carry out some useful modeling of our flotation results. I am indebted to Professor Brian Paddon for valuable assistance and advice at that time.

At that time we were also one of the first groups to use the Leeds flotation cell which was a useful machine for controlled batch flotation experiments. Early on it occurred that the kinetics were not reproducible when experimenters reverted randomly to a prescribed set of conditions. After much investigation it transpired that with time the rotor-stator gap was increasing due to wear and this we believed was resulting in the formation of larger bubble sizes which significantly changed the kinetics.

These two early projects, as well as exposure to the Klimpel model and the Leeds flotation cell observation proved to be fortuitous in establishing in the early days of the flotation research an appreciation of the importance of both chemical and physical effects on flotation as well as of appreciating the synergistic influences of reagents in the pulp. Specifically therefore from the early days it became clear that in flotation research it was important:

- to distinguish the ore type being investigated and also the importance of managing the behaviour of gangue minerals in flotation;
- to appreciate the interaction between collector type and depressant type;
- to understand the difference between the role of polysaccharides as both depressants and dispersants;



- to value the use of good kinetic models in analyzing the flotation process;
- to appreciate how important it was to carefully control or monitor the physical conditions pertaining when a set of experiments were carried out.
- to appreciate the effect of cell design and bubble size on the flotation process.

As a result of this early foray into flotation research, the development of the activities of the flotation research programme rapidly developed a particular focus which will give the structure to this dissertation. These are:

1. The role of reagents and the interactions between the various reagents used in the flotation process, viz. collectors, modifiers, depressants and the role of the various ionic species in the pulp.
2. The importance of understanding the ore type used in the flotation process and its properties at the pH and Eh of the pulp during the process. Although much of the early work was done on pyrite flotation for reasons explained above, later on the major focus moved to platinum group minerals which are a mixture of sulphides, oxides, tellurides, arsenides, etc. The behaviour of these different minerals at various pH's is quite different.
3. The role of physical parameters in the flotation process. These include factors such as bubble size, pulp - froth phase interactions, the hydrodynamic characteristics of the cell, etc.
4. The type and design of the flotation cell used. Although the early work focused on the use of laboratory-size agitated/mechanical cells, later on much research was carried out on the use of column flotation cells which opened up opportunities for using a classical chemical reactor-based modeling approach. This ultimately led to a greater focus on modeling the entire process.

## **2. BACKGROUND TO PUBLICATIONS SUBMITTED**

### **2.1 THE ROLE OF REAGENTS IN FLOTATION**

The most important class of collectors for sulphide minerals are thiol collectors. In the pyrite flotation process the most commonly used collector was sodium-mercaptobenzothiazole (SMBT). In the early 1980s there was considerable interest in the gold mining area of the former Eastern Transvaal, where there was a significant occurrence of arsenopyrite, to seek methods to selectively recover the arsenopyrite into the concentrate. This is unusual since generally methods are used to depress the arsenopyrite in such instances. However in this case the arsenopyrite was particularly rich in gold and the plan was to divert the arsenopyrite-rich concentrate to a bacterial leaching process rather than the usual environmentally complex roasting process. The former Gencor had at the time commissioned their world-first bacterial leaching plant in that area at Fairview Mine (the so-called Biox Process). Considerable success was achieved in using a mixture of dithiophosphates and dithiocarbamates in separating the arsenopyrite into the concentrate from the pyrite [5]. Further work continued at that time on the use of dithiocarbamates on the flotation of pyrite [6] and this eventually became the topic of a PhD dissertation of Dr D J Bradshaw now a Chief Research Officer and Group Leader in the Minerals Processing Research Unit. Once significant work had been carried out using dithiocarbamates it became apparent that it is important to carefully control the use of mixtures of dithiocarbamates with other thiol collectors [8,9,10, 22,23, 36] [37; PhD dissertation: D J Bradshaw]. In carrying out this work it became very clear that it was necessary to gain a greater understanding of the relative adsorption characteristics of these various collectors. Considerable interest was developed during that period on studying the adsorption of collectors on minerals including the use of micro-calorimetry [8, 9]. This led to a greater appreciation of the importance of determining the relative heats of adsorption of thiol collectors onto sulphide minerals. It was hypothesized that given the energetically heterogeneous nature of the surface of a sulphide mineral strong collectors would be preferentially adsorbed onto the high energy sites and that the weakly adsorbing collector would then form either secondary pseudo-layers on the anchored strong collector or otherwise adsorb on the weaker sites and be less effective in enhancing

hydrophobicity. This multi-layer phenomenon was important later on in work carried out looking at bubble loading as a function of dosages of collectors.

As indicated in the introduction to this dissertation, the importance of understanding the interaction of reagents used for the collection of the valuable minerals, typically sulphides in the present instance, with the gangue mineral became increasingly more important. The focus on the use of depressants enjoyed much attention. In fact the economic influence of the need to use depressants such as guar gum arguably led to the demise of the practice of pyrite flotation in South Africa due largely to cost of the depressant being greater than the value of the gold recovered in the process. Notwithstanding the use of other alternatives such as carboxymethylcellulose (CMC) [7; MSc. dissertation: R B Duncan], which was at the time a significant by-product from the pharmaceutical industry, managing the cost of depressants remains a key issue today. Reference has already been made to the kerogen study carried out with the aim of optimizing the relative depressing and dispersing effects of reagents [4]. This gave rise to studies of various dispersant types and also opened up a major area of research in the MPRU in the late 1990s by one of the author's colleagues, Dr D J Bradshaw, who founded the Depressant Research Facility. Although the author has only played a minor role in this activity he has recently co-authored two papers with Professor J S Laskowski, reviewing the properties and applications of various types of depressant and dispersant, both organic and inorganic, in mineral processing [17, 18].

Lately, Dr Bradshaw has also shown how the interpretation of the role of a depressant may best be found in the secondary effect it has on the behaviour of the froth phase as a result of the fact that the nature of the particles reporting to the froth phase may change significantly following the use of a depressant [16,28].

It seems to the author that our understanding of the effect which ions present in the pulp have on the behaviour of various reagents being used will be a fertile area of research in the future. The author in a recent publication [15] has shown how the role of copper ions as gangue mineral activators may possibly be understood by analyzing the chemistry of the aqueous pulp phase. Questions to be addressed in determining the effect of reagents should include analyzing the solution equilibria of

the various species. For example this work showed what major role  $\text{Fe}^{3+}$  ions can have on the concentration of other species in a pulp.

Over the last decade the major focus in the reagent chemistry research has been on platinum group minerals. In particular, one of the major challenges in this process is to minimize the recovery of gangue minerals such as pyroxene and feldspar into the concentrate since for various reasons this will adversely affect the downstream pyrometallurgical processes. In studies of the effect of the various ions in the process water on the overall grades and recoveries [11-15; 56; PhD dissertation: V Malysiak; 57; MSc. dissertation: N J Shackleton] it was shown that these can have a major effect on the relative floatability of a gangue mineral such as pyroxene relative to the valuable such as pentlandite. This has led to a major research activity investigating methods to overcome the effect of the inadvertent activation of the gangue minerals by modifiers such as copper sulphate, which are extensively used in the flotation process to improve the recovery of the sulphide minerals. As referred to in the previous paragraph, recently significant progress has been made in developing a greater understanding of how a suitable modification of the chemistry of the aqueous phase can resolve problems caused by this inadvertent activation of the gangue mineral. Specifically, for example, it was shown that the addition of various amines to the reagent mixture resulted in the inadvertent activation of pyroxene being significantly reduced. This is possibly due to the way in which the amines modify the solution equilibria and the concentrations of various ions in the process. Specifically for example the amines can cause the concentration of  $\text{Cu}^{2+}$  in solution to decrease thus resulting in the re-solubilisation of the weakly bound copper hydroxide species present on the surface of the siliceous gangue mineral.

It may be noted that in the early 1980s, research was carried out investigating the interactions of guar-based depressants on the adsorption of oleates in the flotation of apatite and calcite [6; MSc. dissertation: A Martalas]. The guar was used in that process to depress the calcite but was also found to inadvertently depress the apatite. This work made use of isotopically labeled reagents to determine the relative adsorption characteristics of these classes of collectors on different ores.

Copper sulphate has been widely used in flotation as an activator of sulphide minerals rendering them much more amenable to the adsorption of the collector and thus making them far more hydrophobic. There is much anecdotal data on the role of the copper sulphate which is added variously in the mills or the conditioners or at the entrance to the first rougher cell [2]. What is often not well understood is the role of the copper ions on the activation of the gangue minerals, on the behaviour of the froth phase and its behaviour at different pH values. The work carried out by various researchers under the supervision of the author has recently been able to clarify many of these questions using sophisticated surface analytical techniques such as Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and X-Ray photoelectron spectroscopy (XPS). These methods enable one to not only detect the presence of these ions on the surface of various minerals but also their oxidation state [15].

It has recently been shown in a current project carried out under the supervision of the author on the flotation of pyrrhotite and chalcopyrite, that the pyrrhotite is readily floated under standard conditions. This is contrary to the common perception that it is very difficult to float pyrrhotite. What does, however, become apparent is that when the pyrrhotite is in an aqueous phase which is significantly enriched by ions such as  $\text{Fe}^{3+}$ , the flotation is markedly reduced probably due to the formation of ferric hydroxide and thus it again illustrates the need for a proper understanding and management of the pulp chemistry. Given the critical importance today of water supply in many parts of the world where flotation is practised it seems that there has been an insufficient appreciation of the importance of the role of various ions present in the recycle water on the overall process. Although this is known, the need to make the necessary calculations is important.

## **2.2 FLOTATION OF DIFFERENT ORE TYPES**

As has already been mentioned, much of the early work in the flotation studies focused on pyrite, given that this was the dominant flotation process in South Africa in the late 1970s and early 1980s. Notwithstanding the fact that the pyrite flotation plants eventually closed down, pyrite continued to be a useful probe system to investigate a wide range of parameters in flotation research. So, although many of

the studies focused on the interaction of various reagents on pyrite flotation it also represented a very valuable test system for evaluating the effects of various physical and chemical parameters on flotation as well as on the performance and characteristics of various cell types.

As already mentioned, arsenopyrite enjoyed somewhat considerable interest in the mid-1980s at a time when Gencor was pioneering its use of bacterial leaching of sulphide ores. Unpublished reports were also written at that time on the effect which the flotation reagents, adsorbed on the arsenopyrite, may have on the activity of the bacteria used in the bio-leaching process. This formed part of other unpublished work on the thermal degradation of the thiol collectors adsorbed onto the sulphide minerals. The author also co-authored a series of papers and Conference Proceedings, with Mr. R C Dunne, in the area of gold-bearing pyrite and chalcopyrite [2, 55]. This led to some preliminary investigations, using column flotation cells, into the effect of in-situ sulphidisation procedures to enhance the recovery of such ores. These investigations did not indicate that it may be possible to increase recoveries by this method.

Reference has already been made to the work carried out by the author and his colleagues studying the interactive effect of collectors, modifiers and depressants on various types of gangue minerals. These included work on pyrophyllite (talc), pyroxene, feldspar and calcite [1, 4, 11-16, 24-27]. As already mentioned the use latterly of sophisticated surface analytical methods has assisted considerably in gaining a much better understanding of the surface behaviour of the mineral.

The focus on sulphide minerals created the opportunity for investigations on the effect of oxidation on the behaviour of these minerals which, as is well-known, can occur, for example, through the use of mild steel milling media [8 & 11; MSc. dissertations: L. Barker and A Dimou]. These studies also led to unpublished reports for companies floating copper, lead, and zinc ore bodies, and variously proposed the importance of continual monitoring of dissolved oxygen levels during the process.

Most importantly, the work on pyrite illustrated to a much greater extent an understanding of the importance of particle size and degree of liberation of the ore

particles. In the mid-1990s the author was able to attract to his group Dr M Powell who had an excellent record in the area of comminution. This intervention has proven to be most valuable for the MPRU and the general flotation research activity since it brings together uniquely a flotation and comminution research group. Thus, managing liberation rather than particle size as well as developing better methods for floating coarser particles in which the valuable is liberated/exposed and in which it is not necessary to further comminute becomes a major focal point. This more careful management of the comminution process will also have effects, for example, on the behaviour of the froth phase.

Early work by the author and his colleagues made use of the Hallimond Microflotation Cell. This is a useful device for carrying out exploratory experiments on the relative effectiveness of collectors or other such reagents in the flotation process in a froth-free and quiescent environment. However, with the later development of a method to measure the sizes of bubbles in flotation cells, the author and his colleague Dr D J Bradshaw modified the device to develop what has become known as the UCT Microflotation Cell. This cell is better defined today as a method to measure the relative hydrophobicity of ore particles after various treatments. It also lends itself to the measurement of bubble loading characteristics of a particular ore-reagent-bubble system [10, 35]. Excellent correlations have been observed between the results obtained using the UCT Microflotation Cell to determine relative hydrophobicity and other more classical methods such as contact angle measurements.

In terms of the gangue minerals, the effect of using various polysaccharide depressants on their flotation has enjoyed attention since the early 1980s. Arising out of this interest and following the growing attention being given to platinum group minerals [11-15, 24-27], the MPRU has through the excellent work of Dr D J Bradshaw, developed a world class research facility for the investigation of the role of various polysaccharide depressants as a function of degree of substitution, molecular weight, ore type, reagent suite, and ionic strength in flotation [16]. This has also led to the development and application of methods for the measurement of these properties, including viscosity. This work builds correctly on the theme of

understanding the influence of the chemistry of the aqueous phase on the overall flotation reagent behaviour [15].

Research was carried out in the early 1980s on apatite and calcite flotation [1] and, later, on coal flotation [33]. In 1982, at the invitation of the former National Institute of Metallurgy, the author was invited to begin research in the area of coal flotation. Fortunately, in 1983, Professor J-P Franzidis joined the author's flotation group. Having worked for Anglo Coal he was the obvious person to drive this work beginning the work with Mr R Fickling [MSc.] and later with Mr M C Harris who is today playing a leading role in the MPRU managing the joint venture with the JKMRC. Much of the work focused on the application of new cell technologies such as the column cell [33] and the Jameson Cell.

### **2.3. EFFECT OF PHYSICAL PARAMETERS ON THE FLOTATION PROCESS**

It is well known that the characteristics and behaviour of the bubbles involved in the flotation process play a very significant role. In the mid-1980s the author was faced with a challenge in some of the early work on column flotation cells to measure the size of the bubbles produced from different sparger systems. This was linked with the visible observation of the change in the bubble size in the Leeds Cell referred to earlier and the advent of column cells with a wide range of sparger types. Building on early work carried out at the former National Institute of Metallurgy in the 1970s by Dr P J Harris and Mr R C Dunne, the author proceeded, mainly with Mr C M Goodall [21; PhD, 1992] and Mr E W Randall, a Senior Technical Officer, to develop a bubble-sizing device which has found widespread use around the world today [44, 45, 46, 47, 48]. It is currently believed that his device is being used by 25 research institutions worldwide and has become known as the UCT Bubble Sizer. Although other arguably more robust methods have appeared in recent years this was the probably the first time that a serious programme of research was carried out for a sustained period aimed at measuring bubble sizes as a function of various parameters. It should be noted that in the 1980s Professor G J Jameson from the University of Newcastle, had done photographic measurements in a major study of the effect of high speed conditioning on flotation. The development of this bubble



sizer in a real pulp opened up exciting opportunities to carry out investigations on the influence of various parameters on the sizes of bubbles. Some of the early applications of this device were to investigate the effects of a whole range of physical and chemical parameters on the sizes of bubbles [45, 46]. These included the influence of various flotation reagents and of fluids of different viscosities, as well as the influence of various physical parameters such as temperature. P J Mills [22; PhD dissertation] investigated the use of bubble size in the scale up of column flotation cells [48]. F Sawyerr [MSc. dissertation] and D A Deglon used the device to develop a model for the prediction of bubble size in a mechanically agitated flotation cell [48]. It was also used in studies to determine the influence of a wide range of parameters on the loading of bubbles in a flotation cell [35]. Goodall [PhD dissertation] used it to investigate pulp-froth interactions in a laboratory column flotation cell [30]. Mills [31] studied the effect of temperature on bubble size. Goodall [32] developed an ingenious device which was able to carry out instantaneous cuts of the froth phase enabling the measurement of the amount of solids, liquid and, by inference, gas phase in the froth phase of the cell and using the bubble sizer was able to correlate these parameters to the pulp phase behaviour. In an important study using a Rushton turbine, D A Deglon [39; Ph.D. dissertation 1998] carried out extensive investigations determining bubble size using high speed photographic techniques [64]. This produced a very rich set of data which is still being used by Dr Deglon, presently a Senior Lecturer in Chemical Engineering at UCT and Deputy Director of the MPRU, in his development of a strong new initiative in the MPRU using computational fluid dynamics techniques in the modeling of flotation cells.

Arguably one of the most significant impacts which the development of a robust technique to measure bubble size had on flotation occurred in 1996 when the author's colleague, Professor J-P Franzidis, was on sabbatical leave at the JKMRRC. At this time interest had developed in the use of the bubble surface area flux,  $S_b$  which is a function of air flow rate and bubble diameter, in the characterization of flotation cells and the kinetics of flotation in such a cell. The so-called  $k-S_b$  model which today dominates much of current thinking behind the modeling of the flotation process was considerably enhanced by the ability to measure bubble size [72] and Franzidis, Harris and co-workers later on successfully modeled work done by Mills and Goodall in column cells using their bubble size measurements.

The ability to measure bubble size in the pulp phase opened up the challenge to measure the sizes of bubbles in the froth phase. Seminal work in this regard was done by Professor E T Woodburn at UMIST using sophisticated techniques and later by his successor, Professor J J Cilliers, formerly from the Chemical Engineering Dept. at UCT and now Professor at the RSM. Colleagues of the author went a different route and over the past five or more years Dr D J Bradshaw and Professor G J de Jager of the Department of Electrical Engineering, a leading authority in image analysis, have developed a froth imaging device known as SmartFroth. This system enables a rigorous analysis to be carried out of the characteristics of the surface of the froth. This ability will undoubtedly lead to much research output in the next few years, especially correlating the behaviour of the froth and pulp phases [16].

It is common cause that the froth phase is probably the least well understood aspect of flotation. In a recent set of studies co-supervised with M C Harris attempts have been made to model the froth phase behaviour in a flotation cell [63, 65, 71, 73]. This work has led to much further work by M C Harris of the modeling of phenomena such as entrainment which is a key to developing more robust models for the froth phase behaviour and ultimately for the overall flotation process.

## **2.4 CHARACTERISATION OF FLOTATION CELLS**

As is well-known in the late 1980s, column flotation cells enjoyed widespread interest. The development of these very large flotation cells with their unique bubble generating sparger systems were very amenable to scale-up since they lent themselves to rigorous characterization using classical chemical reactor theory. This was well exploited by G Dobby and J Finch of McGill University in the late 1980s. These cells also proved to be the precursors to the very large agitated flotation cells being used today, the largest currently being close to 300 m<sup>3</sup> in size. These large cells are important in the design of modern concentrators where the huge increase in throughput capacity of the comminution circuits have been the driving force.

The author embarked on a study of the influence of various parameters on the sizes of bubbles in column flotation cells in the mid-1980s. Beginning with the work C.M.

Goodall and P J T Mills [both PhD theses: 1992] the major focus was on the modeling of the solid and liquid phase residence time distributions in a column cell. It had been inferred in the late 1980s that the solid and liquid phases followed similar behaviour. Mills [58, 61] modeled the behaviour of the solid and liquid phases making use of isotopically labeled tracers and by setting up a pilot scale column cell at the former National Nuclear Facility at Pelindaba. This generated a very rich source of data which still lends itself to further investigation. Further work was then done by Goodall [59, 60] and later in collaboration with Professor J Yianatos of the University of Santa Maria in Chile, who had done similar work at the time at Disputada (now Los Bronches) Mine in Chile [62]. Scale-up studies began at the same time and Mills used modeling methods to compare pilot scale cells with large scale cells using actual comparable data from each cell [67].

Much other work was published during this time in various conferences where the emphasis was somewhat different but the theme similar. These included work on coal [33], the effect of using different sparger types in which a large scale test rig was built in the MPRU using commercial Cominco spargers [51, 53], reviews of the current practice both in South Africa and globally using column cells for different ore types [50, 53, 54, 55, 56]. Later in a reversion to a study of froth behaviour in an agitated cell further studies were carried out to analyze their performance [65, 66].

## **2.5 MODELING AND SIMULATION STUDIES**

Modeling has played a significant role in this research [58-73]. As has been referred to above, the author was exposed to the importance and value of modeling the flotation process through early discussions with Professor R Klimpel with whom a lifelong and most rewarding friendship continued until his untimely death. Modeling, of course, is a basic discipline in process engineering and the application of classical reactor theory to the modeling of flotation cells has enjoyed extensive attention in many research groups around the world. As already referred to, the author was able to extend this ability to carry out such modeling often by virtue of the ability to measure the sizes of bubbles in flotation cells. Coupled with a good understanding of the residence time distribution of the solid and liquid phases (direct measurements of the residence time distribution of the gas phase remains an elusive target) it was

now possible to begin using standard methods to characterize the behaviour of flotation cells and to begin to develop scale-up strategies. In the mid 1990s M C Harris, with the author as a co-supervisor, supervised an MSc dissertation of F de Beer [MSc dissertation 1998] the aim being that this should largely be a plant based study. It seemed at the time that it would be useful to characterize various streams by using standard batch scale flotation experiments on samples of ore taken 'hot' from various positions around the circuit on the assumption that the kinetic behaviour of an ore particle in a standard constant-operating batch cell should not change irrespective of its experience moving through the plant. In other words a slow floating particle entering the plant will still be floating when it enters the cleaner circuit. Serendipitously the group at the JKMRRC also began thinking along these lines. The rest is history with M C Harris having taken this concept and used it with colleagues at the JKMRRC as one of fundamental approaches in modeling the behaviour of circuits. This thinking has contributed significantly to the development of the current version of JKSimFloat.

## **2.6 MEASUREMENT TECHNIQUES**

It is worth noting in this dissertation the remarkable developments that have taken place over the last 25 years in our ability to measure the parameters which play such an important role in the flotation process. In the early 1980s the author began using techniques such as EDAX in electron microscopy to attempt to determine the copper surface coverage of particles [3]. The fact that none was observed was later explained through the Healey's solvation effect theory. Currently techniques that the author's students have been using include Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), X-ray Photoelectron Spectroscopy (XPS), Zeta Potential measurements, XRD structure determination and other such solid state characterization techniques [3, 11-15, 24-27, 44-47, 49, 51]. In this way it has now become possible to make very clear determinations of the elemental surface coverage of particles as a function of various treatments. This, coupled with the ability to measure bubble sizes in flotation cells, and also to characterize the behaviour of the froth phase through SmartFroth has greatly enhanced our ability to develop a great understanding of the flotation process. In a joint venture of the MPRU with the JKMRRC and the group of Professor J Finch at McGill University,

considerable progress is being made in carrying out measurements of parameters such as superficial air rate, bubble size using a photographic method, gas hold-up in the pulp phase, etc. The combined effect of these developments will all contribute greatly to a better understanding of this complex process. This is not to exclude the Flotation Characterisation Test Rig (FCTR), a joint venture between MPRU, JKMRC and a manufacturer which is essentially a pilot scale flotation circuit which endeavours to fully characterize the manner in which an ore particle will behave in a real circuit.

The MPRU through the work of Dr D J Bradshaw has recently begun an initiative to incorporate process mineralogy into its research studies. This discipline will greatly assist our understanding the effect of liberation and ore type and surface state on the flotation process and will inevitably provide an excellent linkage between the comminution and flotation research activities.

The MPRU has also through the work of Dr D A Deglon established a strong activity using CFD modeling to characterize the behaviour of flotation cells. This presents a unique set of challenges in regard to measurement and these are being addressed presently.

As already alluded to above the seminal work of M C Harris and his colleagues, both in the MPRU and at the JKMRC, have led to major developments in the ability to model and simulate flotation circuits. This is already having a major impact on operator's ability to better understand the performance of their plant and to begin in a controlled scientific manner to optimize its performance.

## **2.7 SERENDIPITOUS AND MISCELLANEOUS CONTRIBUTIONS**

Appendix C of this dissertation lists the author's research activities in the area of catalysis. This has played an important serendipitous role especially regarding the work on the behaviour of siliceous gangue minerals, but also generally in appreciating the complexity of the solid-liquid-gas interactions which are common to both flotation and heterogeneous catalysis.

In the early 1980s the author began an extensive set of research work on the catalytic behaviour of synthetic mica-montmorillonite [74-77]. This is a 2:1 layer alumino-silicate in which exchange takes place in the octahedral layer rendering the silicate framework negative and thus resulting in the generation of a charge balancing proton which is the basis of the acid catalyst. Talcaceous minerals such as pyrophyllite are also 2:1 layer silicates and the ability to fully understand the importance of how such layered silicates behave opens up the opportunity for gaining a greater understanding of the behaviour of depressants in their interactions with such minerals. The author has addressed some of these issues in his recent papers with Professor J S Laskowski [17, 18].

A number of researchers have over the years used silanisation as a method to produce a fully hydrophobic particle. Serendipitously the author has also done extensive research over 20 years on the important class of catalyst called zeolites, which are porous crystalline alumino-silicates and in that sense also mimic in many respects the behaviour of siliceous minerals in the flotation process. The importance of understanding the external surface behaviour of such catalytic materials has been a major focus of the author's work on zeolites and this has required the development of sophisticated methods to silanize their external surfaces. This has to be done in a carefully controlled manner which is often not appreciated in the flotation literature [78-84].

During the 1980s and early 1990s the author was involved with the Anglo American Corporation in designing and developing procedures for the training of chemical engineering students on mineral processing concentrators. This work, which the author carried out in their Gold and Uranium division for 12 years, led to a significant improvement in the training of metallurgists and chemical engineers in Anglo American Corporation [87]. The MPRU still today is involved in an extensive collaboration with a large international mining company in providing continuing education for metallurgists and metallurgical engineers. This involvement in the education of engineers on concentrators is seen by the author to be a natural outflow of the research that he and his colleagues have carried out over many years.

Finally it is appropriate to mention in this dissertation the outstanding and in many ways unique collaboration which the author has enjoyed with his colleagues at the University of Stellenbosch since 1979. In particular mention must be made of Professors J S J van Deventer and L Lorenzen who have always been enormously supportive of this collaboration. One good exemplar of this collaboration is the Annual Mineral Processing Symposium which continues to be a joint effort and which is this year in its 23rd year of existence [85, 86].

**3. List of Publications Included in this Submission and referred to in Chapters 1 and 2**



### 3.1 Publications referred to in Chapter 1

#### Papers Published in Peer-reviewed Journals

4. C.T. O'Connor and A. van Zyl, The separation of kerogen from pyrophyllite by flotation, *The Journal of the South African Institute of Mining and Metallurgy*, 85 (1985) 357-360

#### Papers Published in Conference Proceedings

29. C.T. O'Connor and A. van Zyl, The separation of kerogen from pyrophyllite by flotation, *The Journal of the South African Institute of Mining and Metallurgy*, 85 (1985) 357-360
42. C.T. O'Connor, R.C. Dunne and A.M.R. Botelho de Sousa, The effect of temperature on the flotation of pyrite from two different ores, *Proceedings of the XVth International Mineral Processing Congress, Cannes, France, 1985*, pages 211-221

### 3.2. Publications referred to in Chapter 2.1 –The Role of Reagents in Flotation

#### Papers Published in Peer-reviewed Journals

1. C.T. O'Connor, R.C. Dunne and A. Martalas, The adsorption of oleate and the guar-based gum, Acrol LG-21, onto apatite and calcite, *Colloids and Surfaces*, 27 (1987) 357-366
2. C.T. O'Connor and R.C Dunne, The practice of pyrite flotation in South Africa and Australia, *Minerals Engineering*, 4 (1991) 1057-1069
3. C.T. O'Connor, C. Botha, M.J. Walls and R.C. Dunne, The role of copper sulphate in pyrite flotation, *Minerals Engineering*, 1 (1988) 203-212
4. C.T. O'Connor and A. van Zyl, The separation of kerogen from pyrophyllite by flotation, *The Journal of the South African Institute of Mining and Metallurgy*, 85 (1985) 357-360
5. C.T. O'Connor, D.J. Bradshaw and A.E. Upton, The use of dithiophosphates and dithiocarbamates for the flotation of arsenopyrite, *Minerals Engineering*, 3 (1990) 447-459
6. D.J. Bradshaw, A.E. Upton and C.T. O'Connor, A study of the pyrite flotation efficiency of dithiocarbamates using factorial design techniques, *Minerals Engineering*, 5 (1992) 317-329
7. C.T. O'Connor and R.C. Dunne, The flotation of gold bearing ores – A review, *Minerals Engineering*, 7 (1994) 839-849
8. D.J. Bradshaw and C.T. O'Connor, The flotation of pyrite using mixtures of dithiocarbamates and other thiol collectors, *Minerals Engineering*, 7 (1994) 681-690
9. D. J. Bradshaw, J.J. Cruywagen and C.T. O'Connor, Thermochemical measurements of the surface reactions of sodium cyclohexyl-dithiocarbamate, potassium n-butyl xanthate and a thiol mixture with pyrite, *Mineral Engineering*, 8 (1995) 1175-1184
10. D.J. Bradshaw and C.T. O'Connor, Bubble-particle adherence: Synergistic effect of reagents, *The Encyclopaedia of Separation Processes*, E.T. Woodburn (ed), Academic Press, 2000, Vol II, 1455-1464
11. V. Malysiak, C.T. O'Connor, J. Ralston, A.R. Gerson, L.P. Coetzer and D.J. Bradshaw, Pentlandite-feldspar interaction and its effect on separation by flotation, *International Journal of Minerals Processing*, 66 (2002) 89-106

12. N.J. Shackleton, V. Malysiak and C.T. O'Connor, The use of amine complexes in managing inadvertent activation of pyroxene in a pentlandite-pyroxene flotation system, *Minerals Engineering*, 16 (2003) 849-856
13. V. Malysiak, N.J. Shackleton and C.T. O'Connor, An investigation into the floatability of a pentlandite-pyroxene system, *International Journal of Minerals Processing*, 74 (2004) 251-262
14. C.T. O'Connor and V. Malysiak, An investigation into the adsorption of cationic species, especially copper, onto pyroxene and feldspar and their subsequent flotation behaviour, *Journal of Ore Dressing*, 6 (2004) 55-60
15. C.T. O'Connor, V. Malysiak and N.J. Shackleton, The interactions of xanthates and amines with pyroxene activated by copper and nickel, *Minerals Engineering* (in Press)
16. D.J. Bradshaw, P.J. Harris and C.T. O'Connor, The effect of collectors and their interactions with depressants on the behaviour of the froth phase in flotation, *Minerals Engineering* (in Press)
17. J.S. Laskowski and C.T. O'Connor, The role of dispersants and depressants in mineral processing. Part I: The mechanisms of interaction with the solid and liquid phases, *International Journal of Mineral Processing* (Submitted for Publication)
18. J.S. Laskowski and C.T. O'Connor, The role of dispersants and depressants in mineral processing. Part II: The applications of dispersants and depressants in the mineral processing, *International Journal of Mineral Processing* (Submitted for Publication)
36. D.J. Bradshaw, P.J. Harris and C.T. O'Connor, Synergistic interactions between reagents in sulphide flotation, *The Journal of the South African Institute of Mining and Metallurgy*, 4 (1998) 187-192

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19. C.T. O'Connor, D.J. Bradshaw and A.E. Upton, The separation of arsenopyrite from pyrite by flotation, *International Colloquium of Developments in Froth Flotation*, Gordon's Bay, South Africa, August 1989
20. C.T. O'Connor and R.C. Dunne, A preliminary survey of flotation practice on south African gold mines, *Randol Gold Forum*, Scottsdale, Arizona, January 1988, pages 233-245
21. C.T. O'Connor, C. Botha, M.J. Walls and R.C. Dunne, The role of copper sulphate in pyrite flotation, *Randol Gold Forum*, Scottsdale, Arizona, January 1988, pages 245-252

22. D.J. Bradshaw and C.T. O'Connor, The synergism of thiol collectors in a mixture used for the flotation of pyrite, *Proceedings of the International XXth Mineral Processing Congress*, Aachen, September 1997, (Eds. H. Hoberg and H. von Blottnitz) GMBH Publishers, Vol 3, pages 343-354
23. C. Helbig, D.J. Bradshaw, P.J. Harris, C.T. O'Connor and H. Baldauf, The synergistic interactions of mixtures of thiol collectors in the flotation of sulphide minerals, *Proceedings of the XXI International Mineral Processing Congress*, Rome, Italy July 2000 (Eds. P. Massaci) Elsevier, pages B8b 1-9
24. V. Malysiak, N.J. Shackleton, D. de Vaux and C.T. O'Connor, Effect of water quality on pentlandite-pyroxene floatability with an emphasis on calcium ions, *Proceedings of the XXII International Mineral Processing Congress*, Cape Town, South Africa September 2003, pages 734-742
25. N.J. Shackleton, V. Malysiak, C.T. O'Connor and D. de Vaux, The role of complexing agents and dispersants in pentlandite-pyroxene separation by flotation, *Proceedings of the XXII International Mineral Processing Congress*, Cape Town, South Africa September 2003, pages 743-752
26. C.T. O'Connor and V. Malysiak, An investigation into the adsorption of cationic species, especially copper, onto pyroxene and feldspar and their subsequent flotation behaviour, *Challenges and Opportunities in Mineral Processing. Proceedings of the Xth International Mineral Processing Symposium*, Izmir, Turkey October 2004, pages 415-426
27. C.T. O'Connor, V. Malysiak and N.J. Shackleton, Study of the adsorption of metal ions onto Pyroxene, *Centenary of Flotation Symposium*, Brisbane, Australia 2005
28. D.J. Bradshaw, P.J. Harris and C.T. O'Connor, The effect of collectors and their interactions with depressants on the behaviour of the froth phase in flotation, *Centenary of Flotation Symposium*, Brisbane, Australia 2005

### 3.3 Publications referred to in Chapter 2.2 – Flotation of Different Ore Types

#### Papers Published in Peer-reviewed Journals

1. C.T. O'Connor, R.C. Dunne and A. Martalas, The adsorption of oleate and the guar-based gum, Acrol LG-21, onto apatite and calcite, *Colloids and Surfaces*, 27 (1987) 357-366
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24. V. Malysiak, N.J. Shackleton, D. de Vaux and C.T. O'Connor, Effect of water quality on pentlandite-pyroxene floatability with an emphasis on calcium ions, *Proceedings of the XXII International Mineral Processing Congress*, Cape Town, South Africa September 2003, pages 734-742
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26. C.T. O'Connor and V. Malysiak, An investigation into the adsorption of cationic species, especially copper, onto pyroxene and feldspar and their subsequent flotation behaviour, *Challenges and Opportunities in Mineral Processing. Proceedings of the Xth International Mineral Processing Symposium*, Izmir, Turkey October 2004, pages 415-426
27. C.T. O'Connor, V. Malysiak and N.J. Shackleton, Study of the adsorption of metal ions onto Pyroxene, *Centenary of Flotation Symposium*, Brisbane, Australia 2005
55. C.T. O'Connor, R.C. Dunne, K.H. Schommarz and C.M. Goodall, Column flotation of gold bearing iron sulphides, *Proceedings of the XVIIIth International Mineral Processing Congress*, Sydney, Australia, May 1993, (Ed. T.Napier-Munn)pp.829-837

### 3.4 Publications referred to in Chapter 2.3 – Effect of Physical Parameters on the Flotation Process

#### Papers Published in Peer-reviewed Journals

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### 3.8 Publications referred to in Chapter 2.7 – Serendipitous and Miscellaneous Contributions

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44. C.T. O'Connor, E.W. Randall and C.M. Goodall, Measurement of the Effects of Physical and Chemical Variables on Bubble Size, *International Journal of Mineral Processing*, 28 (1990) 139-149
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47. C.T. O'Connor and P.J.T. Mills, The Influence of Bubble Size on Scale-Up of Column Flotation Cells, *Minerals Engineering*, 8 (1995) 1185-1195
48. F. Sawyerr, D.A. Deglon and C.T. O'Connor, Prediction of Bubble Size Distribution in Mechanical Flotation Cells, *Journal of the South African Institute of Mining and Metallurgy*, 4 (1998) 179-185

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52. D.A. Deglon and C.T. O'Connor, Hydrodynamic investigation of fine particle flotation in a conventional flotation cell, *Proceedings of the XXth International Mineral Processing Congress*, Aachen, September 1997, (Eds. H. Hoberg and H. von Blottnitz) GMBH Publishers, Vol 3, pages 167-174
53. J.-P. Franzidis, M.C. Harris and C.T. O'Connor, Column Flotation: The South African experience, *Proceedings of the SME Symposium*, Denver, Colorado, February 1991, pages B3 1-33

54. J.-P. Franzidis, M.C. Harris and C.T. O'Connor, Review of column flotation practice on South African mines, *Column 91, Proceedings of an International Conference on Column Flotation*, Ontario, Canada, June 1991, pages 479-493
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59. C.M. Goodall and C.T. O'Connor, Residence time distribution studies in a flotation column. Part 1: The modelling of residence time distributions in a laboratory column flotation cell, *International Journal of Mineral Processing*, 31 (1991) 97-113
60. C.M. Goodall and C.T. O'Connor, Residence time distribution studies in a flotation column. Part 2: The relationship between solids residence time distribution and metallurgical performance, *International Journal of Mineral Processing*, 36 (1992) 219-228
61. P.J.T. Mills and C.T. O'Connor, The use of the axial dispersion model to describe mixing in a flotation column, *Minerals Engineering*, 5 (1992) 939-944
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65. Z.T. Mathe, M.C. Harris and C.T. O'Connor, A review of methods to model the froth in non-steady state flotation systems, *Minerals Engineering*, 13 (2000) 127-140
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67. C.T. O'Connor, P.J.T. Mills and J.J. Cilliers, Prediction of large-scale column flotation cell performance using pilot plant data, *The Chemical Engineering Journal*, 59 (1995) 1-6

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69. C.T. O'Connor and C.M. Goodall, The modelling of the solid and liquid phase residence time distributions in a column flotation cell, *AIME meeting*, Salt Lake City, February 1990
70. C.T. O'Connor and P.J.T. Mills, An evaluation of scale-up procedures using hydrodynamic and kinetic data from pilot plant and full scale pyrite flotation column, *Proceedings of the IV Meeting of the Southern Hemisphere on Mineral Technology*, Chile, November 1994 (Eds. S Castro and J. Alvarez) University of Concepcion Press, Vol 2, pages 137-149
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72. C.T. O'Connor and M.C. Harris, The modelling and simulation of flotation circuits, *New Developments in Mineral Processing, Proceedings of the 9<sup>th</sup> Balkan Mineral Processing Congress*, Istanbul, Turkey, September 2001, pages 419-426
73. Z.T. Mathe, M.C. Harris and C.T. O'Connor, The prediction of continuous flotation cell performance from batch data using a froth recovery model, *New Developments in Mineral Processing, Proceedings of the 9<sup>th</sup> Balkan Mineral Processing Congress*, Istanbul, Turkey, September 2001, pages 437-443

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75. J.C.Q. Fletcher, M. Kojima and C.T. O'Connor, Acidity and catalytic activity of synthetic mica-montmorillonite. Part II: Propene oligomerization, *Applied Catalysis*, 28 (1986) 181-191
76. C.T. O'Connor, L.L. Jacobs and M. Kojima, Propene oligomerization over synthetic mica-montmorillonite (SMM) and SMM incorporating nickel, zinc and cobalt, *Applied Catalysis*, 40 (1988) 277-290
77. A.P. Vogel, C.T. O'Connor and M. Kojima, Thermogravimetric analysis of the iso-butene oligomerization activity of various forms of synthetic mica-montmorillonite, *Clay Minerals*, 25 (1990) 355-362
78. H.P. Röger, K.P. Möller and C.T. O'Connor, The transformation of 1,2,4-trimethylbenzene. A probe reaction to monitor external surface modifications of HZSM-5?, *Microporous Materials*, 8 (1997), 151-157
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82. C.T. O'Connor, K.P. Möller and H. Manstein, The effect of temperature and cyclic alkoxysilane deposition procedures on the silanisation and subsequent catalytic and sorption properties of zeolites, *Journal of Molecular Catalysis A: Chemical*, 181 (2001), 15-24
83. C.T. O'Connor, K.P. Möller and H. Manstein, The effect of silanization on the catalytic and sorption properties of zeolites, *Cattech*, 5 (2003) 172-182
84. H. Manstein, K.P. Möller and C.T. O'Connor, Cyclic chemical vapour deposition of TEOS on ZSM-5: Effect of deposition temperature on shape selective performance, *Studies in Surface Science and Catalysis*, 135 (2001) 207



85. J.S.J. van Deventer and C.T. O'Connor, Spotlight on research into minerals processing, *Journal of the South African Institute of Mining and Metallurgy*, 86 (1986) 463-465
86. C.T. O'Connor and J.S.J. van Deventer, Spotlight on minerals processing in the Western Cape, *Journal of the South African Institute of Mining and Metallurgy*, 87 (1987) 438-440
87. J.-P. Franzidis and C.T. O'Connor, The vacation training of Chemical and Metallurgical Engineering undergraduate students, *5<sup>th</sup> National Meeting of the SAChE*, Vol 3, Pretoria, August 1988, pages T2 0-5

## **APPENDIX B: LIST OF MASTERS AND DOCTORAL THESES SUPERVISED TO DATE**

(\* indicates co-supervision)

	<b>Research Student</b>	<b>Area of Research</b>	<b>Degree</b>	<b>Year</b>
1.	A. van Zyl	The separation of kerogen from pyrophyllite by flotation	MSc	1982
2.	A.M. de Sousa	The effects of temperature on pyrite flotation	MSc	1983
3.	R.E. Fasol	The catalytic conversion of low chain length hydrocarbons to liquid fuels using Zeolite Y.	MSc	1983
4.	J.C.Q. Fletcher	The relationship between the acidity and catalytic activity of synthetic mica montmorillonite	PhD	1984
5.	W.K. Schumann	The conversion of olefins liquid fuels using sulphonic acid resins	MSc	1984
6.	A. Martalas	The adsorption of flotation reagents on calcite/apatite	MSc	1984
7.	R.B. Duncan	The characterization of flotation cell parameter interactions	MSc	1984
8.	L. Barker	The effect of dissolved salts on the recovery of pyrite by flotation	MSc	1985
9.	M.W. Rautenbach	The effect of acidity on the deactivation of mordenite and ZSM-5 in polymerization reactions	PhD	1985
10.	L.L. Jacobs	The oligomerization of propene over Ni-SMM	MSc	1985
11.	A. Dimou	The use of xanthates as pyrite collectors	MSc	1986
12.	D.M.M. McLean	The kinetics of olefin oligomerization over phosphoric acid	PhD	1987
13.	S.M. Harms	The oligomerization of olefins over supported nickel catalysts	MSc	1987
14.	P.M. Dickens	The oligomerization of olefins over cobalt catalysts	MSc	1987
15.	K.P. Möller*	A study of the diffusion characteristics of deactivated zeolites	PhD	1989
16.	R. Hartford	The oligomerization of olefins over pillared clays and RE zeolites	MSc	1989

17.	S. Schwarz*	The synthesis, characterization and olefin oligomerization activity of modified forms of ZSM-5	PhD	1990
18.	B. Andersen	The synthesis, characterization and catalytic activity of boron and phosphorus modified zeolites	PhD	1991
19.	R. Forrester	The evaluation of cetane numbers using small scale analytical techniques.	MSc	1991
20.	K.M. Schommarz	The design of a column cell to beneficiate pyrite	MSc	1991
21.	C.M. Goodall	The effect of various chemical and physical parameters on the performance of a column flotation cell	PhD	1992
22.	P.J.T. Mills	Development of a hydrodynamic and kinetic model for the design of a column flotation cell	PhD	1992
23.	M. van Niekerk*	The conversion of methanol to olefins over zeolites	PhD	1992
24.	S.T. Langford	The conversion of oxygenates over ZSM-5	MSc	1993
25.	J.S. Vaughan*	The synthesis, characterization and catalytic activity of RE exchanged heteropoly acids	PhD	1993
26.	M. Howden	Synthesis and characterization of ZSM-5	PhD	1993
27.	R. Nash*	The conversion of syngas to chemicals	MSc	1994
28.	R. Weber*	The synthesis of ZSM-5 with controlled Si and Aluminium gradients	MSc	1994
29.	C. M'Kombe*	Metal loading of zeolites	MSc	1995
30.	G. Moon	Synthesis of Zeolite Beta	MSc	1995
31.	N.O. Lotter	Quality control model for the development of high confidence flotation test data.	MSc	1995
32.	F. de Beer*	The characterisation of a two stage flotation circuit treating a complex platinum and chromite ore	MSc	1996
33.	A. O'Donovan	The role of extraframe-work aluminium in the activity of zeolites	PhD	1996
34.	G. S.Sewell*	Synthesis of ethylamines	PhD	1996

35.	A.P. Vogel	The kinetics of olefin oligomerization over synthetic and pillared clays	PhD	1996
36.	S.J. Sealy*	The kinetics of olefin oligomerization	PhD	1996
37.	D.J. Bradshaw	The flotation of sulphides using dithiocarbamates	PhD	1997
38.	J. Bunt*	Coal flotation	MSc	1997
39.	D. Deglon	Cell hydrodynamics	PhD	1998
40.	E Theron*	Characterisation and optimisation of flotation columns for the recovery of platinum ore from the UG-2 reef	MSc	1998
41.	C. Tapa*	Investigation of copper flotation at ZCCM	MSc	1998
42.	D Egya-Mensah*	Hydrodynamics and gas dispersion in mechanical flotation cells	MSc	1999
43.	S C W Bunkell*	Investigation into the effect of high intensity conditioning on the flotation performance of a sulphide ore.	MSc	2000
44.	T Mathe*	Modeling froth phase in flotation cells	PhD	2001
45.	R.J. Nash*	Aromatization of higher alkanes	PhD	1997
46.	J.N. Theron*	The partial oxidation of methane	PhD	1997
47.	A.E. Schnitzler*	The kinetics of methanol conversion reactions	PhD	1997
48.	M. Schnobel*	The synthesis of fine chemicals by partial oxidation.	PhD	1997
49.	S. Robertson*	Synthesis of VPO catalyts	MSc	1997
50.	H.P. Röger*	Catalytic activity of inertised zeolites.	PhD	1998
51.	R. Weber*	Inertization of zeolite acidity	PhD	1999
52.	S. Hurgobin	Activity of steamed Beta	MSc	1999
53.	L.H.C.van Steen*	Methanol amination.	PhD	2000
54.	H Manstein*	Silanisation of zeolites.	PhD	2002
55.	G Moon	Alkylation of phenols.	PhD	2003

56.	V Malysiak	Pentlandite-pyroxene and pentlandite-fledspar interactions and their effect on separation by flotation	PhD	2003
57.	N J Shackleton	Role of complexing agents in the Flotation of Pentlandite – pyroxene mixtures	MSc	2003
58.	R Hunt*	The effect of hydrothermal and acid dealumination on the structural, acidic and catalytic properties of mordenite	MSc	2005

## **APPENDIX C: PAPERS NOT INCLUDED WITH THIS SUBMISSION**

### **PAPERS PUBLISHED IN PEER REVIEWED JOURNALS**

1. C.T. O'Connor, M. Kojima and W.K. Schumann  
The oligomerization of C<sub>4</sub> alkenes over cationic ion exchange resins  
Appl. Cat., 16, (1985) 193-207.
2. E.G. Prout, E.G. Shephard and C.T. O'Connor  
The photolysis of barium and strontium azides  
J. Inorg. Nucl. Chem, 43, (1981) 643-652.
3. E.G. Prout and C.T. O'Connor  
Photolysis of lithium azide
4. E.G. Prout and C.T. O'Connor  
The Photolysis and co-irradiated decomposition of calcium azide  
S. Afr. J. Chem., 37 (4), (1984) 193-7.
5. E.G. Prout, C.T. O'Connor, D.W. Lensen and B. Orlandi  
A precise constant temperature water bath  
J. Phys. E.: Scientific Instruments, 17, (1984) 839-840.
6. C.T. O'Connor, R.E. Fasol and G.A. Foulds  
The oligomerization of C<sub>4</sub>-alkenes with calcined NaHY-Zeolites.  
Fuel Processing Technology, 13, (1986) 41-51.
7. C.T. O'Connor, J.C.Q. Fletcher and M.W. Rautenbach  
A simple infra-red cell for solid state catalyst characterization.  
J. Phys. E.: Sci. Instrum., 19, (1986) 367-9.
8. M. Kojima, J.C.Q. Fletcher and C.T. O'Connor  
Acidity and catalytic activity of synthetic mica-montmorillonite, Part I: An infrared and temperature programmed desorption study.  
Appl. Cat., 28, (1986) 169-179.
9. J.C.Q. Fletcher, M. Kojima and C.T. O'Connor  
Acidity and catalytic activity of synthetic mica-montmorillonite, Part II: Propene oligomerization.  
Appl. Cat., 28, (1986) 181-191.
10. M. Kojima, M.W. Rautenbach and C.T. O'Connor  
Acidity characterization of ion-exchanged mordenite, Part I: Temperature programmed desorption of pyridine.  
J. Catal. 112, (1988) 495-504.
11. M. Kojima, M.W. Rautenbach and C.T. O'Connor  
Acidity characterization of ion-exchanged mordenite, Part II: An infrared spectroscopic investigation.  
J. Catal. 112, (1988) 505-515.
12. M. Kojima, M.W. Rautenbach and C.T. O'Connor  
Butene oligomerization over ion-exchanged mordenite.  
Ind. Eng. Chem. Res. 27, (1988) 248-252.

13. C.T. O'Connor, L.L. Jacobs and M. Kojima  
Propene oligomerization over synthetic mica-montmorillonite (SMM), and SMM incorporating nickel, zinc and cobalt.  
Appl. Catal., 40, (1988) 277-290.
14. E.W. Randall, M. Kojima, C.T. O'Connor and K. Herzog  
A capillary gas flow control system for thermal analysis studies.  
S. Afr. J. Chem., 34, 4, (1981) 113-117.  
J. Phys. (E): Sci. Instrum. 21 (1988) 505-507
15. S.M. Harms, M. Kojima and C.T. O'Connor  
Propene oligomerization over nickel-loaded silica alumina.  
Fuel Processing Technology, 31, (1989) 231-243.
16. B. Andersen, M. Kojima, C.T. O'Connor  
Propene oligomerization over boron modified ZSM-5.  
Stud. Surf. Sci. Catal., 49 (1989) 1193-120.
17. S. Schwarz, M. Kojima and C.T. O'Connor  
The effect of silica-alumina ratio and syndissertation time on high pressure olefin oligomerization over ZSM-5.  
Appl. Catal. 56, (1989) 263-280
18. R.W. Hartford, M. Kojima and C.T. O'Connor  
The catalytic activity of Lanthanum ion exchanged on ZSM-5.
19. C.T. O'Connor and M. Kojima  
The conversion of low chain length olefins into liquid fuels.  
S. Afr. J. Chem. Eng., 1, (1989) 23-41.
20. A.P. Vogel, M. Kojima and C.T. O'Connor  
Thermogravimetric analysis of iso-butene oligomerization activity of various forms of synthetic mica montmorillonite.  
Clay Minerals, 25, (1990) 355-362.
21. C.T. O'Connor and M. Kojima  
Alkene oligomerization.  
Catalysis Today, (3) (1990) 329-350.
22. R.W. Hartford, M. Kojima and C.T. O'Connor  
The effect of pillaring montmorillonite and beidellite on the conversion of trimethylbenzenes.  
Ind. Eng. Chem. Res., 28, 12, (1989) 1748-1752.  
J. Catal. 128, (1991) 487-498.
23. S. Schwarz, M. Kojima and C.T. O'Connor  
Effect of stirring, extrusion and pelletizing on high pressure propene oligomerization and xylene isomerization over ZSM-5.  
Appl. Catal. 68, (1991) 81-86.
25. S. Schwarz, M. Kojima and C.T. O'Connor  
The effect of tetraalkylammonium, alcohol and amine templates on the syndissertation and high pressure propene oligomerization activity of ZSM-type zeolites.  
Appl. Catal., 73 (1991) 313-330.

26. C.T. O'Connor, S. Schwarz and M. Kojima  
The effect of various physical and chemical parameters on the syndissertation of ZSM-5 for propene oligomerization.  
Stud. Surf. Sci. Catal., Vol.65, (1991) 491-500.
27. J.S. Vaughan, J.C.Q. Fletcher and C.T. O'Connor  
The oligomerization of olefins over heteropoly acids.  
Prepr.-Am.Chem.Soc.,Div.Pet.Chem., 36(4), (1991) 605-612.
28. C.T. O'Connor, R.D. Forrester and M.S. Scurrrell  
Cetane number determination of synthetic diesel fuels.  
Fuels,71,11, (1992) 1323-1327.
29. M. van Niekerk, J.C.Q. Fletcher and C.T. O'Connor  
Characterization of dealuminated large port mordenite.  
J. Catal., 138, (1992) 150-163.
30. C.T. O'Connor, J.S. Vaughan and L. Petrik  
AlPO<sub>4</sub>, SAPO and MeAPSO - a new family of molecular sieves.  
S.A.Jour. Chem. Eng., 5,1, (1993) 17-35.
31. J.S. Vaughan, C.T. O'Connor and J.C.Q. Fletcher.  
High pressure oligomerization of propene over heteropoly acids.  
J. Catal., 147, (1994) 441-454.
32. K.P. Möller and C.T. O'Connor  
The measurement of diffusion and adsorption using a jetloop recycle reactor.  
Stud. Surf.Sci. Catal., vol. 84 (1994) 1201-1218.
33. J.S. Vaughan, C.T. O'Connor and J.C.Q. Fletcher  
Propene oligomerisation and xylene and methyl-pentene isomerization over SAPO-11 and MeAPSO-11.  
Stud. Surf.Sci. Catal., vol. 84 (1994) 1709-1716.
34. S.J. Sealy, D.M. Fraser, K.P. Möller and C.T. O'Connor  
Equilibrium considerations in the modelling of propene oligomerisation.  
Chem. Eng. Sci., 49,19, (1994) 3307-3312.
35. K.P. Möller, M. Kojima and C.T. O'Connor  
Diffusion and adsorption in HY and HM deactivated by propene oligomerisation and hexane cracking.  
Chemical Engineering Journal, 54, (1994) 115-123.
36. J.N. Theron, J.C.Q. Fletcher and C.T. O'Connor  
Oxidative reforming of methane to syngas over a NiO-CaO catalyst.  
Catalysis Today 21, (1994) 489-494.
37. J.S. Vaughan, C.T.O'Connor and J.C.Q. Fletcher  
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J. Catal., 147, (1994) 441-454.
38. B.W.L. Southward, J.S. Vaughan and C.T. O'Connor.  
Infrared and thermal analysis studies of heteropoly acids.  
J. Catal., 153, (1995) 293-303. [2.037]



39. G.S. Sewell, E.van Steen and C.T. O'Connor  
Reductive ammination of ethanol with silica supported cobalt and nickel catalysts  
Appl. Catal. 125, (1995) 99 - 112.
40. L.F. Petrik, C.T. O'Connor and S. Schwarz  
The influence of various syndissertation parameters on the morphology and crystal size of ZSM-5 and the relationship between morphology and crystal size and propene oligomerization activity.  
Stud.Surf.Sci.Catal., vol. 94 (1995) 517-524.
41. A. O'Donovan and C.T. O'Connor  
The effect of acid and steam treatment of Na- and H-mordenite on their structural, acidic and catalytic properties.  
Microporous Materials, 5,4 (1995) 185 - 202. ]
42. K.P. Möller, J.C.Q. Fletcher, R.J. Becker and C.T. O'Connor  
Residence time distributions in a jet loop reactor  
Chem.Eng.Commun.,137 (1995) 111-118
43. G.S. Sewell, C.T. O'Connor and E. van Steen  
Reductive ammination of ethanol with silica-supported cobalt and nickel catalysts  
Appl. Catal. A: General, 125 (1995) 99 - 112.
44. S.P.J. Smith, V.M. Linkov, R.D. Sanderson, L.F. Petrik, C.T. O'Connor and K. Keiser  
Preparation of hollow-fibre composite carbon-zeolite membranes.  
Microporous Materials, 4,5 (1995) 385-391.
45. M.J. Van Niekerk, J.C.Q. Fletcher and C.T. O'Connor  
The effect of catalyst modifications and reaction conditions on the conversion of methanol to light olefins over SAPO-34.  
Appl. Catal. A: General, 138 (1996) 135 - 145.
46. R.J. Nash, M.E. Dry and C.T. O'Connor  
The aromatization of 1-hexene and 1-octene by gallium/H-ZSM-5 catalysts.  
Appl. Catal.A: General, 134 (1996) 285-297.
47. K.P. Möller and C.T. O'Connor  
Gas solid mass transfer in a jetloop reactor.  
AIChE Journal, 42, 4 (1996) 1187.
48. K.P. Möller and C.T. O'Connor  
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