STRIPPING RARE EARTH ELEMENTS AND IRON FROM D2EHPA DURING ZINC SOLVENT EXTRACTION

by

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Abstract

At Skorpion Zinc mine, in south-west Namibia, zinc oxide ore is refined through sulphuric acid leaching, solvent extraction, electrowinning and casting of the final 99.995 % Zn metal. Over the last four years, the rare earth element concentrations, with particular reference to Y, Yb, Er and Sc, have significantly increased in the circulating electrolyte and the zinc-stripped organic phase streams in the electrowinning and solvent extraction processes. This project had two main objectives: firstly, the effect(s) of rare earths on the zinc solvent extraction and electrowinning processes were to be determined; based on these results, the second objective was to find a suitable method for removing rare earth elements from the organic phase during zinc solvent extraction.

The investigation into the effect of the rare earths on zinc electrowinning showed that an increase of 100 mg/l in the electrolyte Y concentration caused a decrease of 6 % in current efficiency. The elemental order of decreasing current efficiency was found to be: Y > Yb > Er > Sc. In the zinc solvent extraction process, it was found that an increase in the total organic rare earth elements and iron concentration from 3100 to 6250 mg/l resulted in doubled viscosity and an increase in phase disengagement time from 100 to 700 seconds. The organic zinc loading capacity after two extraction stages was reduced by 1 – 3 g/l depending on the pregnant leach solution used.

The detrimental effect of rare earth elements on solvent extraction and electroplating of zinc therefore justified the development of a rare earth element removal process. Stripping of low concentrations of rare earth elements from 40% D2EHPA diluted in kerosene to produce a clean organic for zinc extraction was investigated using bench-scale experiments in a glass jacketed mixing cylinder. For the rare earths, the best stripping agent was found to be H_2SO_4, followed by HCl and then HNO_3. Hydrochloric acid achieved better Fe stripping than sulphuric acid. Acid concentration was tested in the range of 1 to 7 M, organic-to-aqueous ratio for the range of 0.25 to 6.0 and temperatures between 30 and 55 ℃. More than 80% stripping of yttrium and erbium could be achieved at an optimum hydrochloric acid concentration of 5 M and more than 90% rare earth element (specifically Y, Er, Yb) stripping from the organic phase could be achieved with 5 M sulphuric acid.

Stripping was improved by reducing the organic-to-aqueous ratio to as low as 0.5 and increasing the temperature. Stripping increased with increasing temperature in an S-shaped curve, flattening off at 50°C. The effect of O:A ratio was more significant than the effect of temperature on rare earth stripping. The results showed good repeatability, and were not limited by the rare earth concentration, agitation rate or equilibrium time in the range of set points used in the experiments.

Statistical models were compiled to fit the experimental data obtained for Y, Yb, Er and Fe when stripped with sulphuric and hydrochloric acid respectively. All models showed dependence on the acid concentration and squared-concentration and interaction effects between the O:A ratio and temperature and stripping agent concentration were significant. The models were compiled for the experimental data obtained from stripping synthetically prepared organic and then tested on results obtained when stripping the plant organic phase.

The following three process solutions were discussed for implementation on a plant scale for the removal of rare earths from the organic phase during zinc solvent extraction: Sulphuric acid stripping mixer settler or stripping column, improvement of available HCl stripping section and replacement of the organic inventory. The possibility of an oxalic acid precipitation process to obtain value from the rare earths as by-product was also discussed. It was concluded that the current process that uses HCl to strip off iron and rare earths would be the best practically and financially feasible process. Value can be gained from the rare earths if a rare earth element - oxalic acid precipitation section that is financially feasible can be established.

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Opsomming

By Skorpion Zinc myn, in suidwes Namibië, word sinkoksied erts gesuiwer deur middel van swaelsuur-loging, oplosmiddel ekstraksie, elektroplatering en gieting van die finale 99.995 % Zn metaal. Oor die afgelope vier jaar het die seldsame aardmetale konsentrasie, spesifiek Y, Yb, Er en Sc, noemenswaardig in die sirkulerende elektroliet en sink-gestroopte organiese fase toegeneem. Hierdie projek het twee hoofdoelstellings gehad: eerstens moes die effek van seldsame aardmetale op die sink oplosmiddel ekstraksie en elektroplatering prosesse bepaal word; gebaseer op hierdie resultate, was die tweede doelstelling om 'n geskikte metode vir die verwydering van seldsame aardmetale vanaf die organiese fase gedurende sink oplosmiddel ekstraksie te vind.

Die ondersoek na die effek van seldsame aardmetale op sink elektroplatering het gewys dat 'n verhoging van 100 mg/l in die elektroliet Y konsentrasie 'n verlaging van 6 % in kragdoeltreffendheid veroorsaak het. Die element-orde van verminderende kragdoeltreffendheid was Y > Yb > Er > Sc. Vir die sink oplosmiddel ekstraksie proses, is gevind dat 'n verhoging in die totale organiese seldsame aardmetaal- en yster konsentrasie van 3100 tot 6250 mg/l 'n verdubbelde viskositeit en 'n verlenging in faseskeidingstyd van 100 tot 700 sekondes tot gevolg gehad het. Die organiese sink ladingskapasiteit na twee ekstraksie stappe is met 1 – 3 g/l verminder afhangende van die logings oplossing wat gebruik is.

Die nadelige effek van seldsame aardmetale op oplosmiddel ekstraksie en sink elektroplatering het die ontwikkeling van 'n seldsame aardmetale verwyderingsproses regverdig. Die verwydering van lae konsentrasies seldsame aardmetale vanaf die D2EHPA-keroseen organiese fase om 'n skoon organiese fase vir sink-ekstraksie te verkry is ondersoek deur banktoetsskaal eksperimente. Vir die seldsame aardmetale is bevind dat H_2SO_4 die beste stropingsagent is, gevolg deur HCl en dan HNO_3. Soutsuur het beter yster verwydering as swaelsuur bewerkstellig. Suurkonsentrasies van 1 tot 7 M, O:A verhoudings van 0.25 tot 6 en temperature tussen 30 en 55℃ is getoets. Meer as 80% verwydering van yttrium en erbium kon bereik word met 'n optimum HCl konsentrasie van 5 M en meer as 90% seldsame aardmetale (spesifiek Y, Er en Yb) verwydering vanaf die organiese fase met 5 M swaelsuur.

Seldsame aardmetale en yster verwydering kon verbeter word deur die organies-tot-waterfase (O:A) verhouding te verminder tot so laag as 0.5 en deur die temperatuur te verhoog. Stroping het in 'n S-kurwe verhoog soos die temperatuur verhoog het, en het afgeplat teen 50°C. Die effek van die O:A verhouding was belangriker as die effek van temperatuur op stroping. Die resultate het goeie herhaalbaarheid gewys, en is nie deur massaoordrag beperk nie.

Statistiese modelle is saamgestel om die eksperimentele data wat vir Y, Yb, Er en Fe verkry is vir stroping met swaelsuur en soutsuur te pas. Al die modelle het afhanklikheid van die suurkonsentrasie en kwadratiese suurkonsentrasie gewys en interaksie effekte tussen die O:A verhouding, temperatuur en suurkonsentrasie was belangrik. Die modelle is saamgestel vir die eksperimentele data wat verkry is vanaf stroping van 'n sintetiese organiese fase en is toe getoets op resultate wat verkry is vanaf stroping van die aanleg se organiese fase.

Die volgende drie proses-oplossings is oorweeg vir implementering op 'n aanlegskaal vir die verwydering van seldsame aardmetale vanaf die organiese fase gedurende sink oplosmiddel ekstraksie: Swaelsuur stroping menger-afskeidingstenk of stropingskolom, verbetering van die bestaande HCl aanleg en vervanging van die organiese inventaris. 'n Moontlike oksaalsuur presipitasie proses om waarde vanaf die seldsame aardmetale as by-produk te verkry is ook bespreek. Daar is tot die gevolgtrekking gekom dat die huidige proses wat HCl gebruik om yster en seldsame aardmetale van die organiese fase af te stroop, die beste praktiese en finansieel vatbare proses huidiglik is. Waarde kan vanaf die seldsame aardmetale verkry word as 'n seldsame aardmetale – oksaalsuur presipitasie afdeling wat finansieel haalbaar is daargestel kan word.

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Nomenclature

C	concentration
CE	current efficiency
D2EHPA	di-2-ethylhexyl phosphoric acid
EW	electrowinning
F	Faraday's constant
HR	D2EHPA molecule represented by H for the acid proton and R for the organophosphorous part in reactions
i	applied current
mt	metric ton
M	metal, for e.g. Zn, as used in reactions
M_w	molecular weight
n	oxidation state
O:A ratio	organic-to-aqueous ratio
OAC	organic-to-aqueous ratio-concentration interaction
OAT	organic-to-aqueous ratio-temperature interaction
PLS	pregnant leach solution
REE	rare earth element(s)
rpm	revolutions per minute
SX	solvent extraction
t	plating time
T	temperature
Y	yttrium, also representative of rare earths when used in reactions

Chapter 1: Introduction

1.1   Importance of solvent extraction in the metallurgical industry

Solvent extraction is currently one of the most important separation processes in hydrometallurgy and is used in the processing of Cu, Ni, Zn, Co, U, V, Zr, rare earth elements (REE) and the platinum group metals (Flett, 2005). This technology has the ability to selectively extract one element from a mixture of elements under certain pH conditions, enabling the purification of a metal or separation of different metals from one another. Different types of extractants are available, with different selectivities for specific metals. The solvent extraction process can have co-current or counter-current flow, although counter-current flow is more often used industrially (Gupta and Krishnamurthy, 2005).

Commercial solvent extraction bloomed in Southern Africa in the early 1970s, being applied to copper, uranium and the platinum group metals. Solvent extraction is currently still used in this region for gold extraction at Harmony Gold Mine in South Africa, copper extraction in the Copper Belt in Zambia, cobalt extraction at Kasese Cobalt in Uganda, Chambishi Metals in Zambia and Kolwezi Tailings in the Democratic Republic of Congo. Solvent extraction is also used to produce nickel at Tati Nickel in Botswana and to recover nickel and palladium from spent catalyst at Mintek, South Africa. At Anglo Platinum Rustenburg's and Impala Platinum's Base Metals refineries, Cyanex 272 is used to achieve nickel and cobalt separation (Cole *et al*., 2006). The other important application of solvent extraction is the separation of rare earth elements from one another so that value can be gained from the pure product, since most REE applications require high purity rare earth elements as raw material (Gupta and Krishnamurthy, 2005).

Solvent extraction is utilized at Skorpion Zinc to selectively recover zinc from the pregnant leach solution (PLS) produced by leaching of zinc silicate oxide ore. Di-2-ethylhexyl phosphoric acid (D2EHPA), which is a cation exchange extractant, ensures that selective extraction of zinc is achieved, while Cu, Co, Cd and Ni as well as the halides are rejected. Cu, Co, Cd, Ni, Cl and F are detrimental to zinc electrowinning. The solvent extraction process also allows for the solution zinc content to be upgraded from 35 g/l (as a result of the high silica content) in the leach liquor to 115 g/l in the loaded electrolyte. The selectivity of the solvent extraction process therefore allows production of zinc by means of electrowinning despite the large amount of trace impurities present in the leach solution, and it is critical to the existence of Skorpion Zinc mine (Martin, *et al*., 2002 and Cole *et al*., 2006).

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1.2   The Skorpion Zinc process

The Skorpion Zinc process was designed to produce 150 000 mt super high grade zinc per year. The refining process is shown in Figure 1 (Gnoinski, 2007). The refinery is designed to treat 200 t/h zinc silicate oxide ore. After comminution, the ore is leached with sulphuric acid to obtain zinc in aqueous form. After leaching, the slurry is neutralised to a pH of 4.2 to precipitate elements such as Al, Fe and Si which have co-leached with zinc, and then thickened. Approximately 75% of the thickener overflow solution (pregnant leach solution) is clarified and pumped to the solvent extraction process while the other 25% is treated with zinc dust to precipitate Cu, Cd and Ni before being recycled to the process feed. After thickening, the solids are reacidified with sulphuric acid to re-leach precipitated zinc. The slurry is then filtered and the solids disposed of as tailings. The liquid filtrate is treated with limestone and milk of lime to precipitate any remaining zinc as basic zinc sulphate, which is returned to the neutralization section of the plant.

The pregnant leach solution contains approximately 35 g/l Zn. In the solvent extraction process, di-2-ethylhexyl phosphoric acid (D2EHPA) diluted in kerosene is used to selectively extract zinc from the pregnant leach solution at a pH of 4.2 – 4.4 and a temperature of 43°C. The solvent extraction process used at Skorpion Zinc is the modified Zincex process patented by Técnicas Reunidas (Martin, *et al.*, 2002). After extraction of zinc into the organic, the organic phase is washed with demineralised water and spent electrolyte from the downstream electrowinning process to remove impurities. Spent electrolyte from the electrowinning plant is then used to strip the zinc from the D2EHPA and produce loaded electrolyte of a quality which can be fed to the cell house for zinc electroplating. Once the zinc has been stripped, part of the organic phase stream is regenerated with 5 M HCl in order to remove iron, which is co-extracted with zinc.

In the cell house, zinc is plated at 175 kA on aluminium cathodes. The zinc electrowinning plant is very sensitive to impurities such as Ni, Cu, Co and Cd, which lowers the hydrogen overpotential, resulting in excessive hydrogen formation and hydrogen fires in the cell house (Gnoinski, 2007). Through selective extraction of zinc, the solvent extraction plant makes the operation of the zinc cell house possible by effectively reducing the impurity content from the mg/l range in the pregnant leach solution to the μg/l range in the electrolyte. The product from the cell house is super high grade (SHG) zinc cathodes which are then melted to produce ingots or jumbos containing more than 99.995% Zn.
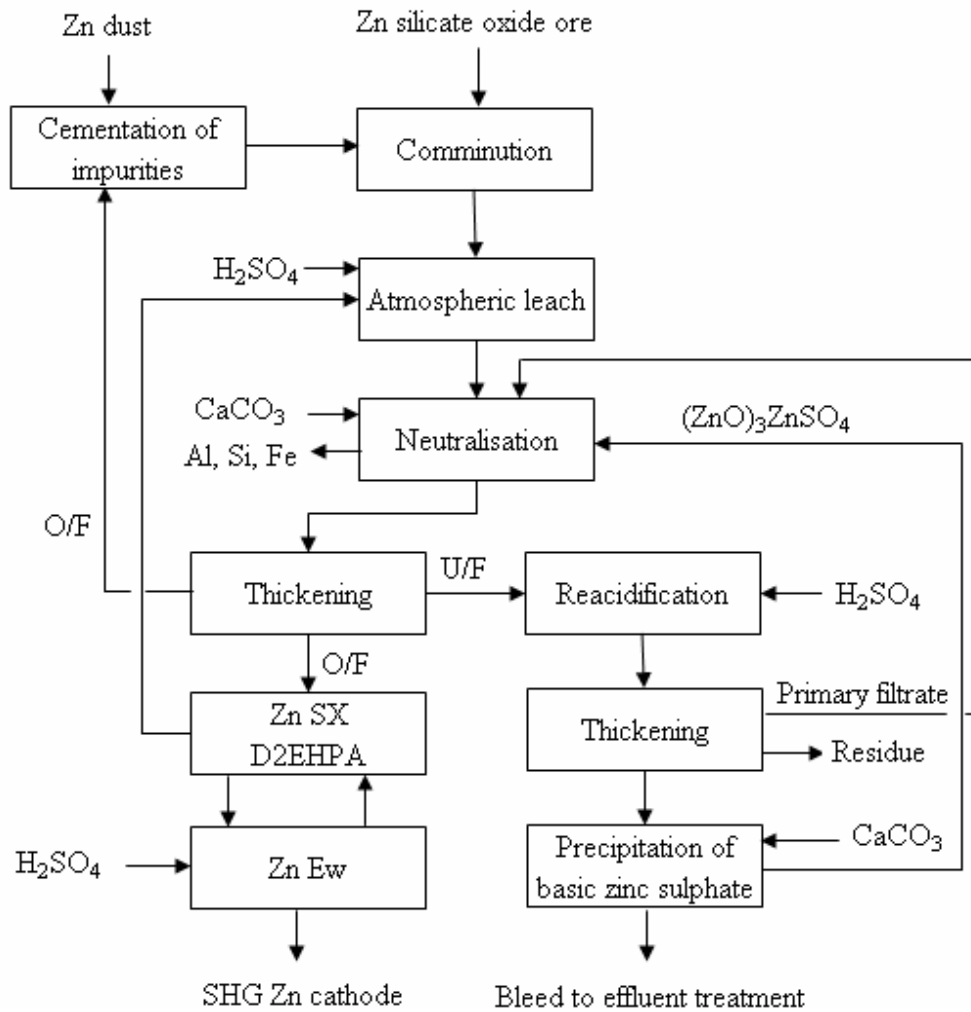
Figure 1: Skorpion Zinc process flow diagram

1.3 Rare earth history

1.3.1 Rare earth occurrence and uses

Rare earths occur in different mineralogical forms, of which carbonatites are the most common. Although the occurrences of rare earths are widespread, rare earths are not always found in high enough concentrations to make mining and refining feasible (Wall, 2011). China is the world's largest rare earth producer, producing 95% of the world supply at its Bayan Obo, Sichuan and Jiangxi mines (Tse, 2011). The United States of America (Mountain Pass in California), Malaysia and Australia also produce rare earths (Gupta and Krishnamurthy, 2005).

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Different rare earth elements have different applications, ranging from magnet manufacturing, petroleum cracking, catalytic converters, radar detection, nuclear plants, ceramics and glass manufacturing, polishing powder and hydrogen storage. While the entire world is dependent on rare earths for many new and green technology applications, China is in a position to govern the rare earth element prices to a large extent given their monopoly on world production of these elements (Tse, 2011 and Hurst, 2010).

1.3.2   Source of rare earths at Skorpion Zinc

Although Skorpion Zinc mine does not produce rare earths, it has been found that certain rare earth elements accumulate in the process streams. An attempt was made to determine what the sources of the rare earths were. Twelve samples were collected from different areas of the Skorpion Zinc mine pit and analysed for rare earth elements in order to determine the origin of the increasing REE concentration seen in some of the refinery process streams. Although twelve samples cannot be considered representative of an entire mining pit with a cross-sectional area of more than 1 km^2, the results gave a better understanding of the possible high-potential REE areas. From Figure 2 it can be seen that the greatest concentration of rare earths occur where the ore body is enriched with manganese and iron in the Core West part of the pit and also in the white schist (SSS) layer in the Central North area of the pit. These are mostly waste areas of ore body. The main elements present are Ce, Y, La, Nd and Er.
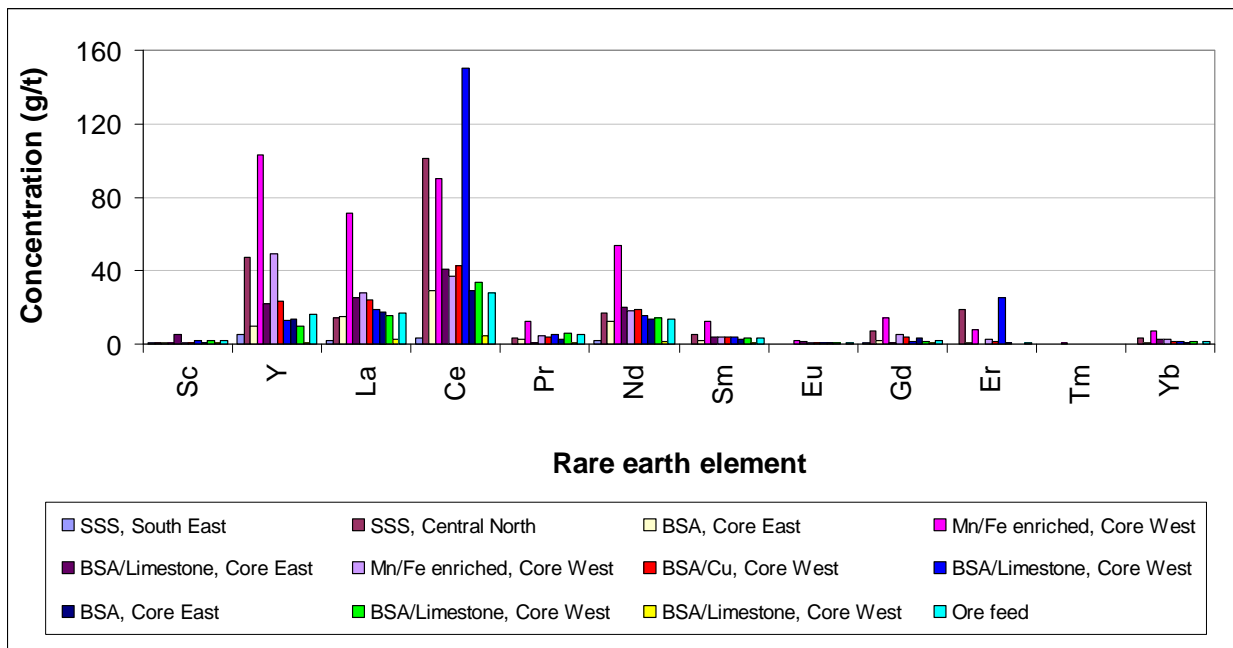
Figure 2: Rare earth concentration of mined material (ore and waste)

As discussed previously, ore fed to the refinery is leached with sulphuric acid and neutralised with limestone. The zinc is contained in the pregnant leach solution while the solids are disposed of as tailings. Comparing the rare earth element concentrations in the liquid and solid streams (see Figure 3) it was seen that the solid streams contain higher concentrations of rare earths. The residue solids after neutralisation with limestone also contain more rare earths than the solids obtained after leaching. This suggests that rare earth precipitation with limestone occurs during neutralisation, reducing the REE concentration in the neutralisation residue liquid (PLS) going to the solvent extraction process.

The percentage of rare earths that are dissolved during leaching and the percentage reporting to the solids are indicated in Figure 4. The percentage in the solids is a combination of rare earths not leached and rare earths precipitated during neutralisation. It was seen that Y, Gd, Er and Yb are easily leached, while the rest of the elements remain in the solids. Y, Gd and Yb are then precipitated again, while Er showed a low tendency to precipitate. However, it should be taken into consideration that the analysis results presented in Figures 3 and 4 were obtained from taking one batch of samples and that it was not verified by taking more samples at other times and operating conditions and comparing the results. However, it does give an idea of the relative dissolution, precipitation and concentration of rare earth elements in the leaching and neutralisation process streams.
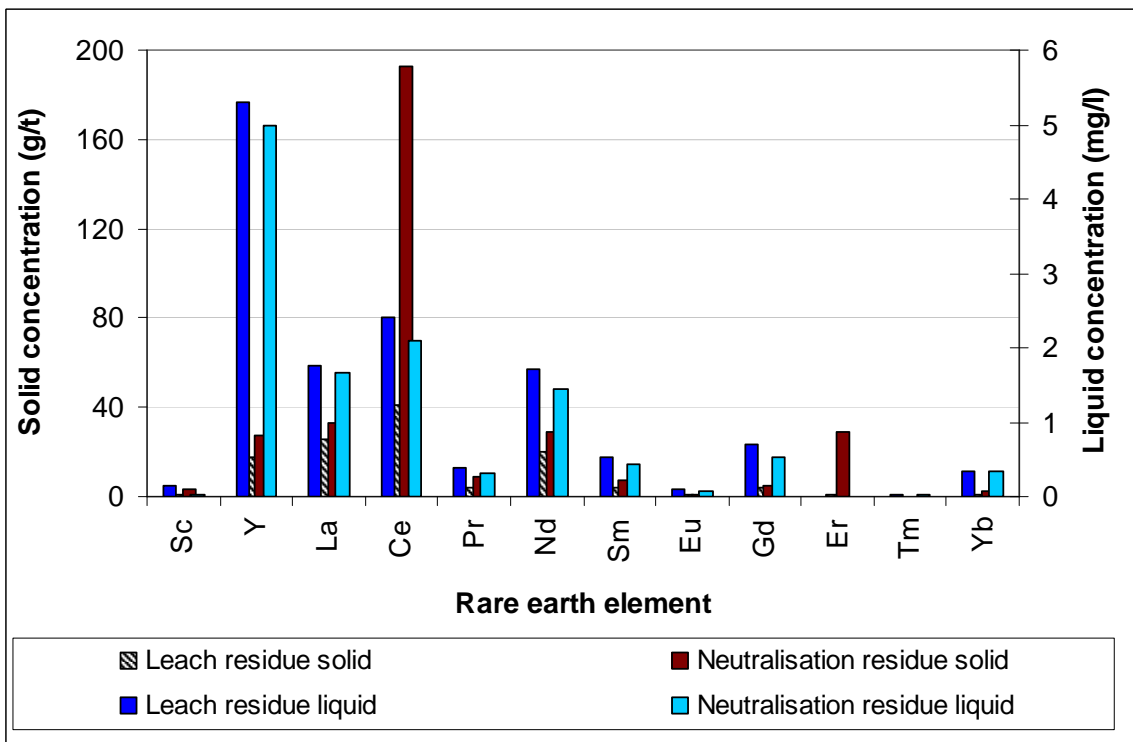
Figure 3: Rare earth concentration of leached and neutralised ore
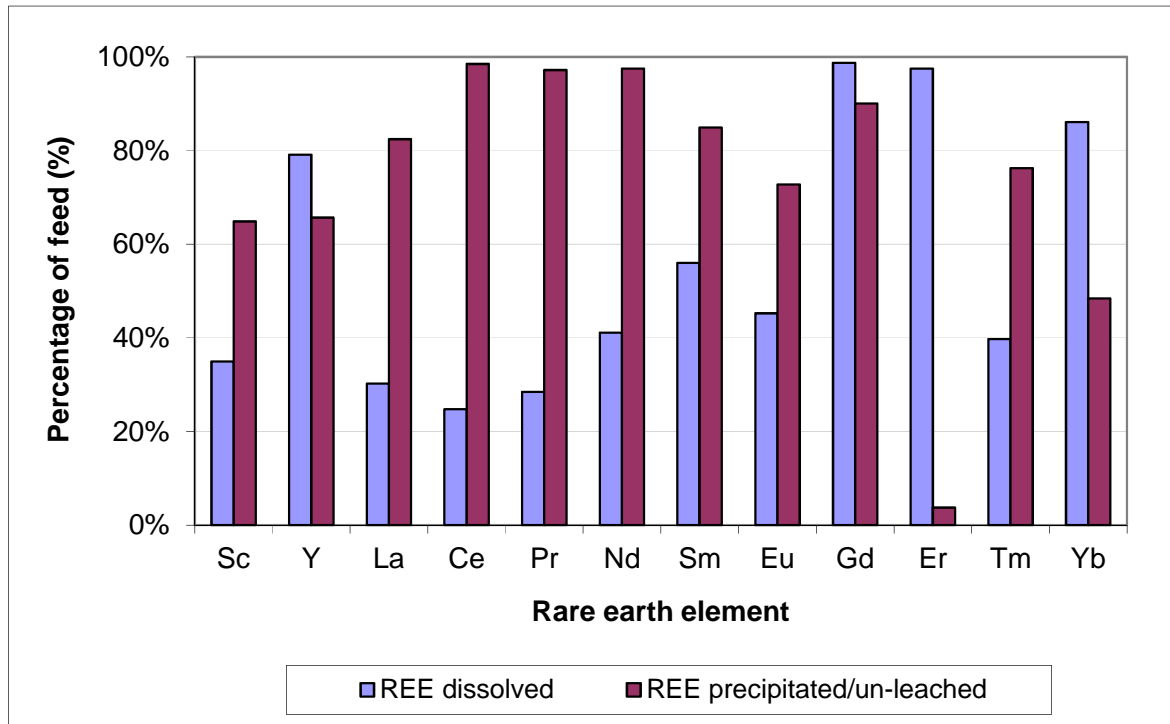
Figure 4: Percentage of REE in ore feed that is leached and precipitated/un-leached

1.3.3 Rare earth concentration in process streams

Figure 5 shows the rare earth concentration of the process streams in the solvent extraction and electrowinning processes. The organic streams (stripped organic and regenerated organic) shows an accumulation of Y, Yb, Er, Sc and Lu, whereas the aqueous streams (spent and loaded electrolyte) shows a build-up of Y, Er, Yb, Nd, Sm, Gd and Ce. Yttrium is therefore present in high concentration in the incoming ore, as well as in all other process streams. Yb, Er, Sc and Lu seem to be more easily extracted onto the organic phase and less easily stripped, while Nd, Sm, Gd and Ce are not easily extracted, but almost all of what is extracted is stripped off and accumulates in the electrolyte streams. The presence of Y, Yb and Er in the bleed stream from the hydrochloric acid plant used for organic regeneration indicates that some rare earths are stripped off during organic regeneration with HCl.
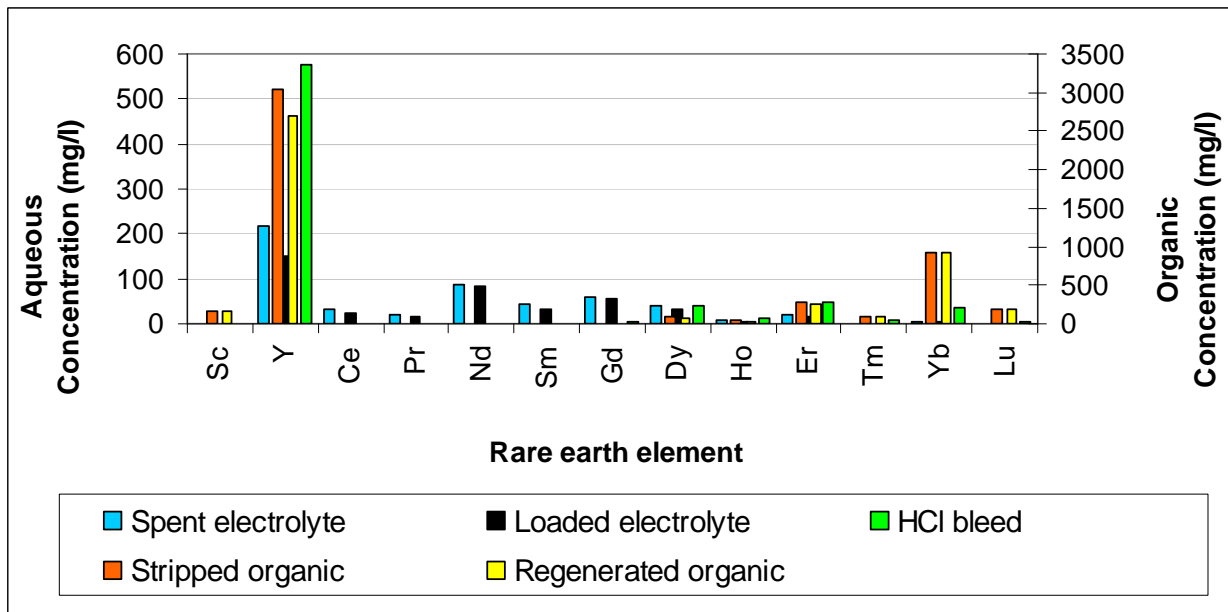
Figure 5: Rare earth concentration of organic and aqueous streams in SX and EW

Figure 6 shows the flow rates and relative concentrations of zinc and rare earths in the solvent extraction and electrowinning process streams as at January 2011. Over the past 4 years it has been found that the concentration of rare earth elements (yttrium in particular) in the zinc-stripped organic phase is increasing (see Figure 7). The rare earths in the incoming pregnant leach solution (PLS) seem to remain constant (see Figure 8), while the electrolyte solution circulating between the solvent extraction plant and the cell house also showed an increase in rare earths, as shown in Figure 9.

Nr	Stream name	Flow rate (m³/h)	Zn (g/l)	Total REE (mg/l)
1	Organic (40%D2EHPA-60%Kerosene)	1400	<1	4750
2	Raffinate	1100	12	15
3	Pregnant leach solution	950	35	20
4	Wash solution	50	30	unknown
5	Loaded electrolyte	300	115	420
6	Spent electrolyte	300	45	540
7	Spent HCl	5	0	unknown
8	Regenerated HCl	5	0	unknown
9	Regenerated organic	20	<1	4350
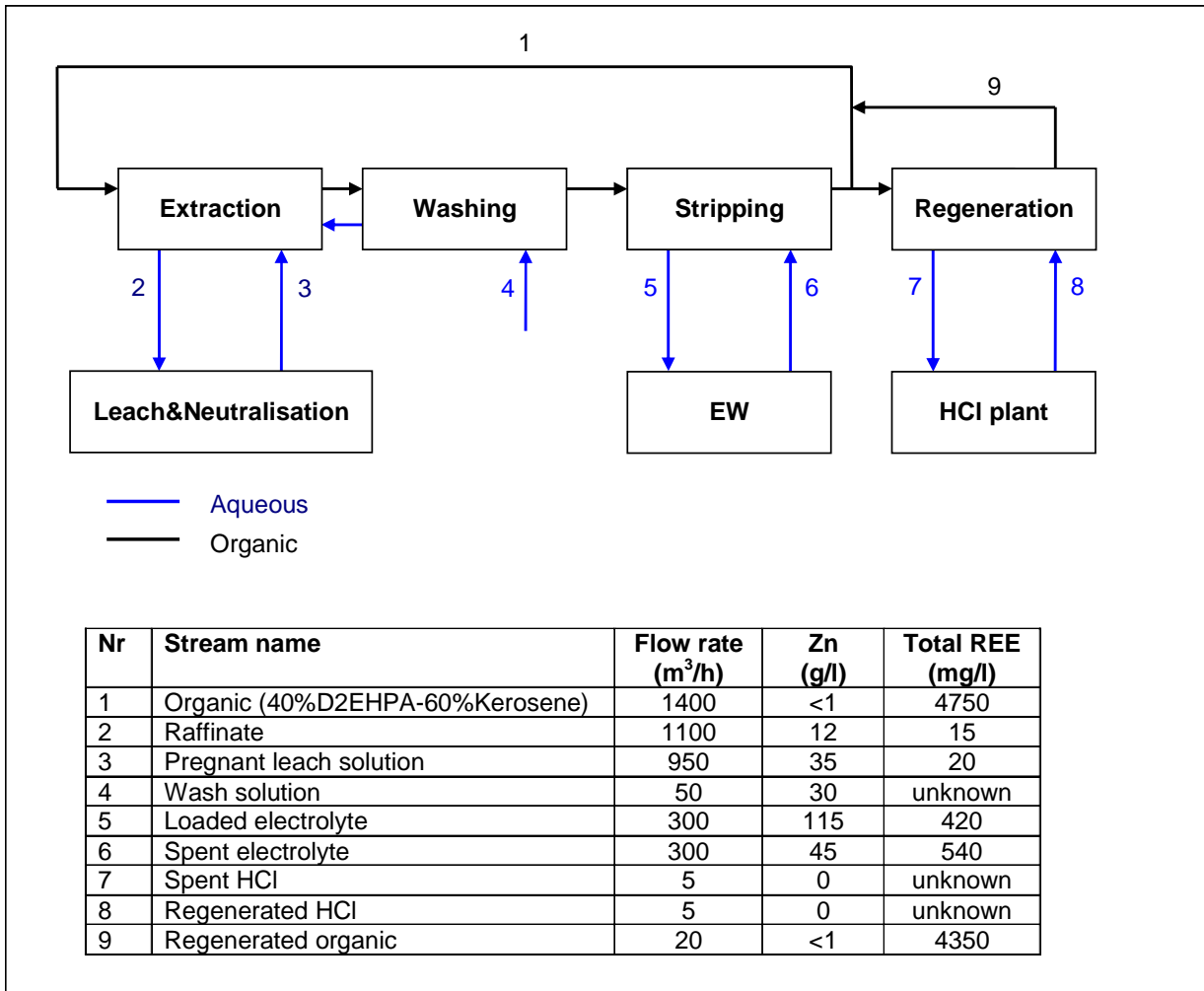
Figure 6: Skorpion Zinc neutralisation, solvent extraction and electrowinning process streams
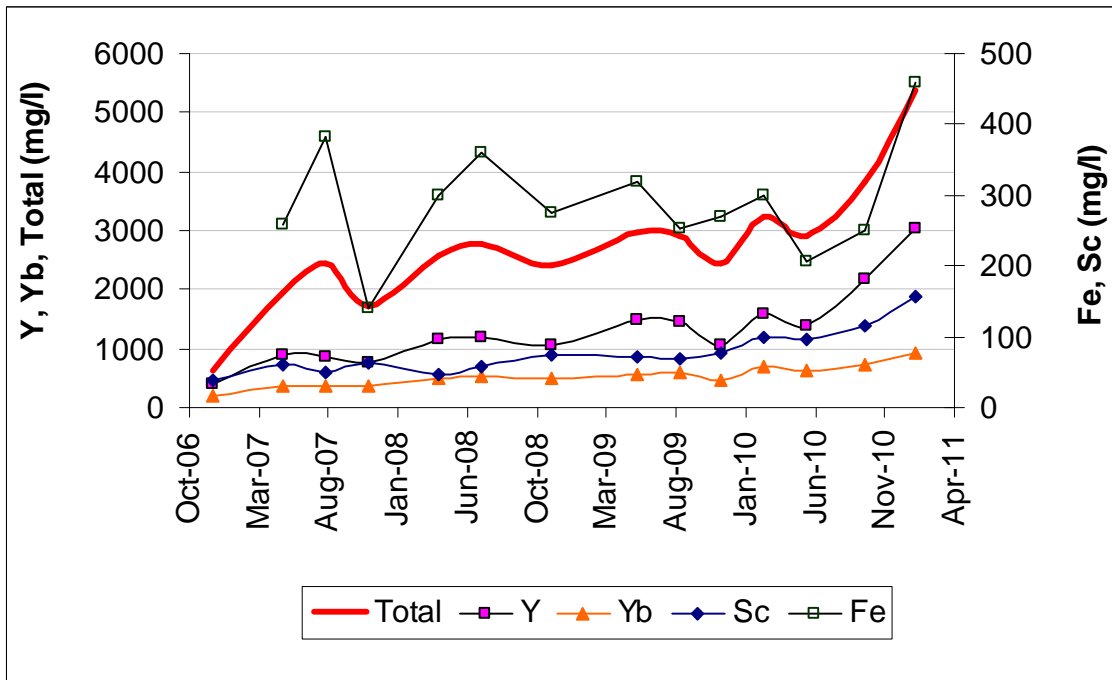
Figure 7: REE analysis of zinc-stripped organic
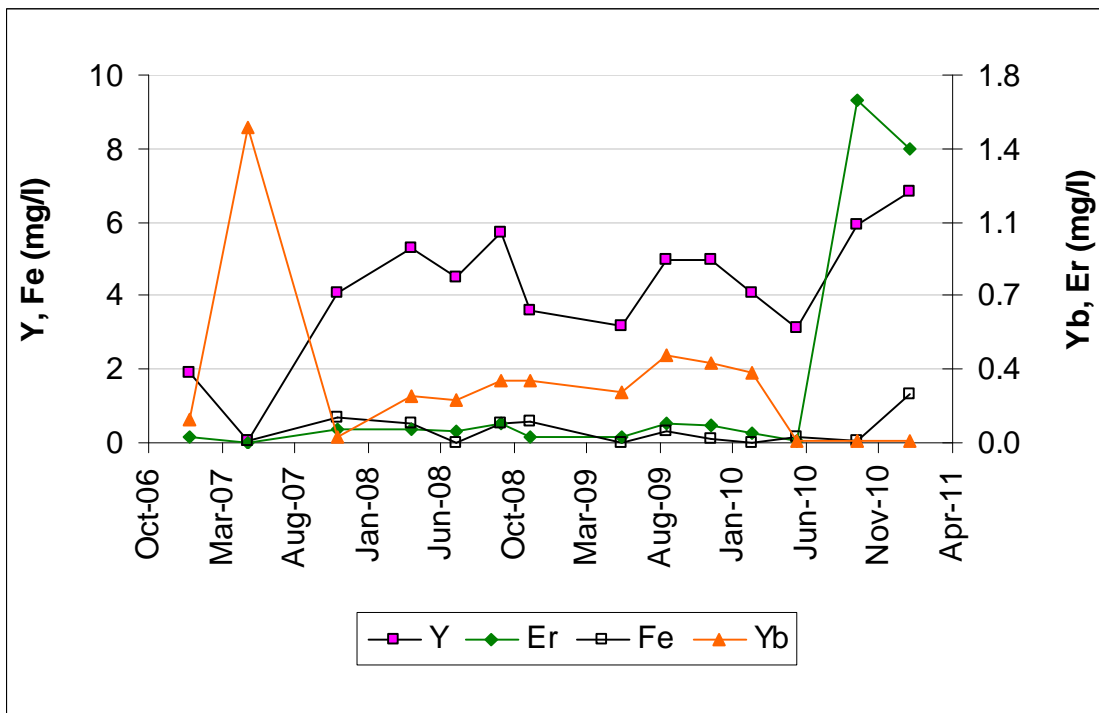
Figure 8: REE analysis of incoming pregnant leach liquor (PLS)
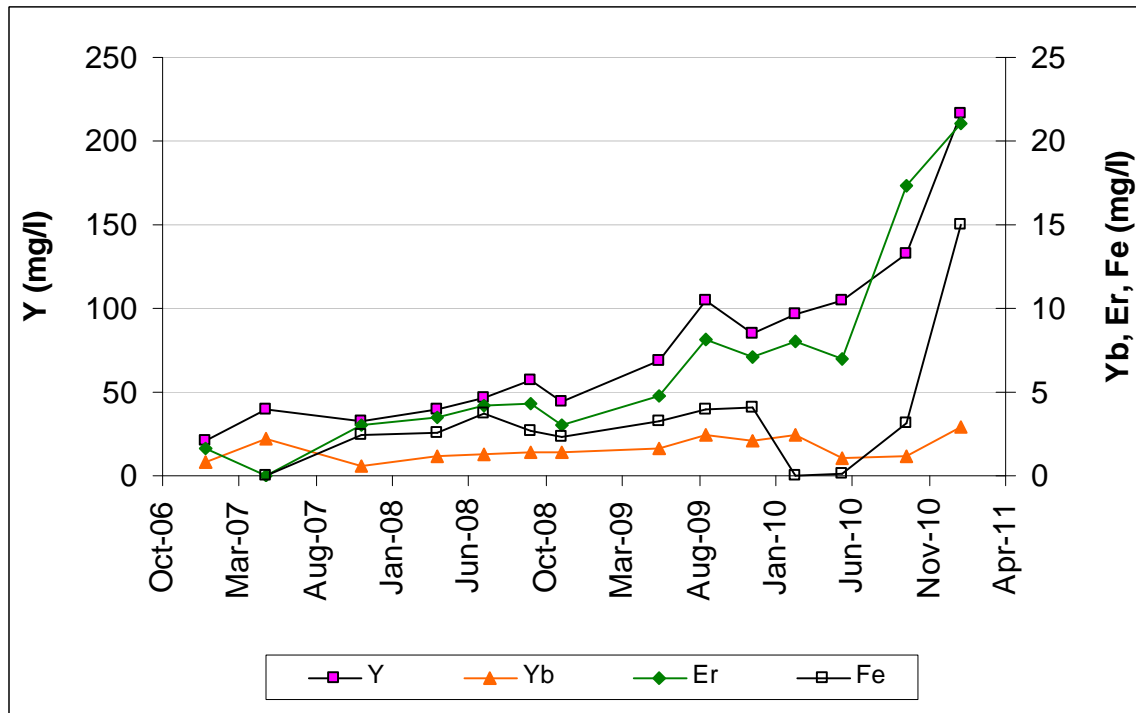
Figure 9: REE analysis of spent electrolyte from the cell house

1.3.4 Relevance of rare earths for Skorpion Zinc

An increase in the concentration of rare earth elements (REE) in the organic phase was a concern for four reasons: firstly, excessive rare earth loading leads to the formation of gel (Sole, 2011), which settles to the bottom of the washing stage settlers and lead to costly clean-up operations. From XRF analysis of the dried gel in February 2010, December 2010 and January 2011, it was found that the gel was mostly composed of the organic phase, zinc, rare earths, particularly yttrium, ytterbium and scandium, and iron (Sole, 2010). The recommended zinc loading on the organic phase is 14 g/l, although the practically possible loading on a plant scale is 18 g/l Zn according to Técnicas Reunidas (Diaz, 2011). As is seen in Figure 7 the current rare earth loading on the organic phase is more than 5 g/l.

Secondly, the high rare earth concentration in the organic phase also means that numerous sites on the organic are occupied by elements such as Y and Yb, reducing the amount of sites available for zinc extraction and therefore reduces the capacity of the solvent extraction process.

Thirdly, apart from causing gel-formation under excessive loading, the effect of the increased presence of REE on the solvent extraction chemistry and phase separation was unknown.

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Lastly, the effect of rare earths on zinc plating and current efficiency in the cell house, if rare earths are transferred from solvent extraction to electrowinning, was not known.

The purpose of this project was therefore to determine the effects of rare earth elements on the solvent extraction and electrowinning processes and to find a suitable process for removal of the accumulated rare earth elements from the organic. Research work on solvent extraction in the rare earth industry has been done by a number of authors (Hirashima *et al.*, 1978, Gupta and Krishnamurthy, 2005, Rachandra Rao, 2006 and Weiwei *et al.*,2006). This literature was used to obtain the basis parameters for the project based on the assumption that stripping REE from an organic phase after zinc solvent extraction is similar to stripping REE from organic during rare earth refining. This assumption was considered valid since the organic phase under consideration was D2EHPA in kerosene, which is commonly used on an industrial scale for rare earth extraction (Gupta and Krishnamurthy, 2005)

1.4 Objectives

The objectives of the project were twofold: firstly, to determine what the effect(s) of rare earths are on the zinc solvent extraction and electrowinning processes, and secondly to find a suitable method for removing rare earth elements from the organic phase during zinc solvent extraction.

The scope of the project is limited to determination of the effect of REE on solvent extraction and electrowinning, detailed stripping tests and proposition of a suitable REE removal process, and does not include detailed design and implementation of such a process.

The following actions were performed in order to achieve the objectives of the project:
- Show the effect, if any, that rare earth elements, particularly yttrium, have on the current efficiency during the electrowinning of zinc.
- Show the effect, if any, that rare earth elements have on the organic phase characteristics during solvent extraction.

- Report on the very basic chemistry involved in REE extraction and stripping.
- Find the optimum stripping agent and stripping agent concentration for the rare earths yttrium, erbium and ytterbium, as well as for iron.

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- Investigate the effect of temperature and O:A ratio and possible interactions between the two on rare earth stripping.
- Compare the rare earth stripping achieved for Skorpion Zinc plant organic phase with that achieved for synthetic organic.
- Provide statistical models for the data obtained.
- Suggest a practically feasible process for rare earth removal that can be implemented on a plant scale.
- Do a preliminary financial feasibility assessment of the process to be implemented at Skorpion Zinc for rare earth removal.

1.5   Thesis Overview

The project first looked at the effects of rare earth elements on the Skorpion Zinc solvent extraction and electrowinning processes. Based on the results, an investigation into the stripping of rare earths from the organic phase used in solvent extraction was justified. The stripping process was investigated on a laboratory scale and a possible plant-scale process is discussed.

The thesis is structured around the project objectives, with the literature review discussed first, followed by the experimental design and method used. Thereafter the experimental results for the effect of rare earths on zinc electrowinning are presented in Chapter 4 and the effect on organic phase health in Chapter 5. Chapter 6 is where the experimental results for stripping rare earths from the organic phase are discussed. The thesis is concluded with possible processes which can be implemented on a plant scale, also including recommendations for further investigations.

Chapter 2: Literature Review

2.1 Zinc Electroplating

The Skorpion Zinc cell house was designed to produce 153 000 mt of cathodic zinc per year at a nominal current density of 400 A/m^2 and a maximum of 460 A/m^2 (Umicore Engineering Process and Operation manual, 2001). The design current efficiency is 90% but the average current efficiency achieved over the last year was 88%. During zinc electroplating the cathodic reaction is:

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad \text{[Equation 1]}$$

The above equation has reversible potential of -0.793 V vs SHE (standard hydrogen electrode). The anodic reaction is:

$$H_2O - 2e^- \rightarrow 2H^+ + \tfrac{1}{2}O_2 \qquad \text{[Equation 2]}$$

Including the anodic and cathodic reaction reversible potentials, overpotentials and resistances involved, the potential needed for zinc metal plating is 3.2 – 3.4 V between the anode and the cathode.

The current efficiency can be calculated from:

$$\%CE = \frac{mass\_plated}{theoretical\_mass\_plated} \times 100 \qquad \text{[Equation 3]}$$

Where the actual mass plated is weighed in grams and the theoretical mass is calculated from:

$$theoretical\_mass\_plated = \frac{M_w\,it}{nF} \qquad \text{[Equation 4]}$$

Where M_w is the molecular weight of Zn in this case, i is the applied current in A, t is the plating time in seconds, n is the oxidation state of Zn and F is Faraday's constant in Coulomb/s.

The effect of rare earth elements, and yttrium in particular, on the current efficiency is not known and no previous work on the subject could be found in literature. No literature could be found on the mechanism by which rare earths influence zinc electrowinning or electrowinning of other metals. The effect of rare earths on zinc electroplating was also discussed with two experts in the field of zinc electroplating (Dewalens, 2011 and Nicol, 2011) and neither could shed light on the mechanisms which might cause the electrolyte rare earth concentration to affect zinc plating or how it would affect zinc plating.

2.2 Organic health

Organic health is the combination of characteristics that quantifies the performance of the organic phase and is measured by measuring its viscosity, zinc loading capacity and the phase disengagement time when mixed with an aqueous phase. Any reference hereafter to "organic health" refers to the viscosity, zinc loading capacity and phase disengagement characteristics of the organic phase.

Standard validation tests (Skorpion Zinc Solvent Extraction Operational Manual, 2003) are used to determine the condition of the organic phase ("organic health") in terms of its characteristic phase disengagement time, viscosity and zinc loading capacity. These organic characteristic properties need to be monitored continuously to ensure that it meets the minimum requirements specified by Técnicas Reunidas for the modified Zincex$^{©}$ process (Martin *et al.*, 2002). The phase disengagement time should be below 200 seconds and the zinc loading at 22 g/l for the laboratory bench scale tests. Viscosity should be less than 5 mPa.s and is usually compared to fresh organic.

The organic phase that is validated is the zinc-stripped organic phase. The viscosity and density of di-2-ethylhexyl phosphoric acid decrease with temperature as shown in Tables 1 and 2 (Rhodia, 2010). Phase disengagement time is affected by the density difference between the liquids in the emulsion, the rate of diffusion and the rate of coalescence. The rate of diffusion is affected by temperature and viscosity. This was confirmed by Musadaidzwa and Tshiningayamwe (2009) who observed that as the viscosity increases, the phase disengagement time increases. One of the factors affecting the rate of coalescence is the pH, with the rate of coalescence increasing as the pH decreases since a reduction in pH causes a reduction in interfacial tension (Hoh *et al.*, 1986). Hoh *et al.* (1986) considered specifically the lanthanum nitrate-D2EHPA-diluent system but the findings indicate that the type of extractant and diluent, and the pH affects interfacial tension and not the specific rare earth element under consideration.

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Mansur *et al.* (2001) found that the zinc extraction reaction kinetics are controlled jointly by both the chemical reaction rate and diffusion, while the stripping reaction is purely diffusion controlled. The increased viscosity of the organic complex when loaded with zinc and the high viscosity of the D2EHPA organic phase limit mass transfer and therefore reduce the reaction rate during extraction and stripping operations (Bart and Rousselle, 1998 and Mansur *et al.,* 2001).

Table 1: D2EHPA viscosity related to temperature

Temperature °C	Viscosity mPa.s
0	160
20	56
40	21
100	4.4

Table 2: D2EHPA density related to temperature

Temperature °C	Density g/cm^3
25	0.974
40	0.952
60	0.937

2.3   D2EHPA and kerosene organic phase characteristics

Di-2-ethylhexyl phosphoric acid (D2EHPA) is used as the extractant of choice for extraction of Zn^{2+} at Skorpion Zinc. It is also widely used in the rare earth industry for solvent extraction of rare earth elements and separation extraction of different rare earths. Kerosene is the diluent of choice used at Skorpion Zinc for zinc solvent extraction, but has been shown to also be the best diluent to use for rare earth extraction (Gupta and Krishnamurthy, 2005). D2EHPA is discussed here to give better insight into the experimental results discussed later in the report.

The industrial D2EHPA used by Skorpion Zinc, and which was also used for the test work in this project, has a 95% di-2-ethylhexyl phosphoric acid (D2EHPA) concentration (minimum), with a maximum of 3% mono-ethylhexyl phosphoric acid (MEHPA) and 5% water. D2EHPA is an acidic extractant which can deprotonate to form the following anion (Rhodia, 2010):

$$(C_8H_{17}O)_2\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{P}}\text{-OH} \leftrightarrow (C_8H_{17}O)_2\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{P}}\text{-O}^- + H^+$$

[Equation 5]

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The anion is hydrophobic and can chelate a cation from an aqueous phase to form an organic-soluble chelate. Extraction by D2EHPA is pH dependant, as discussed in Chapter 2.5, but also depends on the structure of the chelate and the valence of the cation (Rhodia, 2010).

The viscosity of the organic phase increases with loading (Kumar and Tulasie, 2005 and Kolarik and Grimm, 1992). Kumar and Tulasi (2005) proposed a reaction mechanism which involves aggregation of the metal-organic complexes in the bulk organic phase at high zinc loading conditions. The MR_2 complexes (where M is the metal ion and R the D2EHPA anion), formed as discussed below in Chapter 2.5, combine to form larger M_2R_4 complexes which have a severe effect on the viscosity of the organic phase. The viscosity can be decreased by the addition of a small amount of extractant which will break up the large complexes (Kumar and Tulasi, 2005).

A high D2EHPA concentration also increases the viscosity (Mansur *et al.*, 2001). The D2EHPA concentration should be high enough to provide sufficient extraction capacity, but not as high as to compromise viscosity. Kerosene diluent addition is used to maintain the desired D2EHPA concentration.

2.4 Rare earth and iron properties

The rare earth elements are located in the lanthanide series on the Periodic Table. In a phenomenon known as lanthanide contraction, their atomic radii are reduced by the increased effective nuclear charge over the sixth row transition elements (Gupta and Krishnamurthy, 2005). Lanthanide contraction is responsible for the high densities of the rare earths and their very similar chemical properties. Separation of a mixture of rare earths into individual elements is therefore not easy. With the exception of samarium and ytterbium, which have oxidation states of 2+, and cerium, which is tetravalent, all the other rare earth elements, including yttrium, have oxidation states of 3+. The tetravalent ion is preferentially extracted to the trivalent ion, which is again better extracted than the divalent ion (Gupta and Krishnamurthy, 2005).

Yttrium has a similar outer electron arrangement to that of the heavier lanthanides and also a similar size due to lanthanide contraction. Yttrium has properties similar to the heavier lanthanides and is often found with the heavier rare earths in nature. Yttrium is therefore also included as a heavy rare earth, having properties to occur as a pseudo-lanthanide between erbium and ytterbium.

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Based on the concentrations displayed on the graphs in Chapter 1, the elements of main interest for this work are scandium, yttrium, ytterbium and erbium. Table 3 displays some of the properties of these elements. It should be noted that scandium is not strongly affected by lanthanide contraction since it has a very small ionic radius. The chemistry of scandium is therefore very different from the other rare earths and it is not expected to show the same extraction and stripping behaviour.

Table 3: Properties of rare earth elements (Gupta and Krishnamurthy, 2005)

Element	Atomic number	Atomic mass g/mol	Valence	Density g/cm^3
Scandium	21	44.96	2	2.989
Yttrium	39	88.91	3	4.469
Erbium	68	167.26	3	9.066
Ytterbium	70	173.04	3 or 2	6.966

Iron is a transition metal ion and not a rare earth element, but seems to behave similarly to the lanthanides with regard to its extraction and stripping behaviour onto/from the organic phase.

2.5 Solvent extraction fundamental chemistry

During zinc solvent extraction, zinc is extracted according to equation 6, where D2EHPA is represented by *RH* (Skorpion Zinc Solvent Extraction Operational Manual, 2003):

$$ZnSO_4 + 2RH \leftrightarrow R_2Zn + H_2SO_4 \quad\quad\quad \text{[Equation 6]}$$

The zinc-loaded organic phase is then washed with spent electrolyte and demineralised water which removes impurities by the following displacement reaction, where *M* is other base metal ions:

$$R_2M + Zn^{2+} \leftrightarrow R_2Zn + M^{2+} \quad\quad\quad \text{[Equation 7]}$$

After washing, zinc is stripped from the organic to the aqueous phase (namely sulphuric acid spent electrolyte) to produce loaded electrolyte for the downstream electrowinning process:

$$R_2Zn + H_2SO_4 \leftrightarrow ZnSO_4 + 2RH \quad\quad\quad \text{[Equation 8]}$$

However, during the solvent extraction process of zinc, the organic phase is poisoned by other elements, specifically iron, rare earths and scandium, which are co-extracted with the zinc and

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accumulate on the organic. Iron is co-extracted with zinc according to (Skorpion Zinc Solvent Extraction Operational Manual, 2003):

$$Fe_2(SO_4)_3 + 6RH \leftrightarrow 2R_3Fe + 3H_2SO_4 \qquad \text{[Equation 9]}$$

Once the zinc has been stripped from the organic, the organic phase is regenerated by removing the iron with HCl (Skorpion Zinc Solvent Extraction Operational Manual, 2003):

$$R_3Fe + 3HCl \rightarrow 3RH + FeCl_3 \qquad \text{[Equation 10]}$$

Since rare earths are present in low concentrations, it is suspected that the elements are extracted onto D2EHPA to form chain polymer D2EHPA complexes which could have gel characteristics (Anticó *et al.*, 1996). Since Fe^{3+} is also present in low concentrations it may form chain polymers according to equation 11 instead of reacting according to reaction 9. The rare earth extraction or organic poisoning reaction is therefore (Anticó *et al.*, 1996 and Gupta and Krishnamurthy, 2005):

$$(Y^{3+})_{aq} + 3((RH)_2)_{org} \leftrightarrow (YR_3.3HR)_{org} + 3(H^+)_{aq} \qquad \text{[Equation 11]}$$

where rare earths are represented by the symbol for yttrium, Y.

The organic phase can then be stripped of rare earths by the reaction shown in equation 12 (Doyle *et al.*, 1993 and Konishi *et al.*, 1998), where H^+ is provided by an acid such as HCl, HNO_3 or H_2SO_4, or alternatively the H^+ can be replaced by Na^+ when using NaOH. The equilibrium constant for the stripping reaction is given in equation 13. It shows that the reaction is strongly dependent on pH, with the equilibrium constant inversely proportional to $[H^+]^3$.

$$YR_3.3RH + 3H^+ \leftrightarrow Y^{3+} + 3R_2H_2 \qquad \text{[Equation 12]}$$

$$K = \frac{[Y^{3+}][(HR)_2]^3}{[YR_3.3HR][H^+]^3} \qquad \text{[Equation 13]}$$

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To remove rare earths from the after-stripping solution, further processing is possible by precipitation with oxalic acid (Doyle *et al.*, 1993 and Konishi *et al.*, 1998):

$$2Y^{3+} + 3(COO^-)_2 \rightarrow Y_2((COO)_2)_3 \hspace{3cm} \text{[Equation 14]}$$

The rare earth oxalate can then be further converted to an oxide by calcination if desired.

2.6   Variables affecting rare earth stripping

2.6.1   Stripping agent type and concentration

Limited information is available on rare earth removal from the specific D2EHPA-kerosene system of interest here. Similar processes involving other organophosphorous organic phases were therefore considered to provide a basis for test variable values. The literature research focused on the effect of acid concentration on rare earth stripping, differences in extraction or stripping between different rare earth elements and comparison of the results of different acids with each other.

Ramachandra Rao (2006) found that different concentrations of HCl are required to strip different types of rare earths from an organic phase carrying multiple rare earth elements. For example, for 1 M D2EHPA in kerosene, carrying gadolinium, lanthanum and yttrium, 1.3 M HCl strips gadolinium while 7 M HCl is needed for yttrium stripping. Similarly, Geist *et al.* (1999) and Lee *et al.* (2002) found rare earth separation and extraction largely dependent on pH. This would be expected, based on the inverse $[H^+]^3$ dependency of the equilibrium constant in equation 13.

Hirashima *et al.* (1978) also determined that different lanthanides and yttrium showed different distribution ratios, according to atomic number, when extracted from HCl by D2EHPA. Yttrium and erbium showed a similar extractability and ytterbium a slightly higher extractability.   This was further confirmed by Gupta and Krishnamurthy (2005) who found that, for any organophosphorous acid, the extraction efficiency of rare earths increases with an increase in atomic number. This is attributed to an increase in the electrostatic attraction strength between the extractant anion and the rare earth cation as a result of cation decrease over the period. This means that stripping of the relevant rare earth elements should be tested individually and not only one, for instance yttrium, and assumed that it is indicative of the behaviour of all rare earth elements under discussion, although many similarities exist.

Various stripping agents, including H_2SO_4, HNO_3, HCl, KOH, NaOH and NH_4OH can be used to strip rare earth elements from the organic phase, depending on the organic phase under consideration as well as the type of salt the element under consideration occurs in (Desouky *et al.*, 2009, Gupta and Krishnamurthy, 2005 and Mahmoud *et al.*, 2008). Gupta and Krishnamurthy (2005) state that D2EHPA extracts better from chloride than nitrate mediums, but did not compare it with sulphuric acid. Lee *et al.* (2002) found sulphuric acid to be a superior stripping agent compared to hydrochloric acid for the indium and gallium systems. Weiwei *et al.* (2006) found that sulphuric acid gave the best stripping results of ytterbium from Cyanex 923, hydrochloric acid second and nitric acid third. It was found that a low concentration of less than 0.2 M sulphuric acid is sufficient to give high (97 %) stripping percentages of ytterbium from Cyanex 923. Although it is recognised that Cyanex 923 and D2EHPA are not equivalent and do not use the same extraction mechanism (Flett, 2005), results from the Cyanex system are considered as Cyanex is also an organophosphorous acid. Wu *et al.* (2007) mention that, for D2EHPA, higher acidities are required for extraction and stripping than for most other organophosphorous extractants.

From the literature review discussed above it can be concluded that the stripping reaction is highly dependent on pH or, alternatively, acid concentration. It was therefore expected that experimental results would show correlation between the stripping percentage achieved and the initial acid concentration. Based on the literature, lanthanide contraction across the lanthanide period causes differences in extractability and stripping of the different rare earth elements relative to each other. It was therefore expected that, of the elements under consideration for this project, Y and Er will strip easier than Yb, as a result of their relative atomic numbers. Comparing different acids with each other, the literature research indicated that sulphuric acid performs better than HCl or HNO_3 in terms of rare earth stripping. The reasons for this were not explored in the literature reviewed. However, based on the strong dependence of the equilibrium constant on hydrogen ion concentration and relatively more hydrogen ions available in H_2SO_4 than in HCl or HNO_3, this could be expected.

2.6.2 Equilibrium and mass transfer considerations

Desouky *et al.* (2009) and Mahmoud *et al.* (2008) found that the time needed for equilibrium to be reached during yttrium stripping from primene-JMT and trazolopyrimidine are three minutes and five minutes, respectively. Primene-JMT and trazolopyrimidine are other organics also used for rare earth extraction. Weiwei *et al.* (2006) determined that the equilibrium time for ytterbium stripping from Cyanex 923 is 18 minutes. Radhika *et al.*, (2010) did extraction and stripping tests of light and heavy rare earths with TOPS 99 (equivalent of di-2-ethylhexyl phosphoric acid) diluted in kerosene, using

phosphoric acid to provide hydrogen ions and found five minutes to be sufficient for reaching equilibrium. It is therefore expected that the equilibrium time necessary will vary according to the rare earth element to be stripped since the organic phase will be the same (D2EHPA in kerosene) for all the tests. The effects of temperature, agitation rate and the type of agitator should also be considered when determining equilibrium time.

Wang *et al.* (2010) and Wu *et al.* (2007) found ytterbium and yttrium reaction rates are limited by mass transfer and that the stirring speed affects the mass transfer rate below 400 rpm. It is therefore necessary to determine, for a specific experimental setup, the minimum agitation rate above which mass transfer is no longer limiting the reaction rate.

2.6.3   Effect of temperature on stripping

Similar to extraction, stripping involves a change in entropy and enthalpy (Desouky *et al.*, 2009) and is therefore affected by temperature, but the literature review did not deliver specific results as to whether the specific system under consideration would be endothermic or exothermic. However, Wang *et al.* (2010) and Geist *et al.* (1999) found that rare earth extraction and stripping kinetics are diffusion-controlled. Diffusion is affected by temperature since an increase in temperature provides kinetic energy to the molecules, resulting in molecular movement. Based on the literature indication that the reaction rate is influenced by diffusion, it is important to ensure sufficient mass transfer and enough time to reach equilibrium if the effect of temperature is to be determined on the equilibrium composition alone, without the effects that temperature has on mass transfer.

2.6.4   Effect of the organic-to-aqueous (O:A) ratio

Mahmoud *et al.* (2008) found that high stripping percentages of yttrium from triazolopyrimidine are attainable at an O:A ratio of 1:1. Desouky *et al.* (2009) tested O:A ratios of 5:1 to 1:1 for stripping yttrium from primene-JMT and found that stripping increased with a reduction in O:A ratio, with the best stripping achieved at a ratio of 1:1. A review of the kinetics of rare earth extraction with D2EHPA indicated that the reaction occurs mainly on the liquid-liquid interface (Geist *et al.*, 1999). Based on this it would be expected that the organic-to-aqueous ratio would influence the reaction since it affects the effective liquid-liquid surface area.

No literature is available on whether there is any interaction between temperature, O:A ratio and the concentration or type of stripping agent used affecting stripping efficiency. The mass transfer process from the organic to the aqueous phase, through an interfacial layer, as indicated by Wang *et al.* (2010) and Geist *et al.* (1999), would be influenced by all three of these factors. However, this does not imply that there will be interaction effects amongst temperature, acid concentration and O:A ratio at equilibrium.

Chapter 3: Materials and methods

3.1 Assumptions

The project scope was established based on the assumption that yttrium and other rare earth elements could be stripped from the organic phase used in zinc solvent extraction by using the same stripping agents as used in the rare earth industry for stripping during solvent extraction of rare earths. This assumption was considered valid since the organic phase considered was D2EHPA in kerosene, which is used on an industrial scale for rare earth solvent extraction. Also, the purpose of using solvent extraction in the rare earth industry is to concentrate elements which are in low concentration in the feed streams (Gupta and Krishnamurthy, 2005), similar to the case considered here, where rare earths are present in low concentrations in the zinc-rich process streams.

It was further assumed that the laboratory experimental results would give a good indication of the results that the plant process would yield. This was a valid assumption for the stripping and organic health tests, since experience and literature have shown that experimental tests can closely simulate plant conditions in SX (Bart *et al.*, 1991). For the tests involving EW, this was not a very good assumption for precise experimental values since the laboratory scale equipment was not a scaled-down version of the plant size equipment, affecting mass transfer and inter-cathode-anode distance. However, the trends shown by the laboratory data would be indicative of trends that can be expected in the plant, based on literature where researches have tested the effect of other elements on zinc electrowinning (O'Keefe *et al.*, 1990).

3.2 Experimental design and methodology

3.2.1 Current efficiency tests

The effect that an increase in yttrium, erbium, scandium and ytterbium will have on zinc plating current efficiency was investigated by using mini-cells in the laboratory.

The mini-cell set-up is shown in the diagram in Figure 10. The mini-cells consisted of 500 mℓ glass beakers with 1 cm^2 aluminium cathodes and 1 cm^2 lead-silver anodes (see Figure 11). The anode and cathode are mounted in silicone, which is held in place in a Pyrex lid to ensure that the cathode

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and anode face each other and the cathode-anode distance is 0.5 cm. Before placing the electrodes into the solution, both the anode and cathode surface area were polished with fine sandpaper to ensure all residual oxides or contaminants were removed from the electrode surface area. A power supply was used to maintain the current density constant at 500 A/m^2 and a water bath was used to maintain the cells at 36°C. The size of the experi mental equipment limited the number of tests that could be done simultaneously to five.

The five cells were connected in series. The voltages were set to 3.2 V over each cell and would vary according to the solution or plated zinc resistance, but not decrease below 2.8 V, where the plating reaction would stop and lead to zinc dissolution. The cells were allowed to plate for 26 - 28 hours before the electrodes were removed and the zinc stripped. The mass of zinc plated was weighed after each test was completed and the current efficiency calculated using equation 3.
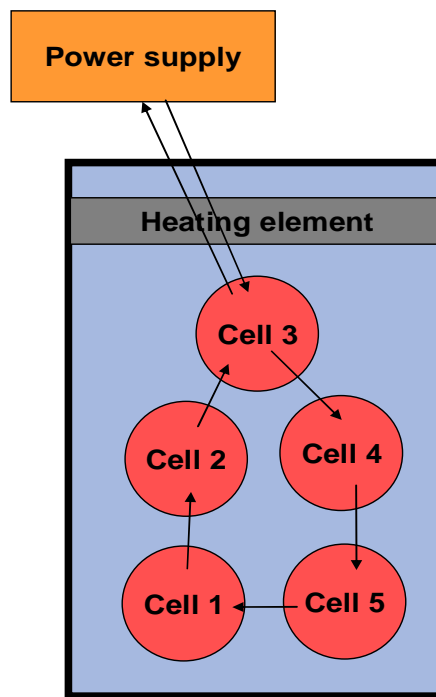
Figure 10: Mini-cell tests set-up
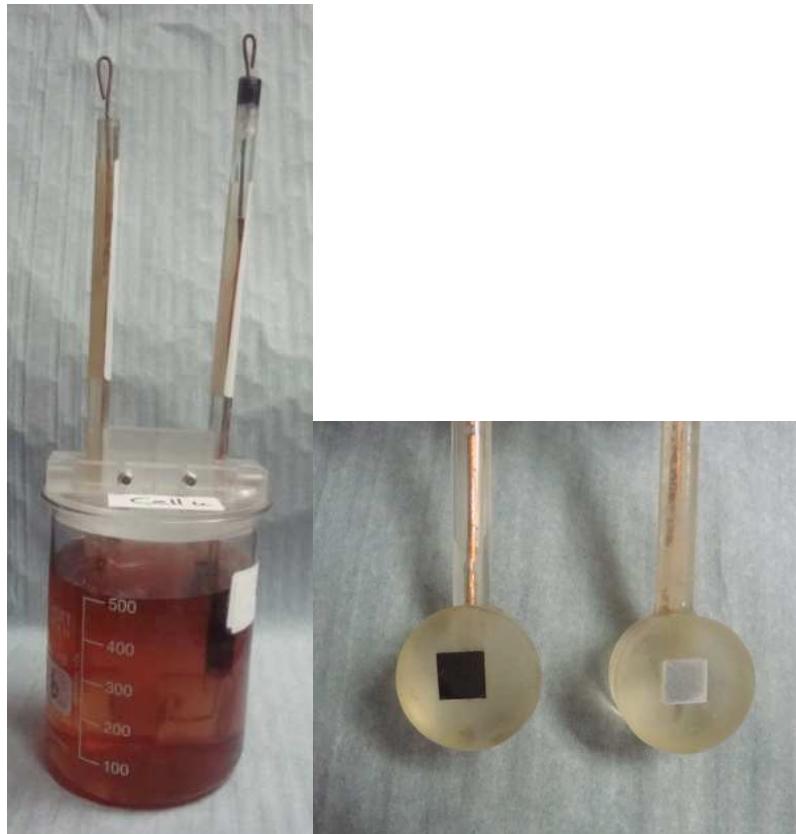
Figure 11: Mini-cell beaker with anode (left) and cathode (right)

Since the objective of this test work was to determine only the effect that rare earth elements have on the electrowinning of zinc, all other variables (temperature, anode-cathode distance, acid concentration and manganese concentration) were kept constant and only the rare earth concentration in the electrolyte varied. Also, to ensure that results could be validated, two blanks (control samples) were included in all batches of tests done to test repeatability of results across batches and across cells within the same batch.

Two tests were done, but in three batches. The first test looked at the effect that different yttrium concentrations have on the electroplating of zinc. The effect that it had was determined by looking at the effect that it had on the current efficiency when plating, as well as visual observations of the plated metal. The yttrium concentration was considered since it is the rare earth present in the highest concentration in the spent electrolyte (see Figure 9). The second test (third batch) considered the effect that the same increase in concentration of the different rare earth elements would have on the zinc plating current efficiency, i.e., which rare earth element would have the most detrimental effect. Table 4 shows the experimental design. The values were selected to see what an increase of 100 mg/l in yttrium's concentration would do to the zinc plating current efficiency. For the batch where

the different elements were compared with each other, the concentration was uniformly increased by 200 mg/l to ensure that some effect is seen.

Table 4: Experimental design for mini-cell tests

Test	Element	Cell	Concentration (mg/l)
1	Y	1	200 (blank)
		2	600
		3	200 (blank)
		4	1000
2	Y	1	200 (blank)
		2	300
		3	200 (blank)
		4	400
		5	500
3	Blank	1	SZ electroyte
	Y	2	SZ electroyte + 200
	Sc	3	SZ electroyte + 200
	Er	4	SZ electroyte + 200
	Yb	5	SZ electroyte + 200

For the first test, plant spent electrolyte (containing 50 g/l Zn, 175 g/l H_2SO_4, 2.5 g/l Mn, trace base metal impurities, 200 mg/l Y, 21 mg/l Er and 3 mg/l Yb) was collected and spiked with 99.999% element standard 100 000 mg/l Y solution to the desired Y concentration. According to Figure 9 the plant spent electrolyte already had a baseline yttrium concentration of 200 mg/l. Y was then added to give solutions containing 200, 300, 400, 500, 600 and 1000 mg/l Y, respectively. The solution containing 200 mg/l Y was therefore the blank solution to which no further Y was added. For the second test, the baseline levels of the rare earth elements were increased by 200 mg/l of Y, Yb, Er and Sc. One cell was the control ('blank'), with no elements added to the spent electrolyte.

3.2.2   Preparation of synthetic organic reagents

Two categories of experiments were performed: one group using organic from the Skorpion Zinc solvent extraction plant and the other using synthetic organic manufactured in the laboratory. This chapter discusses how the synthetic organic phase was prepared.

To manufacture synthetic organic, the rare earths and other ions such as Fe^{3+} and Zn^{2+} had to be extracted from an aqueous phase onto the organic phase to ensure that the elements bind to the organic. This was done in a 250 ml glass jacketed mixing cylinder (see Figure 12) with three baffles.

The baffle width was 5 mm from the inside surface of the cylinder and extended for the full height of the cylinder. The agitator used for mixing had a single impeller composed of two 10 mm vertical rectangular HDPE blades. The impeller-to-vessel diameter ratio was 0.8 and the clearance from the bottom of the vessel to the impeller underside was 20 mm. An agitation rate of 500 rpm was used. The temperature inside the cylinder was maintained with a continuous water stream at a set temperature of 30°C flowing through the jacket.
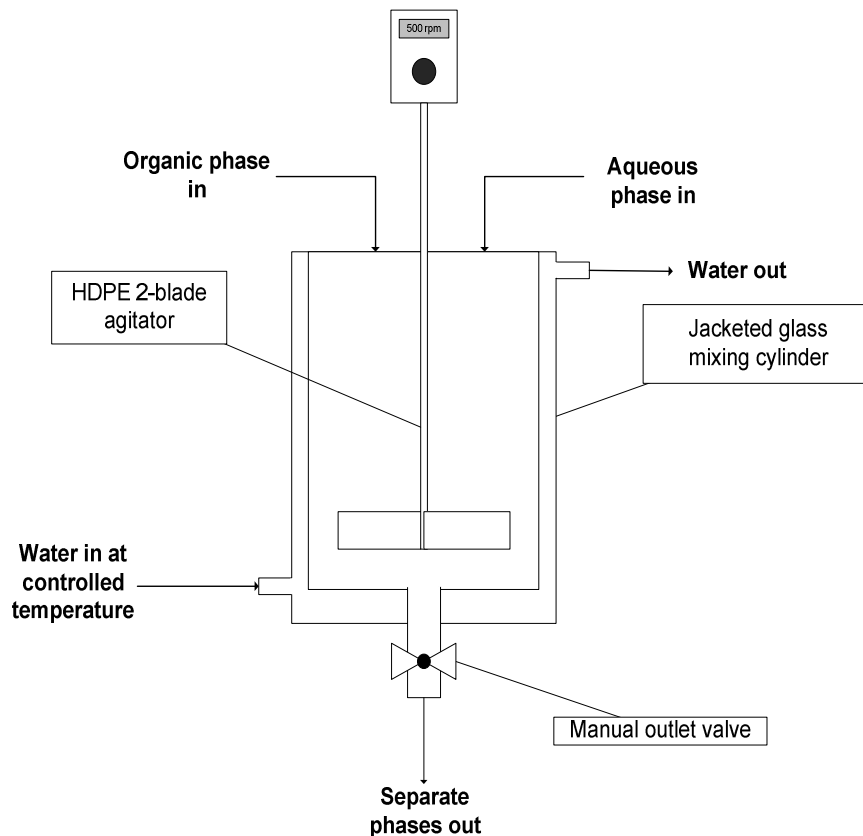
Figure 12: Jacketed glass mixing cylinder used for experiments

Three batches of the synthetic organic phase were required: one with a high concentration of elements bonded to it, one with a middle concentration and one with a low concentration of elements on it. Table 5 shows the desired element concentrations on the organic. It was expected that the exact values in Table 5 would not be obtained. However, the aim was only to produce three variations of organic where there is a clear distinction between low, middle and high element concentrations. It was found that a lower acid concentration increases the percentage extraction (Mahmoud *et al.*, 2008, and Desouky *et al.*, 2009), which is in agreement with equation 11 which shows that a low hydrogen ion concentration favours the forward reaction. It was therefore decided to make up the aqueous phase in 0.5 M H_2SO_4.

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Table 5: Element concentrations on organic

Element	Concentration (mg/l)		
	Low	Middle	High
Y	700	1100	1500
Yb	300	450	600
Er	80	110	140
Zn	1000	1000	1000
Fe	200	300	400
Sc	65	65	65

A factorial design, considering three concentration levels and two temperature levels (see Appendix A), was used to design the experiments for synthetic organic manufacture. The experiments were planned to show the effect of the "concentration" and "temperature" parameters on the response variable, which was "percentage extraction" in this case, as well as interactions between the parameters.   A fractional factorial design was used since the aim was to obtain only a guideline for the extraction that can be expected at different conditions.   The results were used to establish at which conditions sufficient extraction of rare earths onto the organic will be obtained to give the desired organic phase for use in the test work.

The following experimental method was followed to manufacture synthetic organic containing rare earths of a desired concentration: Firstly, a synthetic aqueous phase with a composition of 1200 mg/l Y, 500 mg/l Yb, 120 mg/l Er, 300 mg/l Fe, 70 mg/l Sc, 1000 mg/l Zn and 0.5 M H_2SO_4 was manufactured. For each test, 100 mℓ of the synthetic aqueous and 100 mℓ of pure organic phase (giving an O:A ratio of 1:1, as is used in the Skorpion Zinc process for zinc extraction) were mixed together.

The aqueous phase consisted of 99.999% element standards of Y, Yb, Er, Fe, Sc and Zn diluted in demineralised water to the desired concentrations. The organic phase consisted of 40 wt% D2EHPA and 60 wt% kerosene, with a D2EHPA specification of 95 wt% D2EHPA (minimum), 3 wt% MEHPA (maximum) and 5 wt% water (maximum).

The solution was mixed for 12 minutes where after two minutes were allowed for phase disengagement. Based on literature that report five minutes to be sufficient to reach equilibrium (Radhika *et al.*, 2010), 12 minutes were selected as an adequate mixing time.   The aqueous and organic phases were collected separately and the organic phase filtered through silicon dioxide-

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coated filter paper to remove any entrained aqueous. The samples were then dispatched for ICP-OES analysis of the rare earth element and iron concentrations.

Once the effect of different conditions had been determined on the extraction behaviour of rare earths, a large volume of organic was manufactured with as close as possible to the desired element concentrations, so that all the tests discussed below could be done with the same organic, eliminating inaccuracies introduced by changes in the organic phase.

3.2.3   Organic health tests

Organic health tests involved determining the phase disengagement, viscosity and zinc loading characteristics of the organic phase. These characteristics were measured when zinc was extracted from pregnant leach solution (aqueous phase) onto the organic phase. Using the method discussed in chapter 3.2.2, three synthetic organic phases with "low", "medium" and "high" concentrations of rare earths and iron relative to plant organic were prepared. Clean organic, containing only D2EHPA and kerosene and no rare earths, and plant zinc-stripped organic were the other two organic phases used.

The tests were done using the same mixing cylinder and associated equipment as displayed in Figure 12. Zinc was extracted onto the organic phases from plant pregnant leach solution and synthetic PLS containing 31 g/l Zn, 0.5 g/l Cu, 0.5 g/l Cd, 0.5 g/l Ni and 0.5 g/l Ca in sulphate solution with a pH of 4. For the nine experiments that were performed (see Table 6), the type of PLS and organic phase used were varied. The temperature was kept constant at 43°C and the O:A ratio at 1:1.

Table 6: Organic and aqueous phases used for phase disengagement tests

Test	Organic phase	Organic phase composition (mg/l)					Pregnant leach solution
		Y	Er	Yb	Sc	Fe	
1	Low REE	2000	130	700	70	200	Plant
2	Medium REE	3000	200	1000	100	300	Plant
3	High REE	4000	300	1500	150	400	Plant
4	Clean organic	below detection					Plant
5	Plant Zn-stripped	not determined					Plant
6	Low REE	2000	130	700	70	200	Synthetic
7	Medium REE	3000	200	1000	100	300	Synthetic
8	Medium-High REE	3500	250	1250	125	350	Synthetic
9	High REE	4000	300	1500	150	400	Synthetic

For each test, 200 mℓ of the aqueous and 200 mℓ of the organic phase were added together in the mixing cylinder and agitated for 15 minutes at 620 rpm where after agitation was stopped. The following procedure was followed to determine phase disengagement time: a vertical strip of tape was stuck onto the outside of the mixing cylinder. Once the agitation was stopped, the level of the mixture was marked with a pen. As time progressed, the level of the emulsion band was marked off on the strip every 10 seconds using a stopwatch. Once the emulsion band was zero, the stopwatch was stopped and the total phase disengagement time was recorded. A plot of the emulsion band level against time yielded the disengagement profile. This was the first loading stage and simulated the first stage in an extraction operation.

The aqueous phase was then drained and another 200 mℓ of fresh aqueous phase added. The mixture was again agitated for 15 minutes and the phase disengagement time measured. This was the second loading or second stage in a mixer-settler operation. After the second loading stage, the aqueous phase was drained and the organic phase collected.

10 mℓ of the organic phase was used to measure the kinematic viscosity with an Anton Paar Stabinger SVM 3000 viscometer (0.35% accurate on kinematic viscosity measurements and to 0.0005 g/cm^3 on density measurements). The organic sample was then analysed for Zn to determine the amount of zinc that had been loaded onto the organic phase after two extraction stages. The results were compared for the different organic and aqueous phases used.

3.2.4 Stripping tests

The experiments were divided into 4 groups, namely A to D. The groups are defined in Table 7 and the experimental variables that were used for each test are indicated in Appendix A.

Table 7: Definition of experiments

Group	Definition
A	Optimum stripping agent type and concentration with O:A and temperature interactions
B	Optimum stripping agent concentration (more detail)
C	Results validation: Agitation rate, Equilibrium time, REE concentration
D	Optimum O:A and temperature (more detail)

Stripping agent concentration, O:A ratio and temperature were identified as the key variables influencing REE stripping. The experimental design used was a factorial design looking at four levels

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for stripping agent type, three levels for acid concentration, two levels for O:A ratio and two levels for temperature (see Appendix A).

Based on the literature review, the stripping agent type and the acid concentration were seen to be the most influential in the stripping percentage achieved, and therefore the factorial design increased the levels of these two parameters. Four stripping agents were tested, the O:A factor at a "high" and "low" value and the temperature (T) parameter at a "high" and "low" value. The concentration parameter was tested on "high", "middle" and "low" values to eliminate the possibility of a polynomial relationship between percentage extraction and concentration being distorted as a linear relationship when only two values are tested. The fractional factorial design would also indicate any interactions between any two parameters, affecting the response variable.

This experimental design would show which stripping agent is the most effective at "high", "middle" and "low" concentrations and whether the temperature and the O:A ratio affect stripping. It would show whether there is any interaction between temperature, O:A, concentration and the concentration of stripping agent used.

The same equipment was used for the stripping tests as was explained in Chapter 3.2.2 and Chapter 3.2.3. For the "A" tests as indicated in Appendix A, the following experimental method was followed to strip rare earths from synthetic organic: aqueous solutions of HCl, HNO_3 and H_2SO_4 at 1 M, 3 M and 5 M were made up and NaOH at 20%. 70 mℓ of the aqueous phase and 140 mℓ of the synthetic organic phase were added together for an O:A ratio of 2:1 or 140 mℓ of aqueous and 70 mℓ of the synthetic organic phase for an O:A ratio of 1:2.

The mixture was agitated for 12 minutes at 500 rpm in the jacketed glass mixing cylinder (see Figure 12) where after agitation was stopped and two minutes allowed for phase disengagement. The temperature of the glass mixing cylinder was maintained at a desired temperature between 30°C and 50°C. The aqueous and organic phases were collected separately and the organic phase filtered through silicon dioxide-coated filter paper to remove any entrained aqueous. Samples were then dispatched for ICP-OES analysis of rare earths.

The same method and equipment were used for the "B","C" and "D" experiments indicated in Appendix A, with only the parameters changing as indicated.

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3.2.5   Stripping tests variables

The values of the variables that will be investigated are discussed below. The choice of values was based on the literature discussed in Chapter 2.6 and practical considerations.

Stripping agent type

HCl, HNO_3 and NaOH were tested as stripping agents on a bench scale to determine the most effective one for the current REE element concentrations and also taking into consideration the Skorpion Zinc process. H_2SO_4 was investigated based on the literature from Weiwei *et al.* (2006) and Lee *et al.* (2002), and since it is of high availability at the Skorpion Zinc refinery which has a sulphuric acid plant as an auxiliary plant to the main zinc refining process.

Stripping agent concentrations

For this test work, HNO_3, HCl and H_2SO_4 were investigated in the range of 1 – 7 M and NaOH at concentrations of 20 – 30 %.

Equilibrium and mass transfer considerations

Test work was done with mixing times of 12 minutes. According to literature, equilibrium is achieved in five minutes (Radhika *et al.*, 2010); the selected mixing time would hence be long enough to achieve equilibrium.

Agitation rates of 400, 500 and 600 rpm were investigated to ensure that the stripping reaction was not mass transfer limited and that the results achieved were not influenced by the agitation rate.

Effect of temperature on stripping

Temperatures of 30 – 55°C were investigated since these temperatures span the temperature range of 40 – 45°C that is maintained in the zinc solvent extraction plant at Skorpion Zinc.

Effect of the Organic:Aqueous (O:A) ratio

Preliminary tests were done at O:A ratios of 1:2 (low) and 2:1 (high) to determine whether there were any interactions between the different variables. Thereafter, the range of O:A ratios from 0.25 to 6.0

were tested to establish whether the test results correlate with the trend from literature as mentioned in Chapter 2.6.4.

Chapter 4: Effect of rare earths on zinc electroplating

4.1   Introduction

The effect that the rare earth element (particularly Y, Yb, Er and Sc) concentration has on electrowinning was determined by investigating the current efficiency of zinc plating obtained in the presence of different concentrations of Y, Yb, Er and Sc.   Current efficiency is affected by many factors, including temperature, acid concentration, zinc concentration, mass transfer, plating area, applied current, type of electrode and other impurities present.   For this test work, only the rare earth concentration was varied.   Interaction effects between the different factors and the rare earth concentration were therefore not accounted for as the aim was only to determine whether rare earths affect zinc current efficiency and if so, whether the effect is positive or negative.

4.2   Effect of yttrium on zinc electrowinning

Table 8 shows the current efficiency results obtained for the blank samples (mini-cells with plant circulating electrolyte without any additions).   The first two blank cells were included in the first batch of five mini-cells and the blank cells three and four in the second batch of four mini-cells. The current efficiency results for the four blank cells showed good repeatability between different cells and across different batches.

Table 8: Results for four blank samples

Blank	%CE
1	96.2
2	97.4
3	96.1
4	96.1

Figure 13 displays the current efficiency obtained for different yttrium concentrations in the electrolyte. An average cell voltage of 2.94 V was obtained at a current density of 500 A/m^2.   The high current efficiencies of 96% for the blank plant samples can be attributed to the high current density of 500 A/m^2 that was used for the test work.   For the increase in Y concentration from 200 to 300 mg/l, an average reduction of 5.9% in current efficiency was seen.   The graph shows a linear relationship between yttrium concentration and current efficiency.   Visual observations of the plated zinc found the zinc deposit formed in the high-yttrium electrolytes to have a very smooth morphology compared to the morphology of zinc plated in low-yttrium electrolyte.   No literature could be found on the

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mechanisms by which yttrium affects zinc plating. However, the smooth morphology might be indicative of hydride formation, but this has not been proven yet.
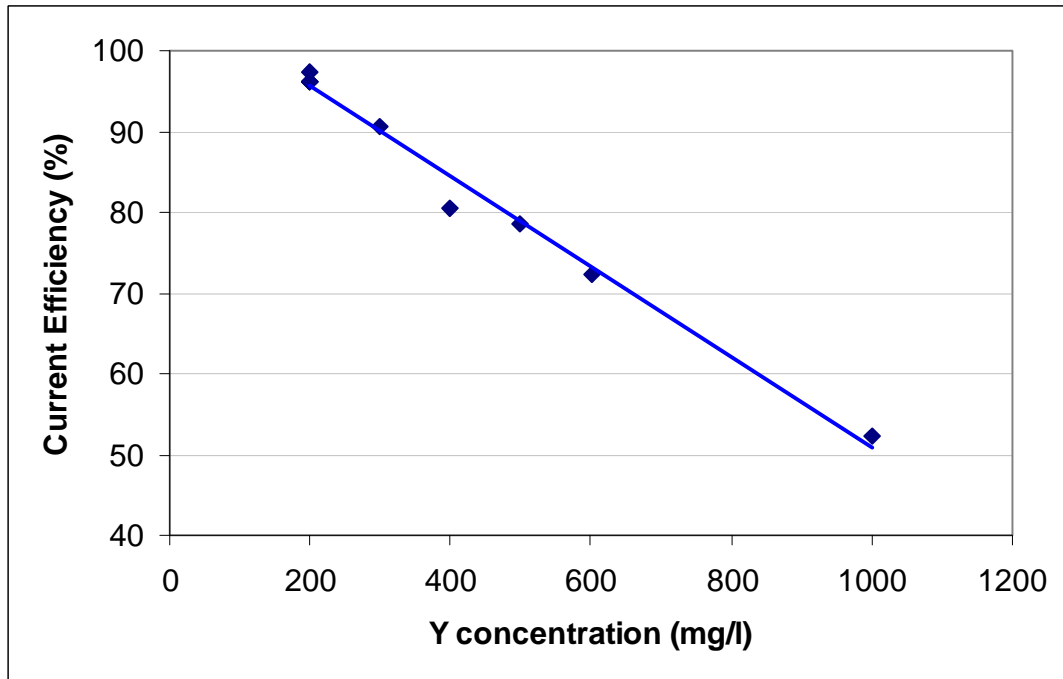
Figure 13: Current efficiency as a function of Y concentration in spent electrolyte

4.3 Effect of different rare earths on zinc electrowinning

Mini-cell tests were also done where 200 mg/l of different rare earth elements were added to the circulating electrolyte from the plant. From the calculated current efficiencies displayed in Figure 14, an increase in the scandium concentration had the most detrimental effect, reducing the current efficiency by 38%. In order of decreasing current efficiency the elements tested showed: Y > Yb > Er > Sc.
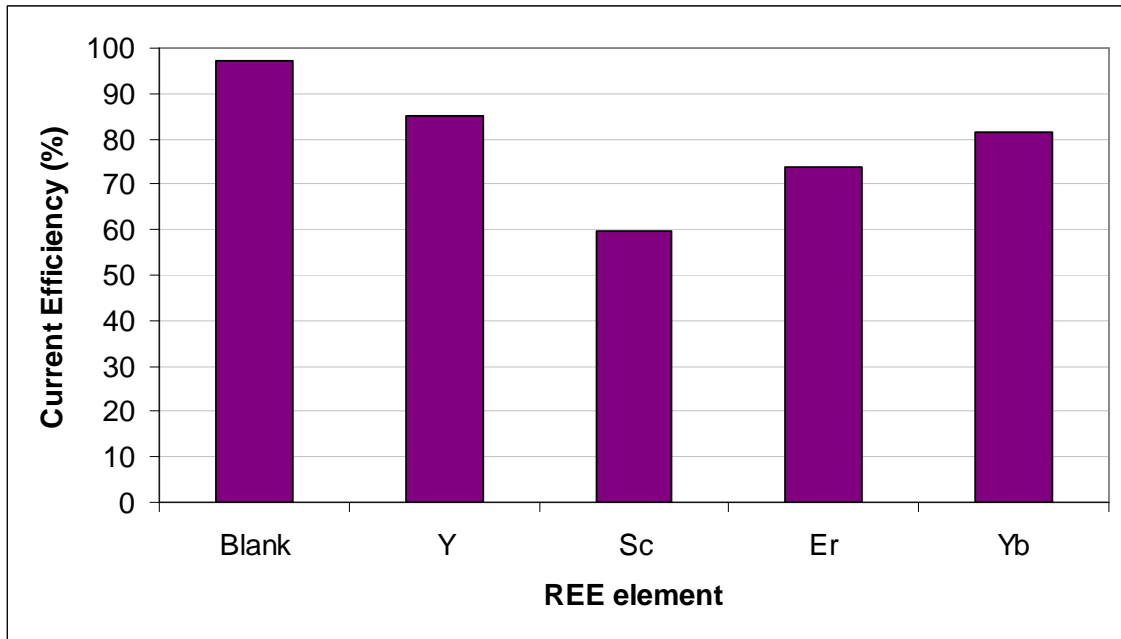
Figure 14: Current efficiency for different REE increased by 200 mg/l

4.4   Conclusions

From the results an increase of 100 mg/l in the electrolyte yttrium concentration caused a decrease of 5 % in current efficiency. Current efficiencies for cells containing REE elements showed that Sc had the most detrimental effect, followed by Er, Yb and Y. The mechanism by which these elements affect zinc plating is not known. The presence of rare earth elements in the electrolyte is possibly originating from rare earth elements stripped with Zn from the loaded organic phase in SX. In order to reduce REE levels in EW it is therefore first necessary to reduce the concentration on the organic phase in SX. Once incoming concentrations on the loaded electrolyte are lower than that in the spent electrolyte, rare earths in accumulation will be reduced by the bleed stream to SX.

Chapter 5: Effect of rare earths on organic phase health

5.1   Introduction

The effect that rare earth elements have on the viscosity, phase disengagement time and zinc loading capability of the organic phase was investigated. Organic phases containing different concentrations of rare earths were firstly prepared and then loaded with either synthetically manufactured leach solution or leach solution from the Skorpion Zinc process plant. Only the effect of the organic rare earth element concentration was investigated, although it is recognised that a number of factors, including temperature, pH and mixing, affect organic viscosity, phase disengagement time and zinc loading.

5.2   Synthetic organic manufacture

Clean industrial-grade kerosene (60%) and D2EHPA (40%) were contacted with an aqueous solution of rare earth elements containing different concentrations of Y, Er, Sc and Yb, and also Fe and Zn to prepare a synthetic organic phase with specific rare earth concentrations. The aqueous solution contained 0.5 M H_2SO_4. The results are plotted in Figure 15. Tests one and two were done with an aqueous solution having a "low" concentration of rare earths, tests three and four with a "middle" amount of rare earths compared to the current levels in the plant and tests five and six with an aqueous phase containing a "high" amount of rare earths. O:A ratios of 1:1 were used in all tests. Tests one, three and five were performed at 30°C an d tests two, four and six at 50°C.
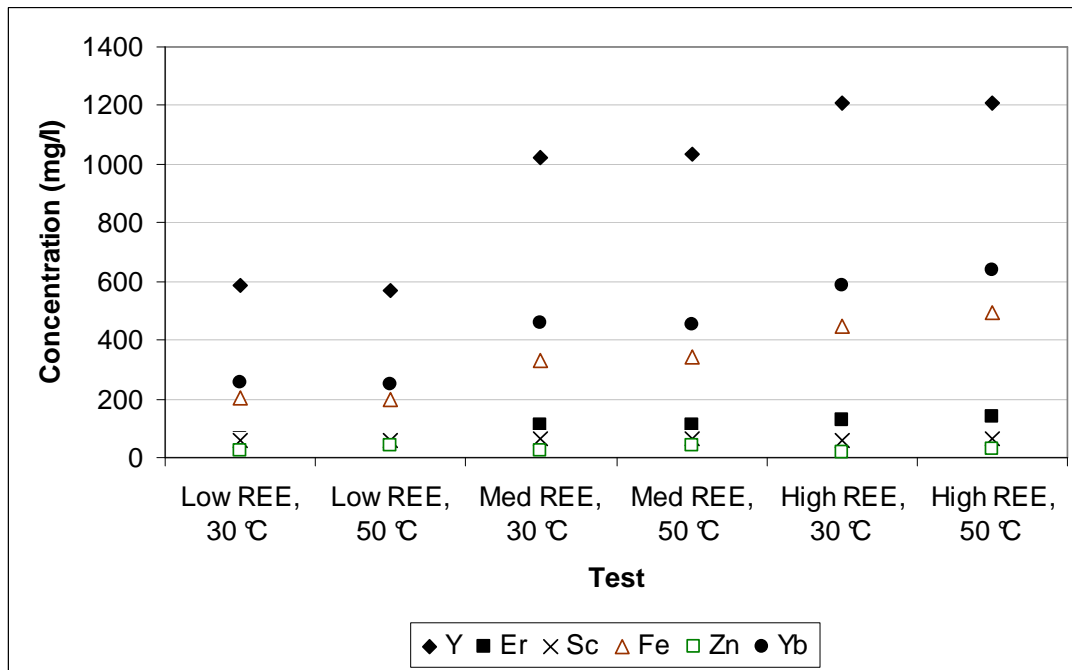
Figure 15: Rare earth, iron and zinc concentration on synthetic organic

From Figure 15 it can be seen that the temperature difference did not significantly affect extraction of the elements from the aqueous to the organic phase. The results showed that the average percentage extraction was 85% for the rare earths and yttrium and 100% for iron.

Zinc did not extract well (only 5% extraction) onto the organic, yielding concentrations of 20 – 50 mg/l and the desired 1000 mg/l as in the plant could not be achieved. The reason for the poor zinc extraction is attributed to the hydrogen ion concentration. Based on the Zn and REE extraction reactions given in equations 6 and 11, respectively, the equilibrium constant for the Zn extraction reaction is dependent on the square of the hydrogen ion concentration and while the equilibrium constant for the rare earth extraction reaction is dependent on the third power of the hydrogen ion concentration. This means that for a hydrogen ion concentration of less than one mol per litre, the REE extraction reaction would be favoured. The test work was continued with the low zinc concentration on the synthetic organic since the main focus was the rare earths and not the zinc as the process solution under consideration was the zinc-stripped organic. However, this should be taken into account when comparing results for plant- and synthetic organic.

The results were used to prepare the synthetic organic phases containing different concentrations of Y, Yb, Er, Sc and Fe needed for the stripping and loading tests.

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5.3   Zinc loading

Zn was extracted from plant PLS containing 32 g/l Zn onto the synthetically manufactured organic phases discussed in the previous chapter. The organic phases were also loaded with synthetic PLS containing 31 g/l Zn, 0.5 g/l Cu, 0.5 g/l Cd, 0.5 g/l Ni and 0.5 g/l Ca. Figure 16 gives the Zn loading obtained after two extraction stages.
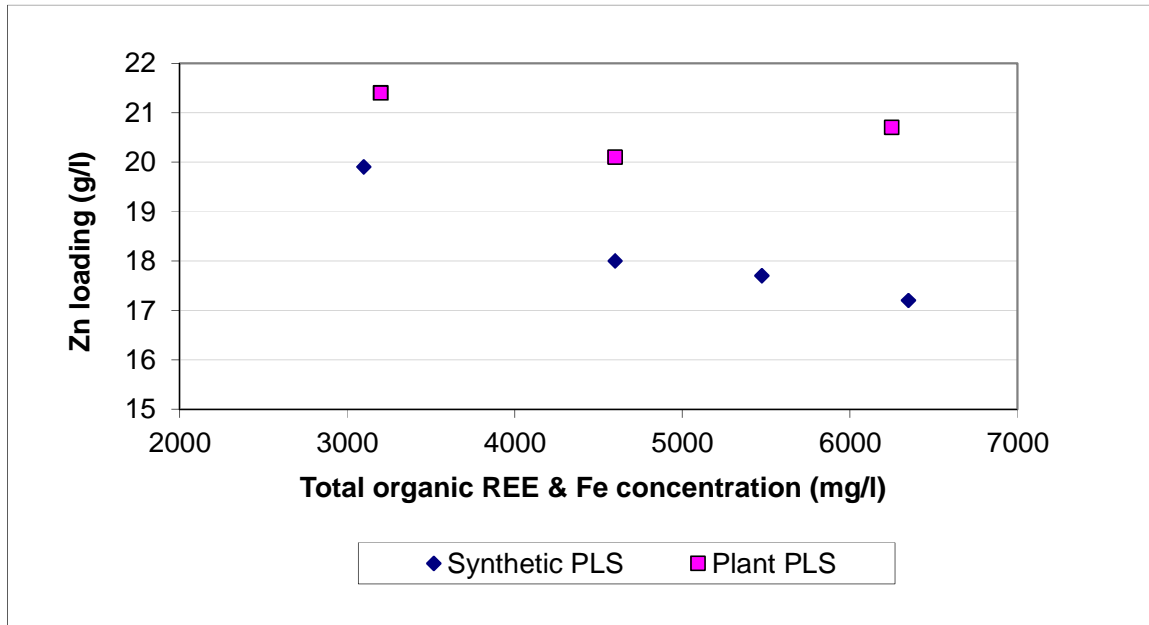
Figure 16: Effect of total REE concentration on zinc loading

At 3000 mg/l REE and Fe, plant PLS loaded 21.4 g/l Zn onto the organic phase, while the synthetic PLS only loaded 19.9 g/l Zn. The synthetic PLS contained 30 g/l Zn (0.46 mol/l) while the plant PLS contained 32 g/l Zn (0.49 mol/l) at the time of sampling. Consider the Zn extraction reaction again:

$$ZnSO_4 + 2RH \leftrightarrow R_2Zn + H_2SO_4 \qquad\qquad\qquad \text{[Equation 6]}$$

The organic phase used contained 40 wt% D2EHPA, which presents 2 mol/l D2EHPA (indicated by *RH* in the equation). D2EHPA was therefore in excess while zinc was the limiting reactant, explaining why the plant PLS achieved a higher zinc loading on the organic phase. Based on the equilibrium constant, an increase in D2EHPA concentration would drive the extraction reaction forward. However, the D2EHPA concentration used in these experiments was the same for extraction with plant- and synthetic PLS, therefore the zinc concentration is the only variable.

When synthetic PLS was used, zinc loading reduced with an increase in rare earth concentration. Plant PLS also followed a decreasing trend for the first two REE concentrations tested, but this was not supported by the third point. The tests with plant PLS should be repeated to verify the trend. Converting mass concentrations to molar concentrations, 3000 mg/l REE would present 0.03 mol/l rare earth elements on the extractant and 6000 mg/l REE would present 0.07 mol/l rare earths. Considering the stoichiometry in equation 11, 0.2 mol/l D2EHPA would be consumed at 3000 mg/l REE and 0.4 mol/l D2EHPA at 6000 mg/l REE if a theoretical 100% conversion is considered D2EHPA would therefore still be in excess. However, as the rare earth concentration increases it has the potential to start competing with Zn for D2EHPA. Based on the stoichiometry, it is not expected that Zn loading will increase at higher REE and iron concentrations, indicating that the third point on Figure 16 for plant PLS is an outlier. The available results for synthetic PLS give sufficient indication of the negative effect of the REE concentration on zinc loading to motivate removal of the rare earths.

Figure 17 aims to compare the results obtained in the lab when using synthetic organic, with clean organic and zinc-stripped organic from the solvent extraction plant. The zinc-stripped plant organic produced results similar to the synthetic organic phase, but the pure organic phase extracted only 11.6 g/l Zn. The poorer zinc loading of the ”clean” organic in Figure 17 can possibly be attributed to a lower extent of hydrogen bonding to improve the ease of metal loading, since the ”clean” organic did not have previous exposure to acid such as the other organic phases used for this test work.
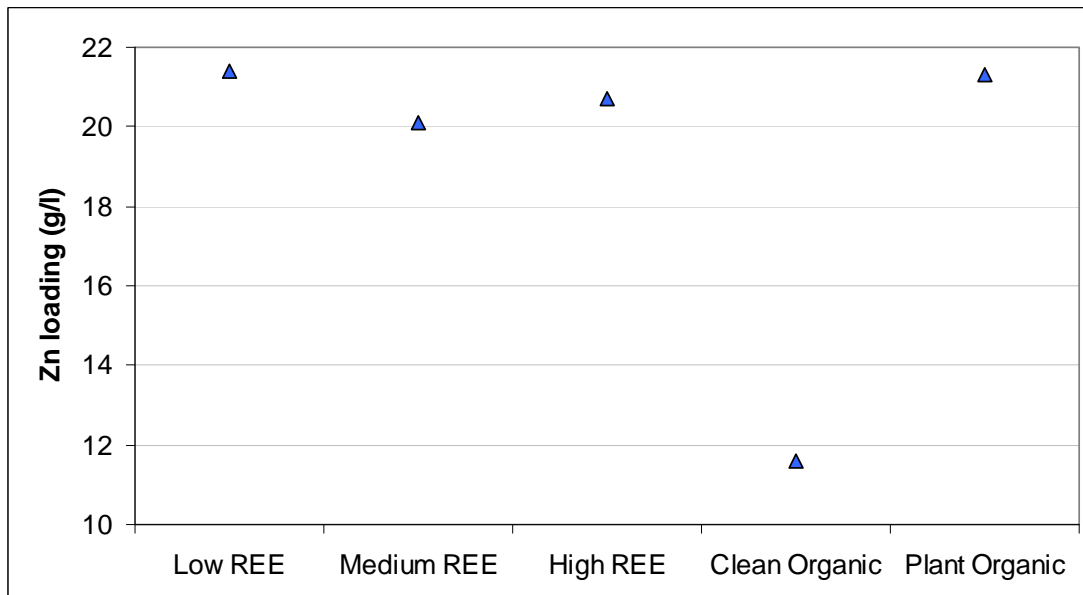
Figure 17: Maximum zinc loading after two extraction stages

5.4   Organic phase viscosity

Viscosity was measured after the second extraction stage. For organic loading with synthetic PLS, the organic phase viscosity increased linearly with an increase in the rare earth and iron concentration (see Figure 18). Since the most common complex formed in rare earth extraction is *(YR$_3$.3HR)$_{org}$* compared to *R$_2$Zn* that is formed during zinc extraction, it was expected that the viscosity would increase due to the bulkier complex as rare earth co-extraction increased at higher rare earth concentrations.

After extraction from plant PLS, the organic viscosity also showed an increase of viscosity with REE and Fe concentration. The first two points show good comparison between the results obtained for synthetic and for plant pregnant leach solution. Since the third point was considered an outlier in Figure 16, it might have a higher viscosity due to combined high Zn and REE and Fe loadings, and would therefore also be considered an outlier on Figure 18.

Plant PLS contained additional elements such as Mn, Mg, Ca and Al not present in the synthetic PLS. However, of these, only Mn and Mg were present in significant concentrations in the PLS and do not extract onto D2EHPA. The co-extractable elements such as Cu, Cd, Ni and Ca were present in approximately the same concentrations in the synthetic and plant PLS. Chloride and fluoride as well as suspended solids were also present in the plant PLS, but were of low extractable concentration. From visual observations during the experiments it was also noted that at higher viscosity air and aqueous could be seen to be entrained in the organic phase, as would be expected.
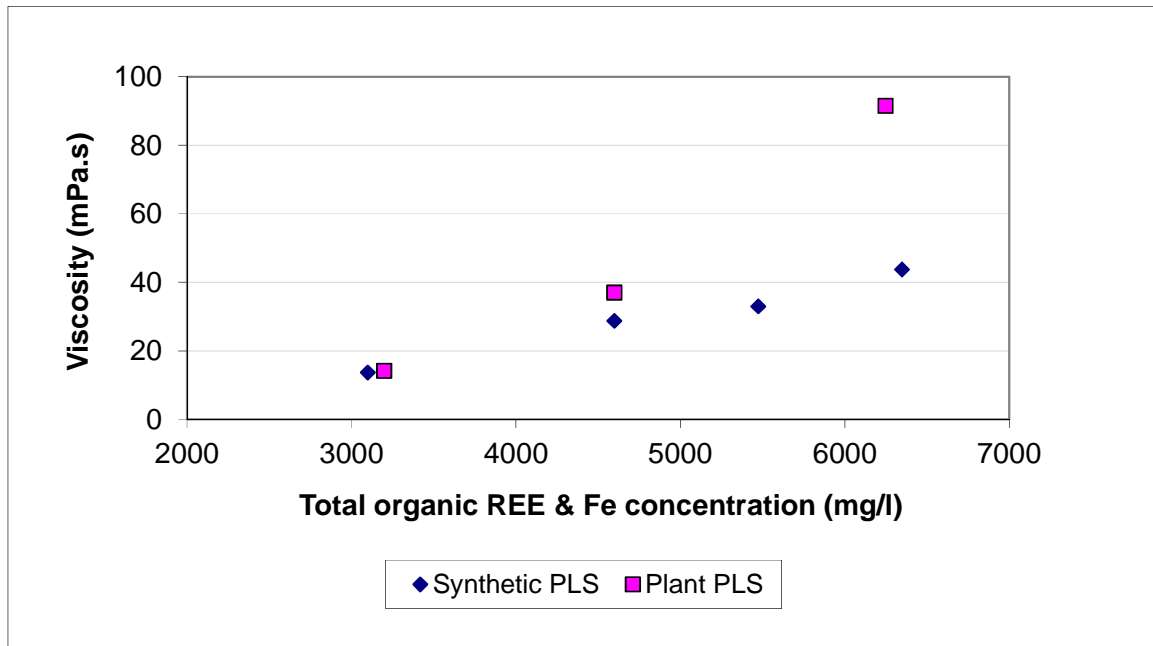
Figure 18: Viscosity vs organic phase rare earth concentration

Viscosity was found to be a linear function of organic phase density (see Figure 19). The increase in density is very small, but more than the 0.0005 g/cm^3 accuracy error that the viscometer is expected to contribute. The increase in density as the rare earth loading increases was expected since the $(YR_3.3HR)_{org}$ complex bonds twice the amount of organic that Zn does in R_2Zn. The small increase in density was possibly due to the low concentration of rare earths complexes.

The viscosity is influenced by the type of bonding between the metal element and the extractant. When the metal ion is extracted, it reacts on the liquid-liquid interface to form the $MR_2(HR)$ complex, (where M is the metal ion and R the D2EHPA anion). The additional HR carries the complex into the bulk organic phase. At low metal loading conditions, $MR_2(HR)$ break up to release the carrier molecule and form MR_2 in the bulk phase, decreasing viscosity as MR_2 have a similar size to the D2EHPA dimer, $HR-RH$, existing in the organic bulk phase.

However, at high metal loading conditions, the carrier complex, $MR_2(HR)$ will aggregate in the bulk phase to form M_2R_4 and release the carrier molecule for extraction (Kolarik and Grimm, 1976 and Kumar and Tulasi, 2005). Since the rare earths utilise more D2EHPA per mole of metal than zinc, it increases the possibility of "high loading" conditions for the rest of the D2EHPA. Aggregation would significantly increase viscosity and explains why the viscosity increased in Figures 18 and 19 as the rare earth loading increased.
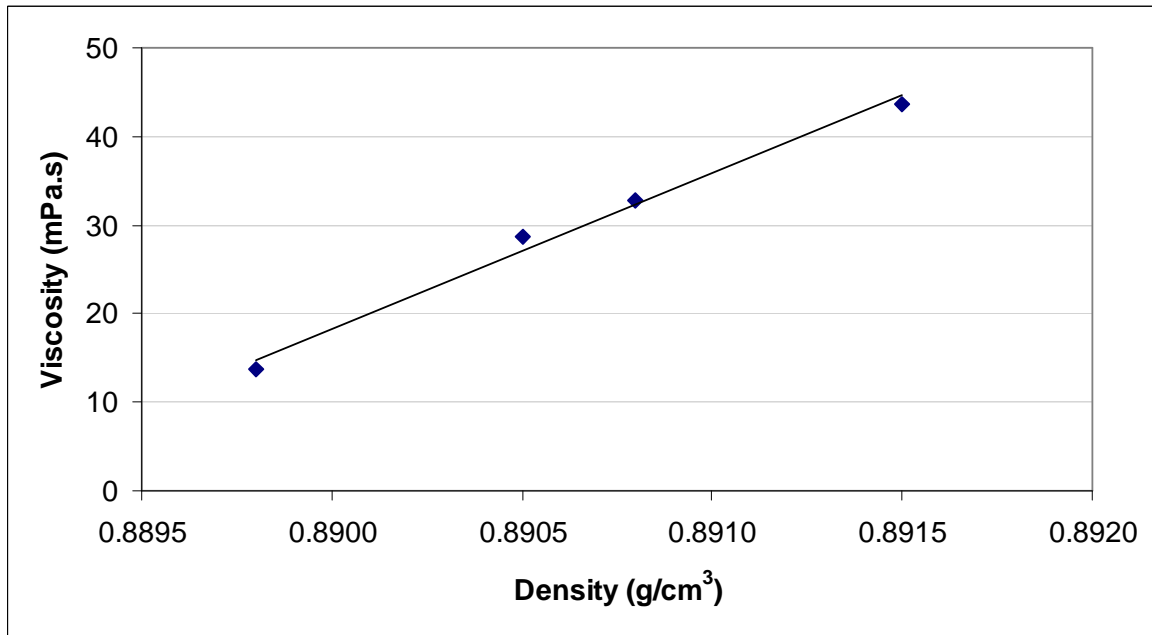
Figure 19: Relationship between organic phase viscosity and density

5.5 Phase disengagement time

The effect that the rare earth element concentration has on the phase disengagement time of the organic phase was determined when zinc was extracted from plant and synthetic pregnant leach solution onto organic. Synthetic organic containing different concentrations of rare earths and iron were used (as indicated in Table 6). The time needed for the organic and aqueous phases to completely separate after the first extraction stage was measured. Phase disengagement time measurement was repeatable to within 5 seconds.

The disengagement profiles for extraction from synthetic PLS are shown in Figure 20. The samples for "low" and "medium" rare earths, as well as the "clean organic" and "plant organic" samples in Figures 20 and 21 show typical separation profiles, with initial slow separation, followed by faster separation and slow separation at the end; this observation is in agreement with results published by Musadaidzwa and Tshiningayamwe (2009). Initial disengagement is slow as the interfacial surface area where interfacial tension has to be overcome is large, slowing coalescence (Hoh *et al.*, 1986). As the interfacial surface area reduces coalescence becomes easier and the greater areas of bulk phase allow the effect of density difference to separate the phases. Disengagement rate decrease at the end since the drive for density difference is less as the emulsion height is small, with diffusion ensuring that the last droplets are coalesced. As the rare earth and iron concentration increased the

phase disengagement profile was stretched as the viscosity increased and a more stable emulsion formed. This resulted in a phase separation time of 15 minutes which would be problematic for mixer-settler operation.
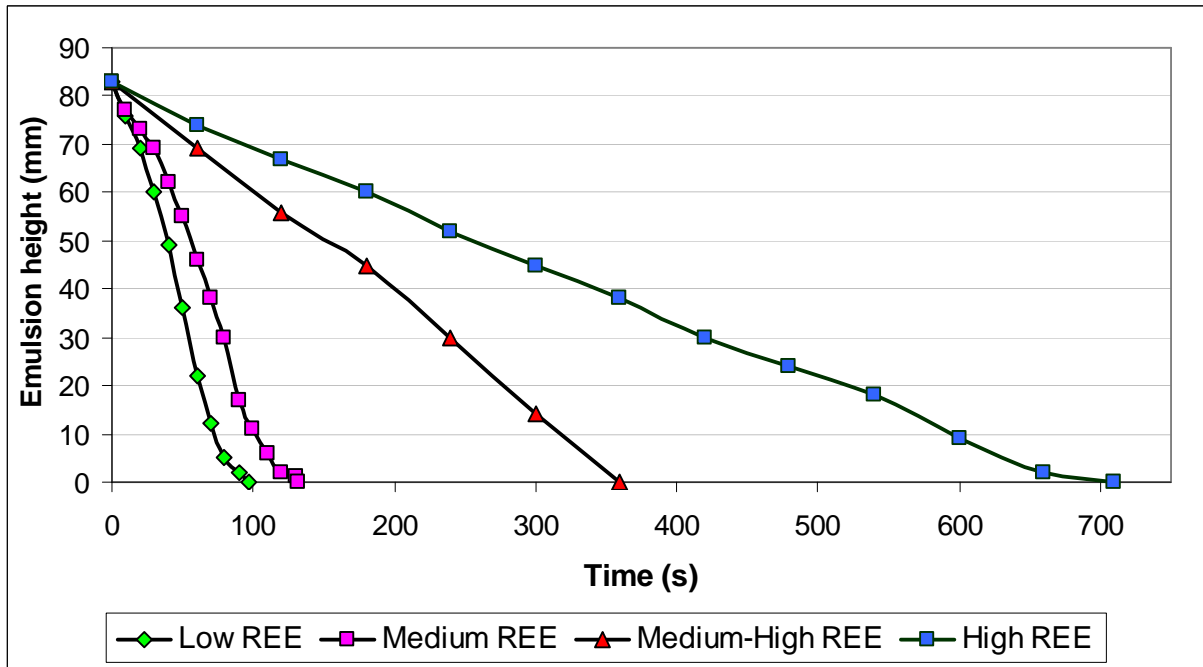
Figure 20: Phase disengagement times for organic after first zinc loading with synthetic pregnant leach solution

The phase disengagement profiles for extraction from plant PLS are shown in Figure 21 and are similar to that for the synthetic PLS with the phase disengagement time increasing with an increase in the organic phase rare earth concentration. Disengagement times were faster when using synthetic PLS than when plant PLS was used. Plant PLS also contained chlorides and fluorides which might form chloro-complexes with the organic phase; however, this is not expected to occur in major concentrations.

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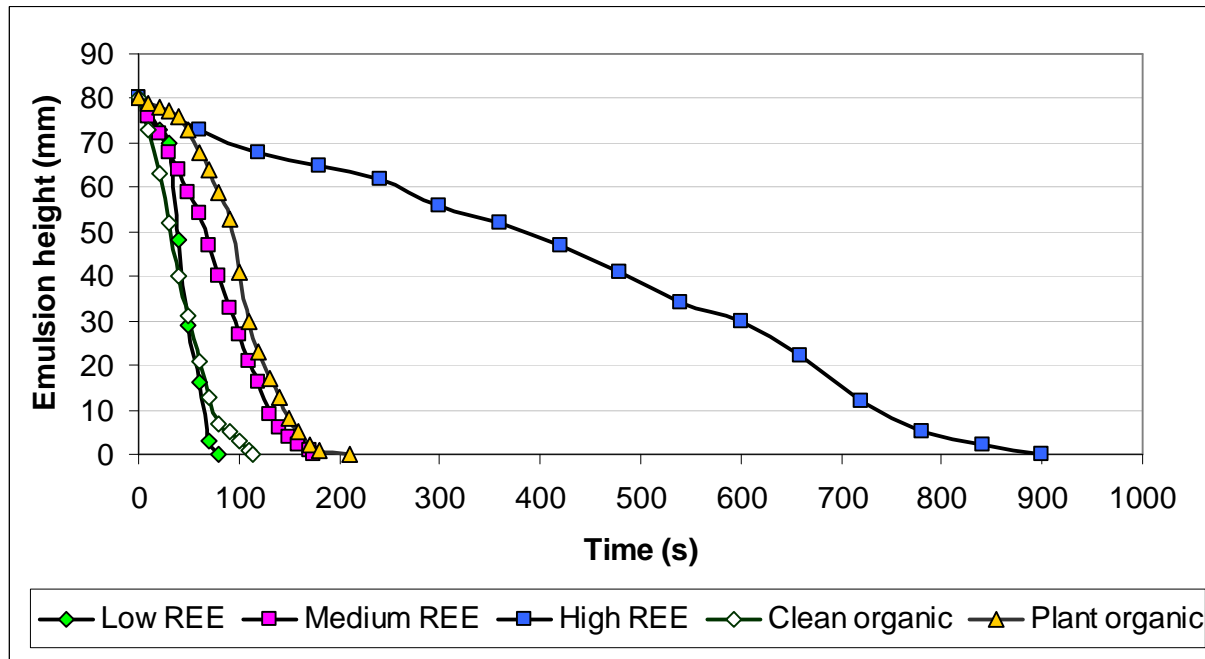
Figure 21: Phase disengagement times for organic after first zinc loading with plant pregnant leach solution

Figure 22 plots the phase disengagement time after the first loading and second loading stages. For the first stage, phase disengagement time increased as the rare earth and iron concentration increased. After the second stage, phase disengagement time was high at low rare earth concentrations, decreased for medium concentrations and then increased again for high rare earth concentrations. At high rare earth concentrations or high zinc loading (at low rare earth concentrations) it was expected that aggregation would occur, viscosity would increase and phase disengagement time should increase. However, according to Figures 23 and 24, the viscosity was low at low organic rare earth and iron concentrations. This low viscosity was not expected at the high zinc loading conditions where non-ideal behaviour would occur in the organic phase (Bart *et al.*, 1992 and Kumar and Tulasi, 2005).
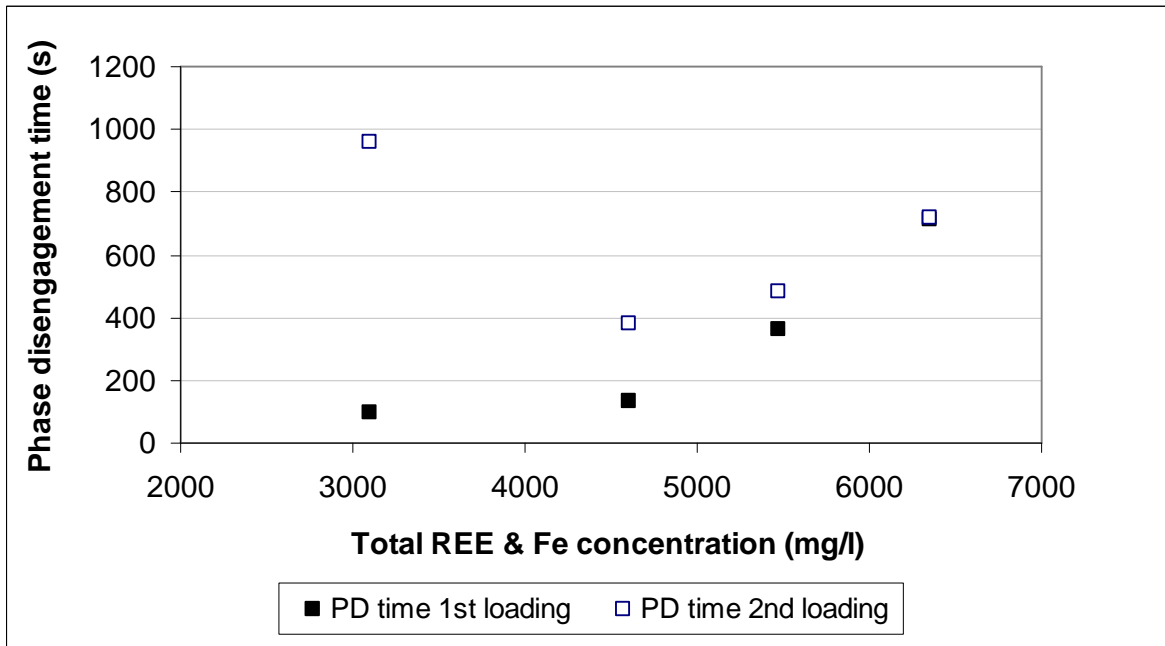
Figure 22: Phase disengagement time after 1ˢᵗ and 2ⁿᵈ zinc loadings

Figure 23 shows that that the plant zinc-stripped organic had a similar phase disengagement time as the synthetic organic phase containing "medium" concentrations of rare earths. The clean organic phase had the lowest viscosity and phase disengagement time as would be expected due to the low zinc loading on the clean organic phase.
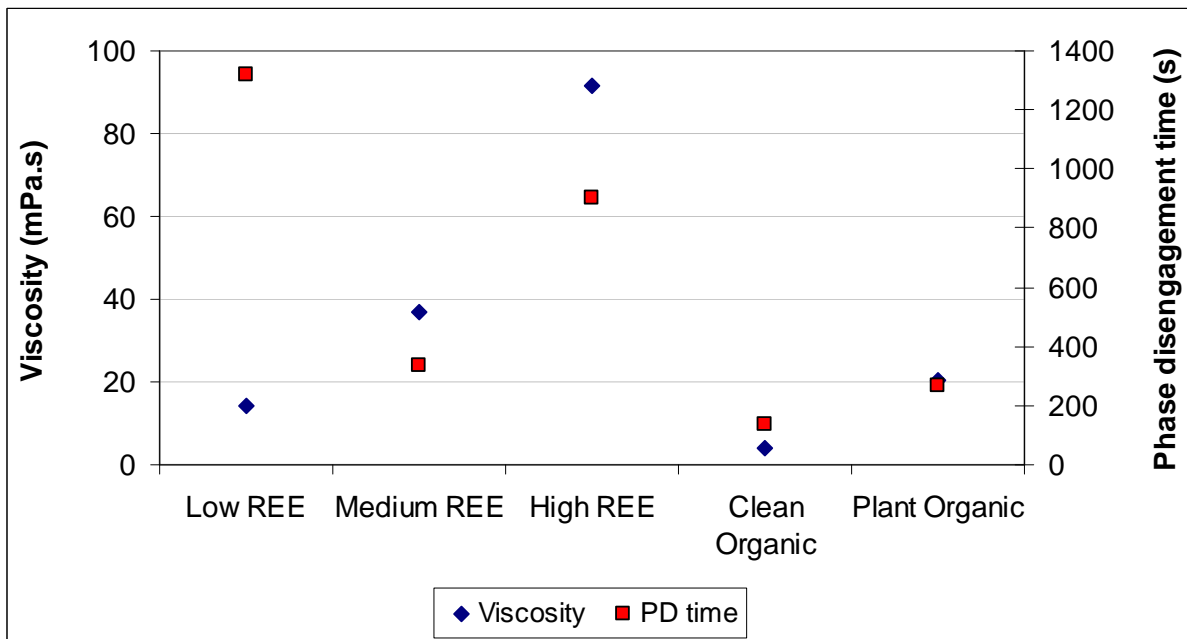
Figure 23: Viscosity and phase disengagement times after first Zn loading for different organic phases
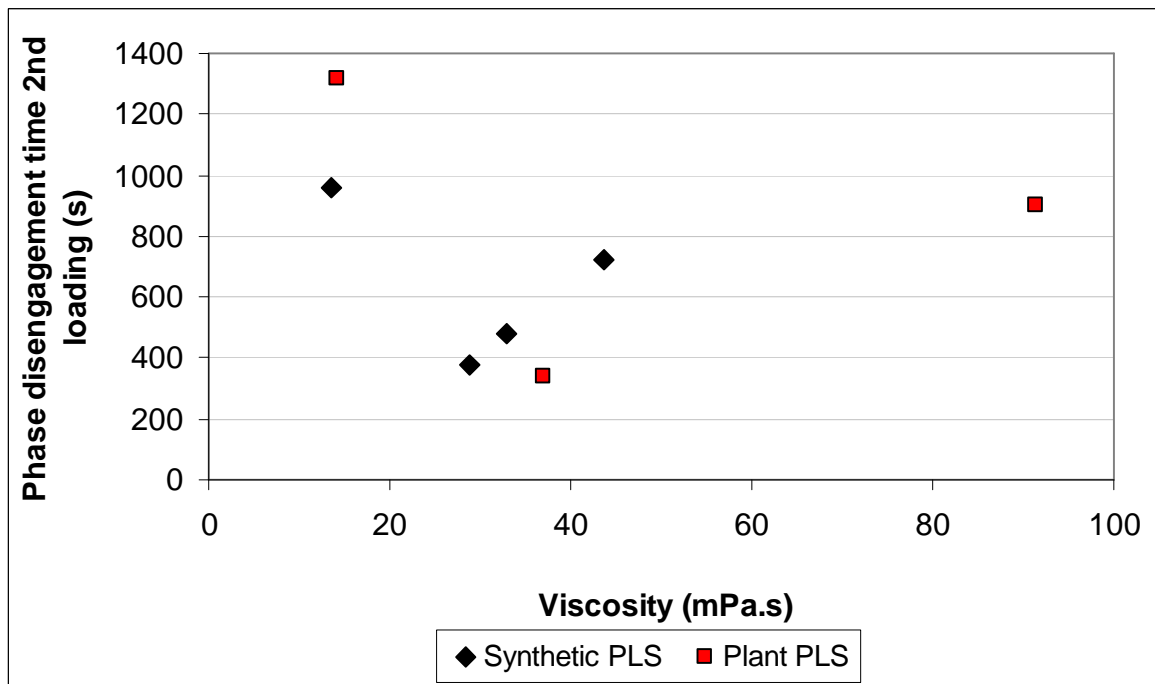
Figure 24: Phase disengagement time against viscosity

5.6   Conclusions

Based on the results discussed above for the organic health test work, it can be concluded that the rare earth loading reduces the organic phase zinc loading and competes with Zn for D2EHPA so that "high loading" conditions arise, causing aggregation of the Zn-D2EHPA complex formed. Increased aggregation results in increased organic phase viscosity and increased phase disengagement time.

As the rare earth loading doubled from a total of 3100 mg/l to 6250 mg/l, the organic phase viscosity after the second loading stage doubled and the phase disengagement time increased from 100 to 700 seconds. The zinc loading after two extraction stages with synthetic PLS decreased from 19.9 to 17.2 g/l. The zinc loading for plant PLS also decreased from 21.4 g/l to 20.1 g/l as the organic REE and Fe concentration increased from 3200 to 4600 mg/l. Higher rare earth element concentrations in the organic phase therefore have a detrimental effect on the organic phase characteristics and should be removed.

Chapter 6: Stripping rare earth elements from the organic phase

6.1   Introduction

Based on the negative effect of rare earths on the organic phase discussed in the previous chapter, a process for stripping rare earths from the organic phase was investigated. The laboratory test work first considered removal of rare earths from a synthetically manufactured organic phase where after the same experiments were attempted with zinc-stripped organic from the Skorpion Zinc solvent extraction plant.

6.2   Rare earth and iron stripping from synthetic organic

Stripping was first tested with an organic phase that had been prepared in the laboratory by loading industrially pure D2EHPA and kerosene with Y, Yb, Er, Sc and Fe. Experimental results can be found in Appendix B.

6.2.1   Stripping agent type and concentration

Figures 25 – 28 show the effect of different concentrations of stripping agents on the stripping of yttrium, erbium and ytterbium from organic.
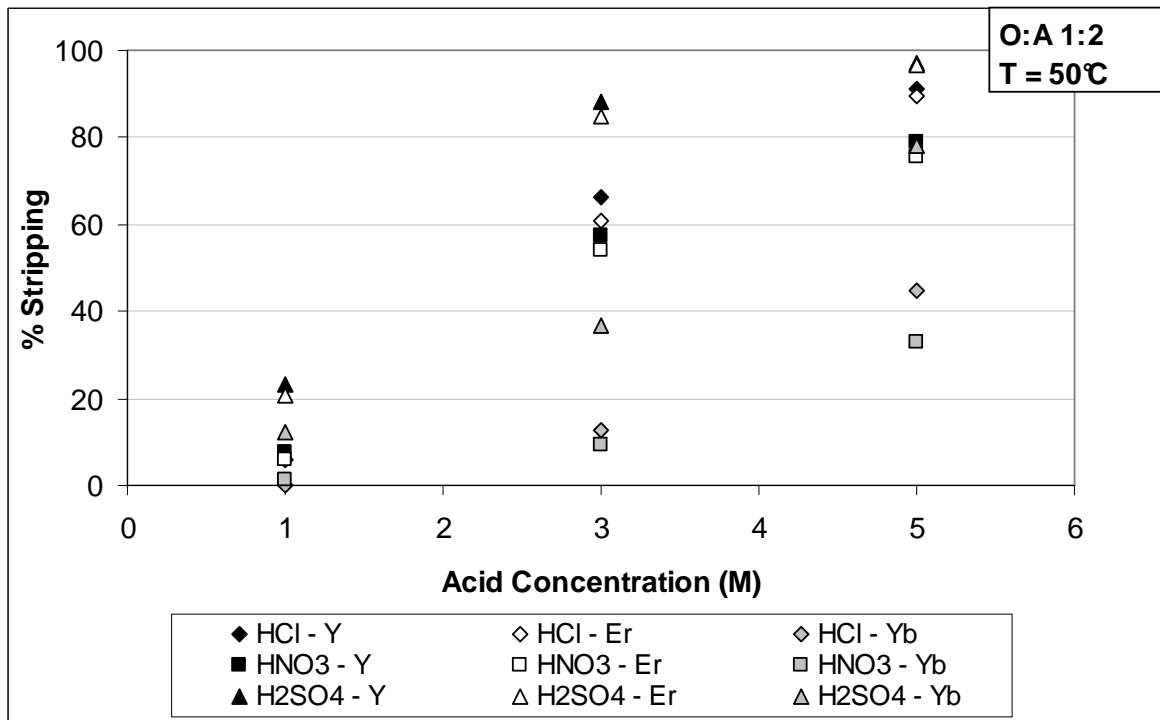
Figure 25: Rare earth stripping from synthetic organic at O:A 1:2 and T = 50℃ for different acid concentrations
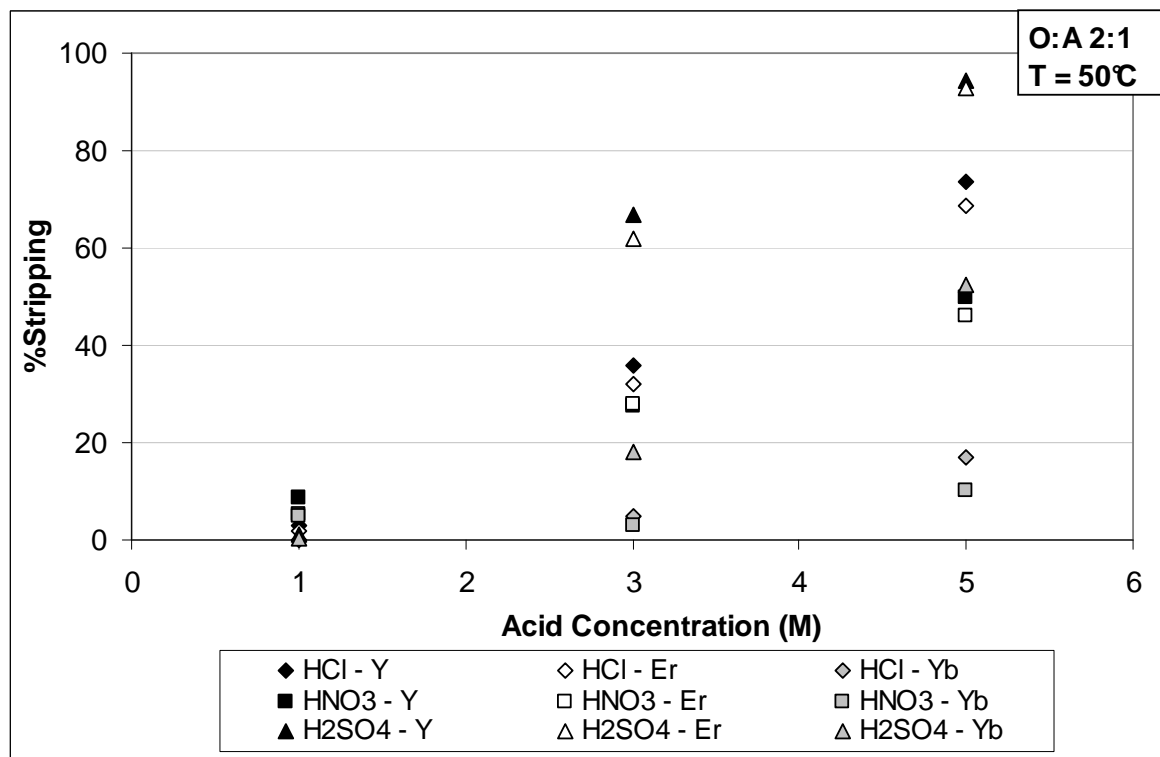
Figure 26: Rare earth stripping from synthetic organic at O:A 2:1 and T = 50℃ for different acid concentrations
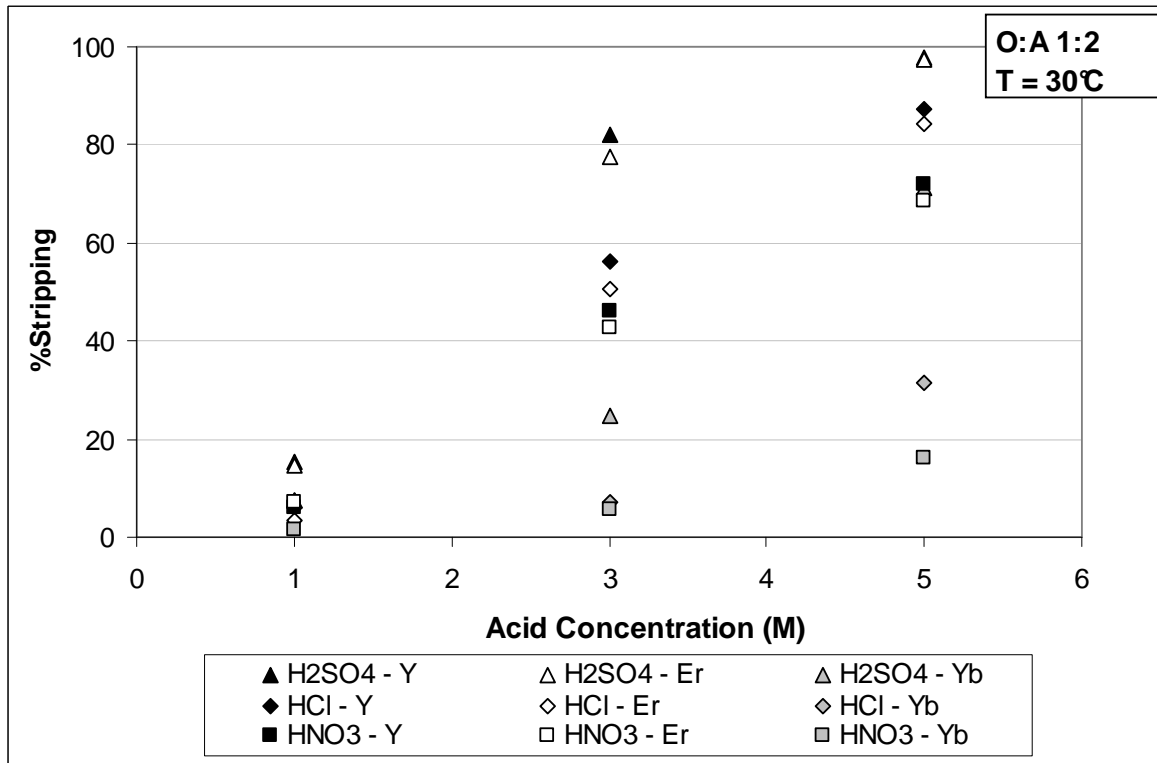
Figure 27: Rare earth stripping from synthetic organic at O:A 1:2 and T = 30℃ for different acid concentrations
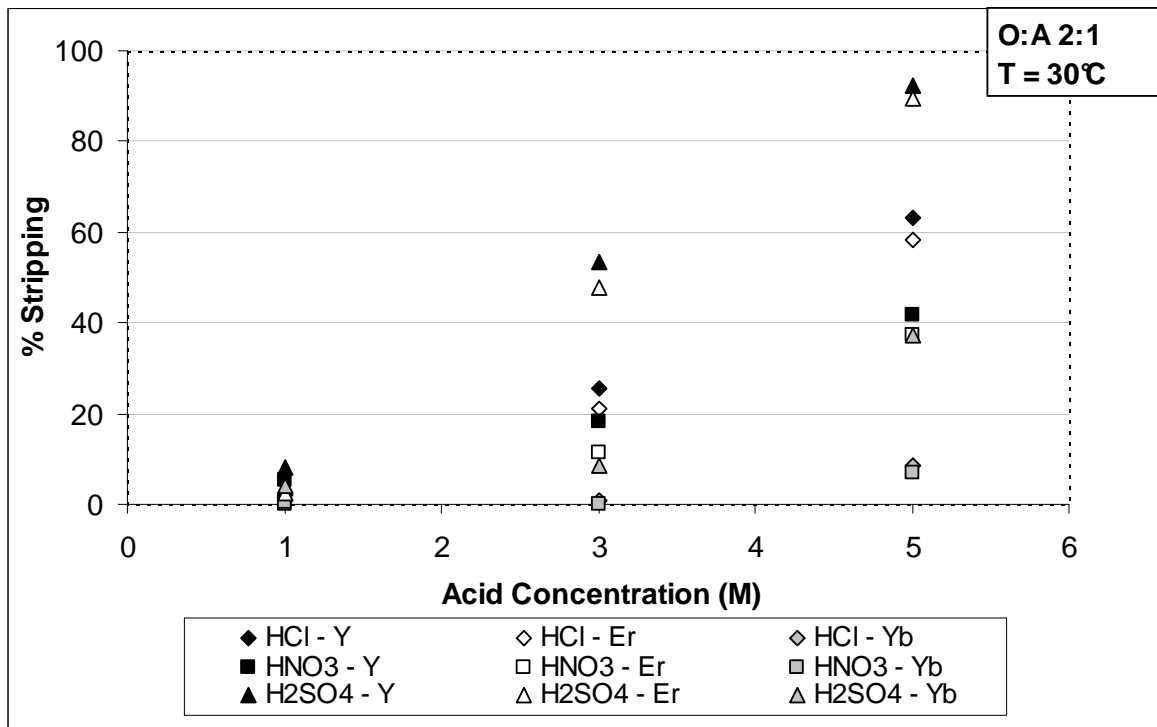
Figure 28: Rare earth stripping from synthetic organic at O:A 2:1 and T = 30℃ for different acid concentrations

From the plots it can be seen that the best stripping was achieved with H_2SO_4, followed by HCl and then HNO_3. This order correlates to the results found by Weiwei *et al.* (2006) for Cyanex 923 and Lee *et al.* (2002). Sulphuric acid achieved stripping percentages of 97% for Y and Er at 5 M and 78% for Yb. Hydrochloric acid achieved 91% stripping for Y, 89% for Er and 45% for Yb at 5 M while nitric acid could only strip 79% of the loaded Y, 76% of the Er and 33% of Yb. The percentage stripping of all three of yttrium, erbium and ytterbium from organic increased with increasing concentration of stripping agent.

The rare earth stripping reaction was considered again to determine the stoichiometric constraints in the system:

$YR_3.3RH + 3H^+ \leftrightarrow Y^{3+} + 3R_2H_2$ [Equation 15]

Converting mass to molar concentrations, it was calculated that 0.023 mol/l of *YR₃.3RH* were available in the system to be converted and this would require 0.07 mol/l of *H⁺*. Based on the stoichiometric requirement, the hydrogen ion concentration was in excess and the acid concentration should not have limited stripping. However, based on the equilibrium constant for the stripping reaction (refer back to equation 13), which is inversely proportional to $[H^+]^3$, it was expected that an increase in acid concentration would drive the stripping reaction forward. Better stripping by sulphuric acid can be explained by the potential of H_2SO_4 to supply two hydrogen ions, compared to HCl and HNO_3 which can only supply one hydrogen ion each.

Yttrium and erbium were stripped easily at high acid concentrations, while ytterbium showed lower stripping performance. Based on the distribution ratio trend with atomic number found by Hirashima *et al.* (1978) it could be expected that ytterbium would not strip as easy as yttrium and erbium.

Figure 29 plots percentage iron stripping against acid concentration and differs from the plots for Y, Er and Yb in that hydrochloric acid is the best stripping agent. Similar to the above plots, iron was increasingly stripped from organic as the acid concentration was increased.

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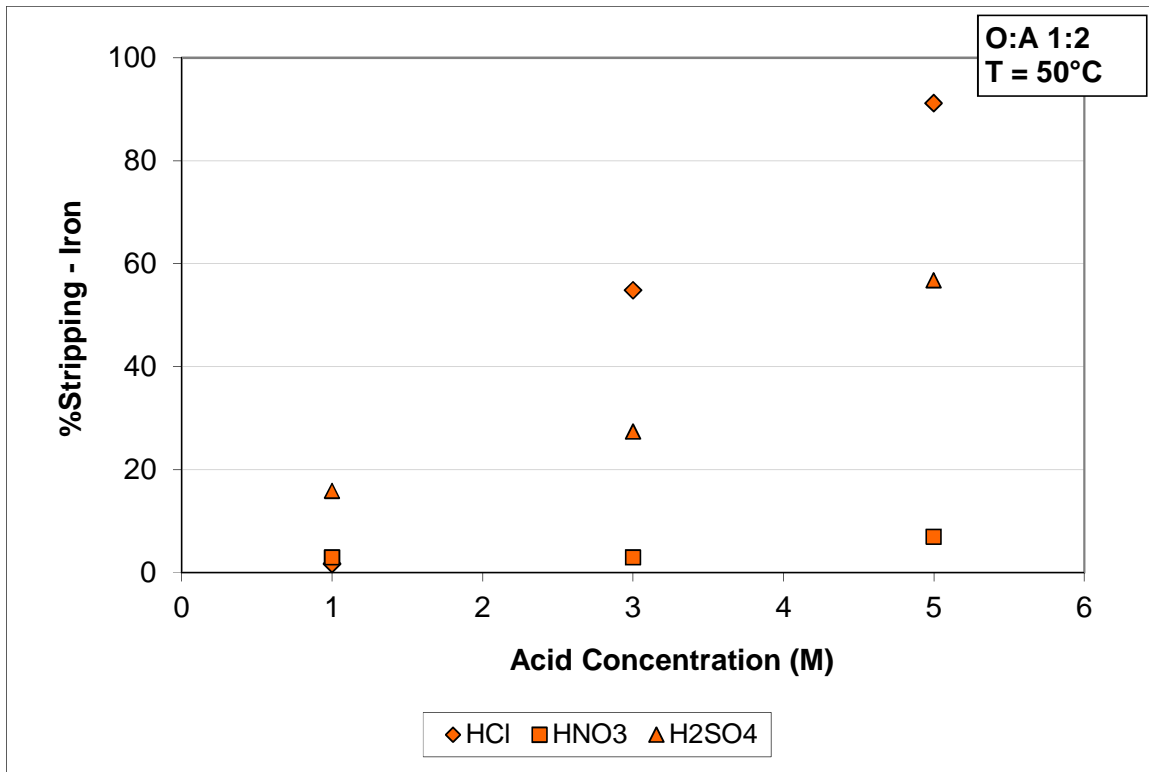
Figure 29: Iron stripping from synthetic organic vs acid concentration, at O:A ratio of 1:2 and a temperature of 50 °C

Based on Figure 30 no conclusive statement can be given on the relationship between stripping agent concentration and scandium stripping from organic. All the tests showed that HCl achieved the lowest stripping of scandium. However, there is no clear indication of which of the other two acids performed the best and the highest stripping obtained was 17.5%, which is very low.

A possible contributor to poorer scandium stripping is that it is present on the organic in lower concentrations than the other elements discussed and that it therefore competes with the Y, Yb and Er ions. However, even at high acid concentrations where most of the other elements are stripped off, Sc still only achieved 8 % stripping at best. Scandium therefore did not behave similar to Y, Yb and Er and further investigation into a process for scandium stripping is required. As it is not present in very high concentrations, it was decided to only consider the other elements for the rest of the project.

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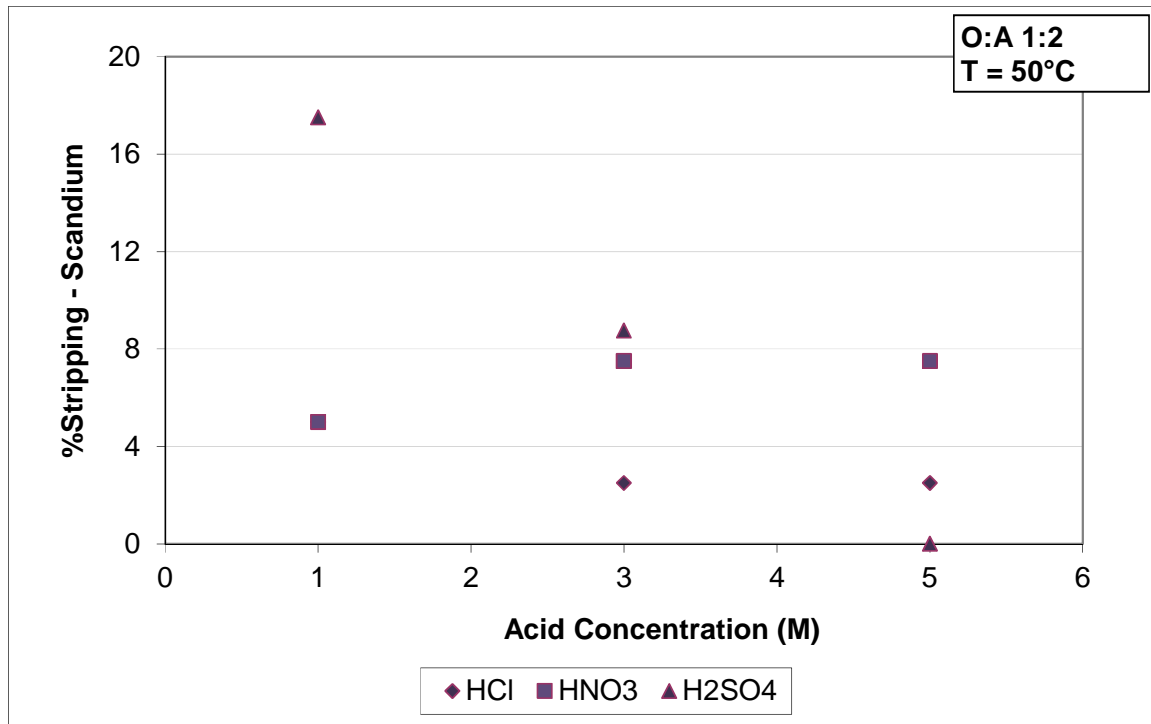
Figure 30: Scandium stripping from synthetic organic vs acid concentration

99% of the zinc present on the organic was stripped off with all three acids at all three concentrations. This could possibly be attributed to the lower oxidation state of zinc, which forms Zn^{2+} ions relative to the other elements such as Y, Er and Fe on the synthetic organic which have oxidation states of three.

When NaOH was used as the stripping agent, it was noticed that the organic phase turned into a dark brown-red gel. No solids were observed in solution. It is suspected that an ester is formed according to the following reaction:
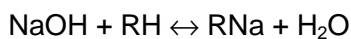
$$NaOH + RH \leftrightarrow RNa + H_2O$$ [Equation 16]

To recover the organic phase, the RNa has to be hydrolysed by aqueous sulphuric acid (Gupta and Krishnamurthy, 2005). On average, 80% rare earth stripping was obtained before hydrolysis and 65% when the organic had been restored. It is suspected that some of the rare earths remained in the aqueous phase entrained in the gel-like structure which then recombined with the D2EHPA molecules once it were hydrolysed. However, although this process is possible, it was decided to reject NaOH as a candidate stripping agent since the gel-like substance poses practical difficulties for handling in the plant. Organic health might also be negatively affected.

6.2.2 Experimental results verification

Repeatability of experiments

Three experiments were repeated at the same concentration and conditions for H_2SO_4 and two for HNO_3 and HCl each. The results below show good repeatability. The three repeated experiments for H_2SO_4 had an average standard deviation of 0.5 and a sample variance of 0.4 for yttrium, erbium and ytterbium stripping. It was therefore assumed that the results obtained for the rest of the experiments were repeatable within a 5 % accuracy range.

Table 9: Repeatability of experiments

Stripping agent	%Sc stripping	Std dev	Var	%Y stripping	Std dev	Var	%Er stripping	Std dev	Var	%Yb stripping	Std dev	Var	%Fe stripping	Std dev	Var
HCL	2.5	3.5	12.5	73.5	0.5	0.3	68.7	0.0	0.0	17.0	2.6	6.9	74.9	0.0	0.0
HCL	7.5			74.2			68.7			20.7			74.9		
HNO_3	8.75	1.8	3.1	49.8	0.1	0.0	46.1	1.2	1.5	10.4	0.5	0.3	3.6	0.2	0.1
HNO_3	6.25			49.9			44.3			9.6			4.0		
H_2SO_4	3.75			94.3			92.8			52.4			29.4		
H_2SO_4	6.25	1.3	1.6	94.8	0.3	0.1	93.4	0.4	0.1	54.3	1.0	1.0	31.4	1.1	1.1
H_2SO_4	5			94.7			93.4			53.9			29.7		

Effect of rare earth concentration on stripping

Synthetic organic phases with different concentrations of rare earths were stripped to determine the effect of the amount of rare earths on the stripping percentage that can be achieved. The high REE, medium REE and low REE organic phases contained 2000 mg/l, 1250 mg/l and 1000 mg/l yttrium and 175 mg/l, 115 mg/l and 108 mg/l erbium, respectively.

Based on equation 12, the stoichiometric amount of acid required for Y stripping at a concentration of 1000 mg/l Y is 0.034 M, indicating that *YR₃.3RH* was the limiting reagent. However, from Table 10 it is seen that the same degree of stripping was achieved for the same conditions (O:A ratio, temperature and acid concentration), irrespective of the concentration of rare earths on the organic. The standard deviations between the stripping percentages for the three rare earth concentrations tested at each set of conditions were low for Y and Er and acceptable for Yb if a standard deviation of 5% is taken as acceptable experimental error and not indicating an effect. Although the stoichiometry acid requirement for the reaction was met, a significantly higher acid concentration is required to drive the reaction forward since the equilibrium constant is inversely proportional to $[H^+]^3$.

Table 10: Stripping % for different rare earth concentrations

Rare earth concentration	Stripping agent	O:A	T	C	% Y Stripping	% Er Stripping	% Yb Stripping	Std dev % Y strip	Std dev % Er strip	Std dev % Yb strip
High					62.2	58.6	11.2			
Medium	H_2SO_4	2	50	3	66.6	61.7	18.0	2.5	2.2	4.5
Low					62.6	57.4	9.6			
High					93.0	92.0	45.8			
Medium	H_2SO_4	2	50	5	94.8	93.4	54.3	0.9	1.0	4.5
Low					93.9	93.9	47.4			
High					86.7	84.5	28.1			
Medium	H_2SO_4	0.5	50	3	88.1	84.9	36.7	0.9	0.2	4.3
Low					86.5	84.7	32.2			
High					98.1	100.0	75.3			
Medium	H_2SO_4	0.5	50	5	96.9	96.7	78.1	0.8	1.9	1.5
Low					98.5	99.8	77.6			

Agitation rate

It was found that the agitation rate from 400 to 600 rpm did not significantly influence the stripping percentages achieved (see Figure 31) when all other conditions were kept constant. It can therefore be concluded that, for the equipment used in the experiments under discussion, sufficient agitation was provided if the agitation speed was above 400 rpm so that mass transfer limitations did not occur.
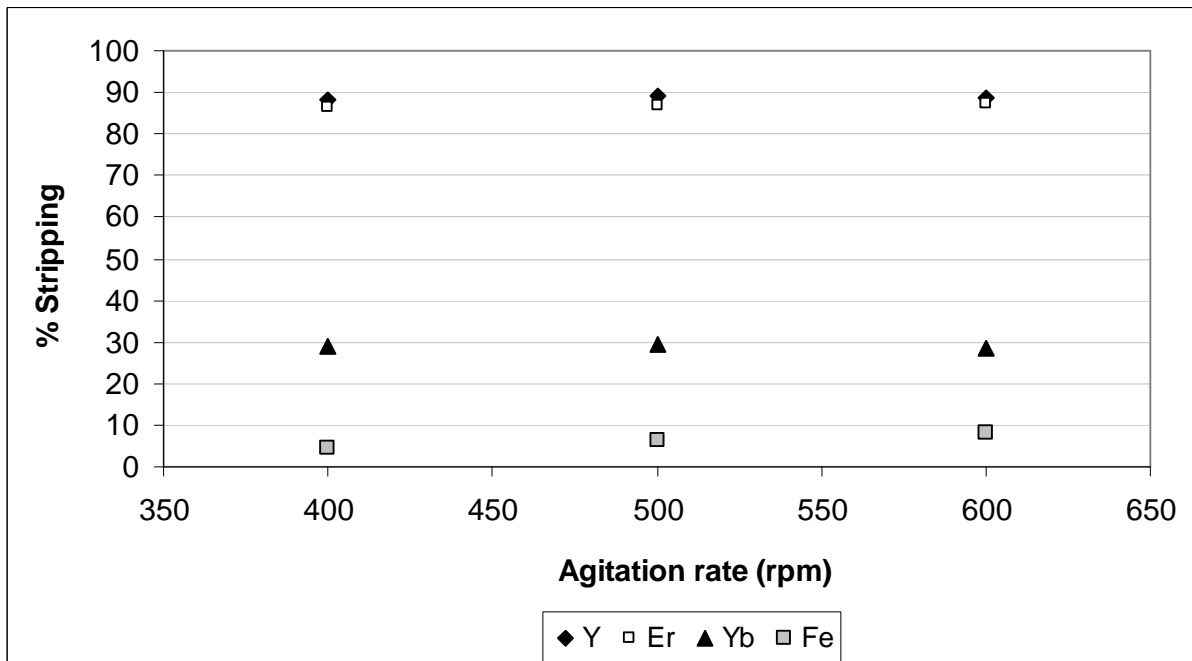
Figure 31: Stripping percentages for 5 M H_2SO_4 at 45 °C and an O:A ratio of 2:1 at different agitation rates

Equilibrium time

Figure 32 plots the stripping percentages achieved when the stripping reaction was allowed different amounts of time, at a constant sulphuric acid concentration of 5 M, O:A ratio of 2:1 and a temperature of 45°C. It can be seen that the curves for yttrium and erbium flatten out from nine minutes onwards, with only a 0.5% increase in stripping percentage from 9 to 12 minutes. For the purpose of this test work it can therefore be assumed that the yttrium and erbium stripping reactions had reached equilibrium at 12 minutes.

The ytterbium curve also flattens off, with a change of 1.6% in the last three minutes. Comparing this with a change of 6.1% between six and nine minutes, it can be said that equilibrium was not yet attained, but no more than a 1% change will happen for reaction times greater than 12 minutes. The iron stripping reaction with H_2SO_4 was not close to equilibrium after 12 minutes. However, the plant already has an existing regeneration circuit that uses HCl for iron removal from the organic phase and therefore the iron results were only necessary for comparison. It can be concluded that the equilibrium time for H_2SO_4 stripping of Y, Er and Yb was sufficient for the reactions to reach equilibrium or be close enough to equilibrium that equilibrium could be assumed for the experimental work.
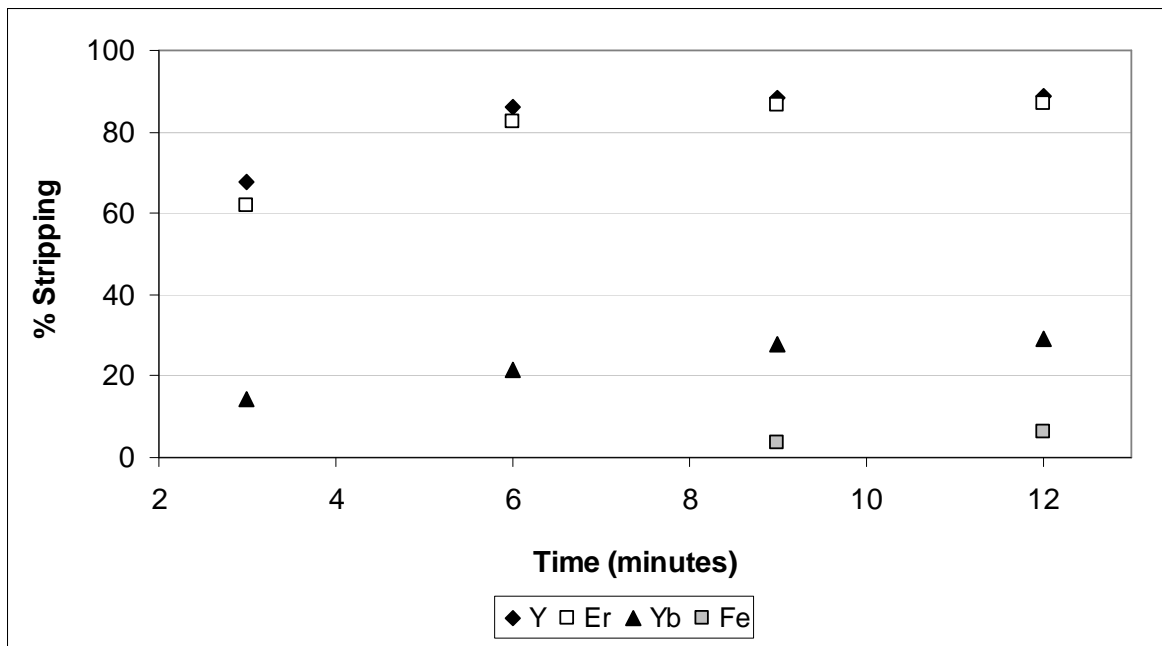
Figure 32: Stripping rare earths and iron from synthetic organic with H_2SO_4 plotted against reaction time

6.2.3   O:A ratio and stripping

Figures 33 and 34 below compare the effect of O:A ratio on the stripping achieved with 5 M H_2SO_4 at 30 and 50°C. Rare earth stripping increased when the O:A ratio was reduced. This was expected, since a reduction in O:A ratio increases the amount of aqueous relative to the organic phase, which increases interfacial contact between the organic molecule containing the rare earth ion and the H^+ ion in the aqueous phase. H^+ ions drive forward the stripping reaction 12. The results also correlate to the trend found by Desouky *et al.* (2009).

Figures 33 and 34 show the effect that the O:A ratio had on stripping rare earths off synthetic organic with sulphuric acid, at a constant concentration of 5 M.
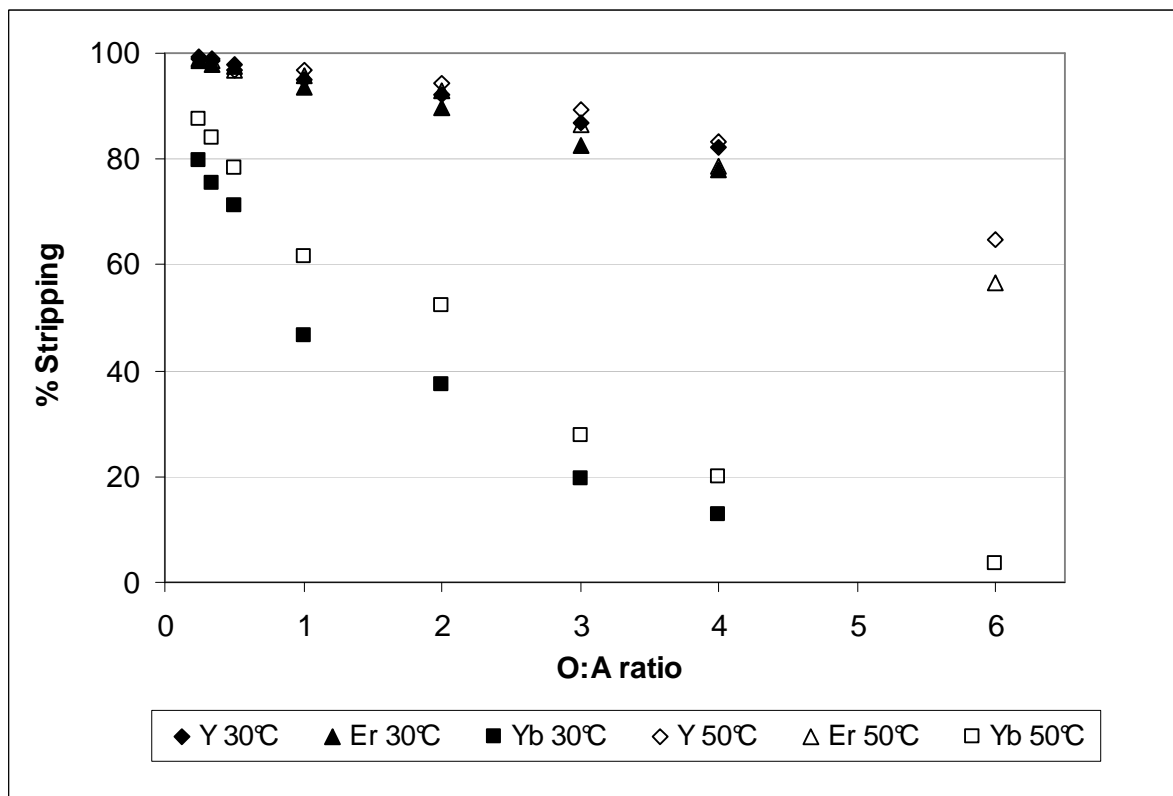
Figure 33: Stripping Y, Er and Yb from synthetic organic with 5M H_2SO_4 at different O:A ratios
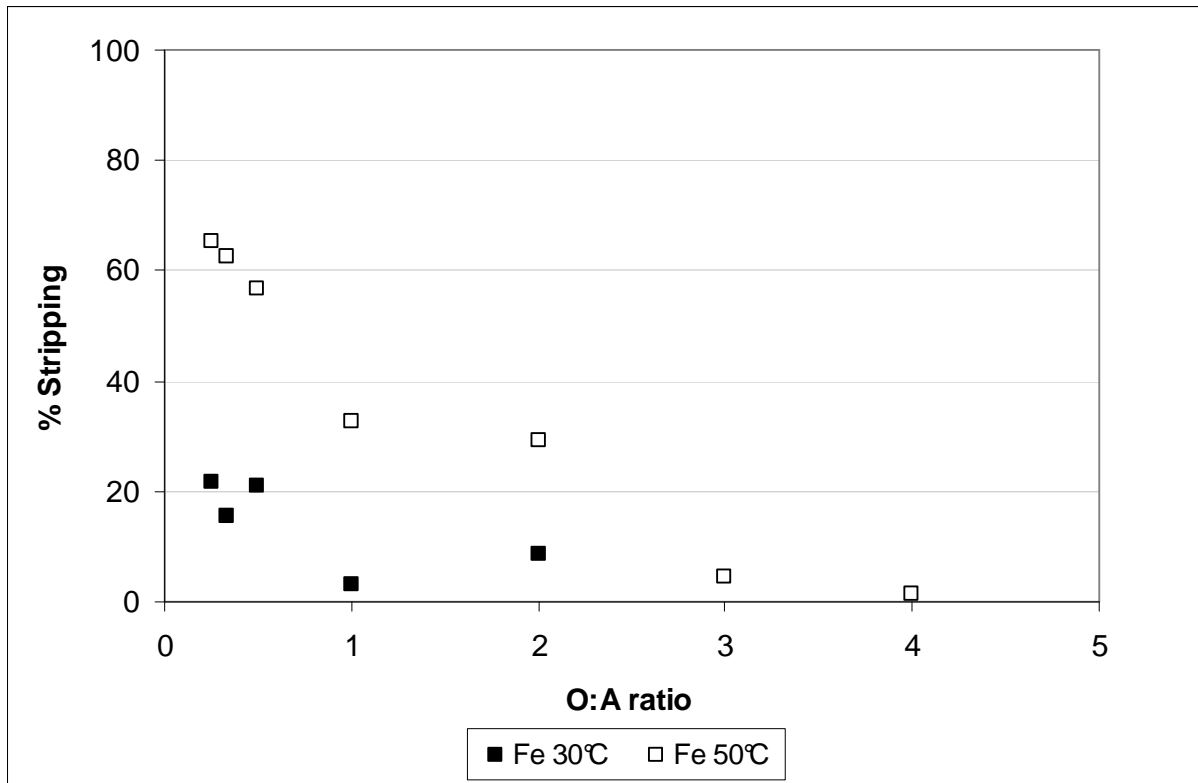
Figure 34: Stripping Fe from synthetic organic with 5M H_2SO_4 at different O:A ratios

Figures 33 and 34 indicate that stripping decreased significantly with increasing O:A ratio. For yttrium and erbium stripping, stripping performance decreased slower at low O:A ratios and decreased more rapidly at O:A ratios of 4:1 to 6:1. Ytterbium stripping, on the other hand, decreased rapidly with increasing O:A ratio at low O:A ratios and tend to steady out at O:A ratios of 5:1 and 6:1. Iron stripping showed the same trend as ytterbium, however, the points were more scattered. For Y and Er the availability of aqueous at high O:A ratios seem to be a limiting factor, which decreases as the O:A ratio decreases. Ytterbium and iron stripping seem to be limited by the available aqueous even at low O:A ratios.

Figures 35 and 36 show the effect of O:A ratio when HCl is used instead of H_2SO_4.
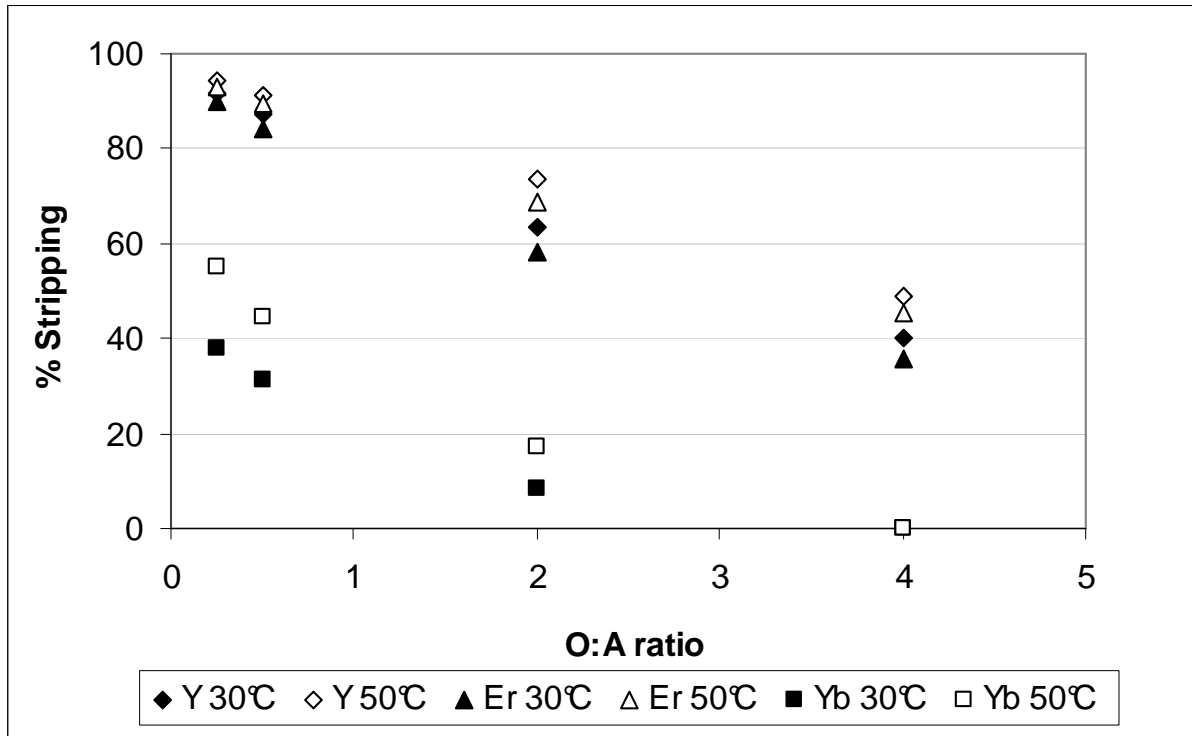
Figure 35: Stripping Y, Er and Yb from synthetic organic with 5M HCl at different O:A ratios
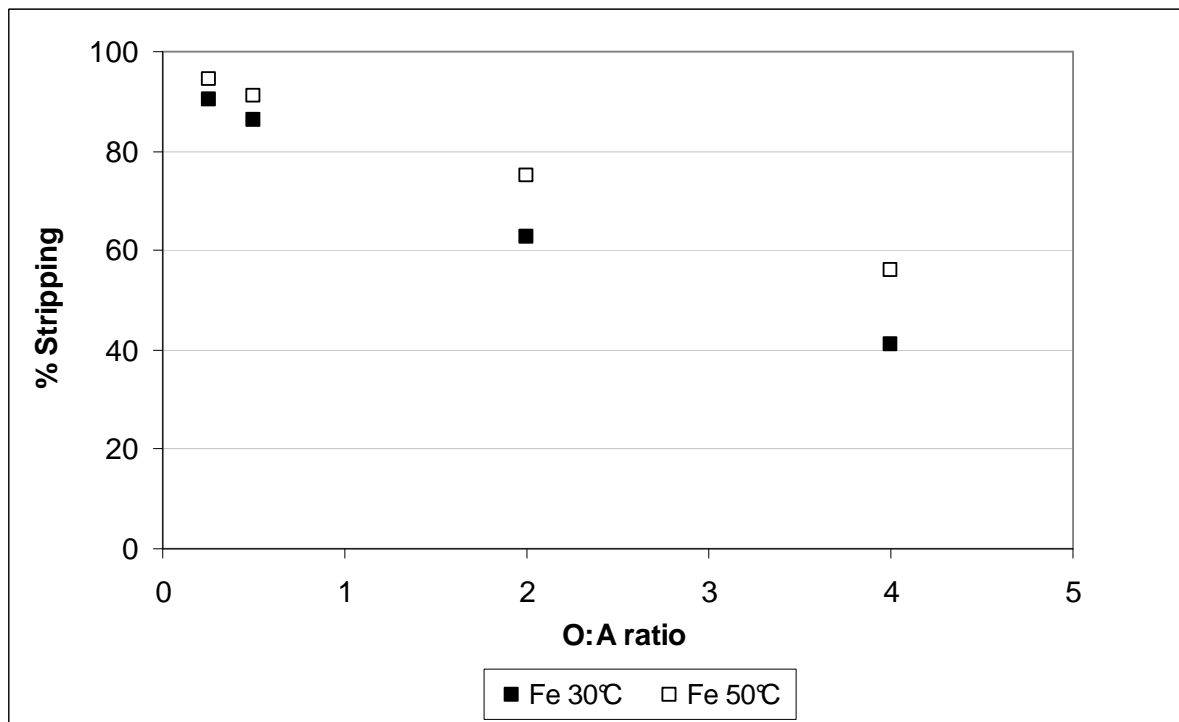
Figure 36: Stripping Fe from synthetic organic with 5M HCl at different O:A ratios

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Stripping yttrium, erbium, ytterbium and iron with HCl, the stripping percentage obtained decreased on average by 10% for every increase of one in O:A ratio. The decrease was also much steeper than when sulphuric acid was used. Stripping percentages of above 40% could be achieved for Y, Er and Fe at an O:A ratio of four, while ytterbium required a lower O:A ratio of two to attain the same percentage stripping.

6.2.4 Temperature

Stripping increased as the temperature was increased. Assuming that the reactions had reached equilibrium, an increase in stripping efficiency with an increase in temperature indicates that the stripping reaction is endothermic. Stripping increased with increasing temperature in an S-shaped curve (see Figure 37). However, the increase in stripping achieved when increasing the temperature from 30 to $55°C$ was only 10% for ytterbium and only 2% for yttrium and erbium. The effect of O:A ratio is therefore more significant than the effect of temperature on rare earth stripping. Increasing the temperature from 30 to $55°C$ increased iron stripping by between 20 and 40%, showing that iron stripping is more severely influenced by temperature than the rare earths.
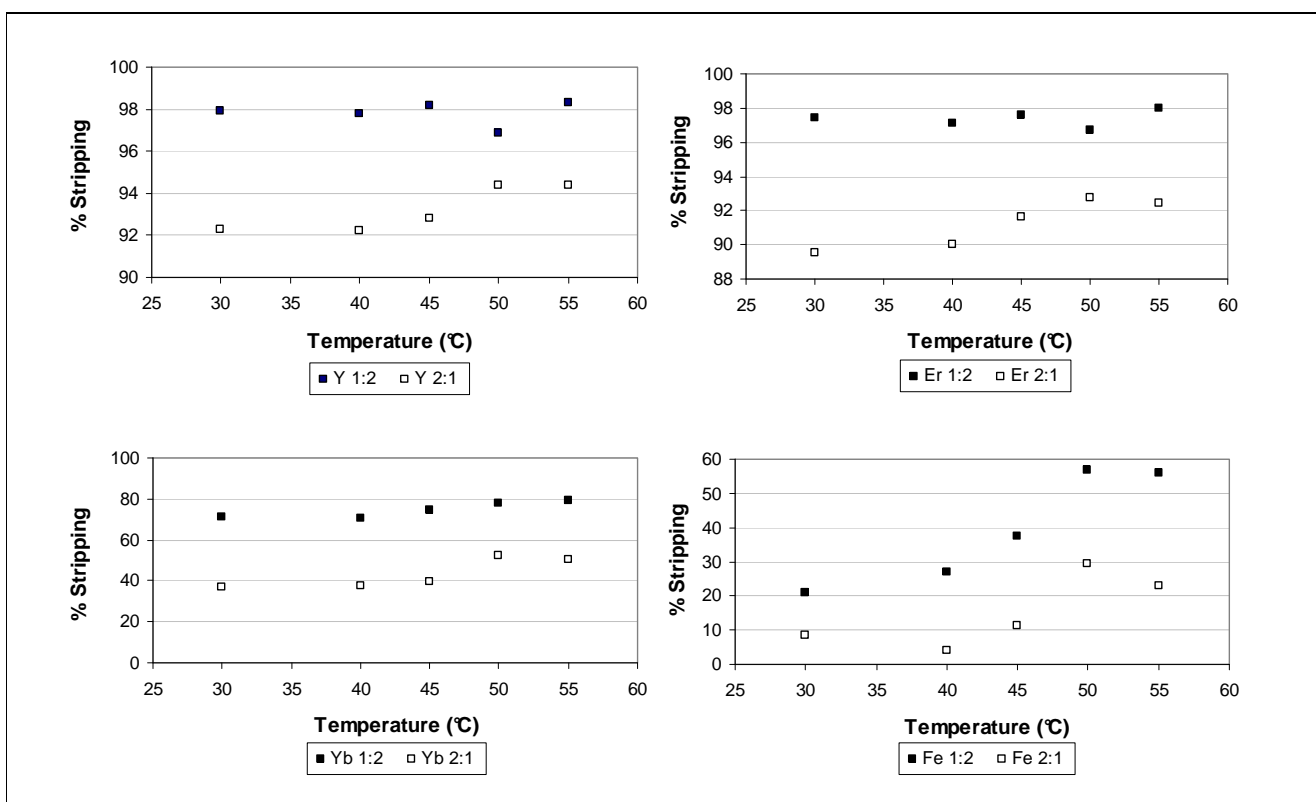
Figure 37: Rare earth stripping from synthetic organic with 5 M H_2SO_4 as a function of temperature, for O:A ratios of 1:2 and 2:1

6.2.5   Interaction effects in rare earth stripping

Regression was performed on the results to determine which variables had the greatest influence on stripping. The ANOVA tables can be found in Appendix C and are discussed in Chapter 6.4. *C* indicates acid concentration, *OA* the O:A ratio and *T* temperature, with *OAC*, *OAT* and *TC* as the interaction terms between the different variables.

When sulphuric acid was used as the stripping agent, *C* and C^2 were found to be the most important variables for yttrium and erbium stripping, while C^2, *TC* and *OAC* were the most influential in ytterbium stripping. When hydrochloric acid was used as stripping agent, *C* and *OAC* were the most important for yttrium and erbium stripping and *OA*, C^2, *TC* and *OAC* for ytterbium. The significant variables in iron stripping with H_2SO_4 were *OA*, *C*, C^2, *OAT*, *OAC* and *TC* and for iron stripping with HCl, C^2 and *OAC*.

It was therefore seen that stripping for all the elements tested was greatly influenced by the stripping agent concentration. The interaction term O:A ratio-concentration (*OAC*) was also important. Since the stripping reaction takes place on the interface of the organic and aqueous droplets it was expected that the interaction between the O:A ratio and acid concentration would play a role. It also means that during plant operation, it is important to not only control the O:A ratio or the acid concentration, but to have both at the desired set points so that the interaction effect will also positively influence the reaction. Iron and ytterbium stripping further also showed the temperature-concentration (*TC*) interaction term to be significant.

6.3   Rare earth and iron stripping from plant organic

6.3.1   Stripping agent concentration: sulphuric acid

Figures 38 and 39 show the effect of different concentrations of sulphuric acid on the stripping of the different elements from Skorpion Zinc plant zinc-stripped organic. At 30 °C, the plots for yttrium and erbium are S-curves with initial slow increase in stripping at low acid concentrations, a steeper increase from 3 to 5 M then stripping percentage flattens off from 5 to 7 M H_2SO_4. The total *YR₃.3HR* concentration in the plant organic was calculated to be 0.04 mol/l. Based on the stoichiometry in equation 12, 0.11 mol/l hydrogen ions would be required to strip off all the rare earth elements. Similar to what was seen for the synthetic organic, stripping of the plant organic was also not

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stoichiometrically limited by the hydrogen ion concentration but the hydrogen ion concentration affected equilibrium.

At 50 ℃, the slow increase in stripping percentage from 1 to 3 M acid seen at a temperature of 30 ℃ was not observed, indicating that, for these low acid concentrations, the reaction equilibrium was limited by both the acid concentration as well as the temperature or energy supplied.

The curves are therefore very similar to that obtained for synthetic organic as was seen in Figures 25 – 28. The synthetic organic phase was only stripped with acid concentrations up to 5 M. The tests with plant organic have indicated that only 3 – 5 % increase in stripping percentage was obtained for an increase in acid concentration from 5 to 7 M. Taking the cost of sulphuric acid into account, it is therefore satisfactory to design the rare earth stripping unit to operate at 5 M.

Ytterbium stripping shows a slow increase in stripping at low acid concentrations and a faster increase from 3 M to 7 M.   The optimum acid concentration for Yb stripping is therefore greater than 7 M. Therefore any process constructed for Yb stripping will cost significantly more than for Y and Er stripping, due to the high acid concentrations that will be required.
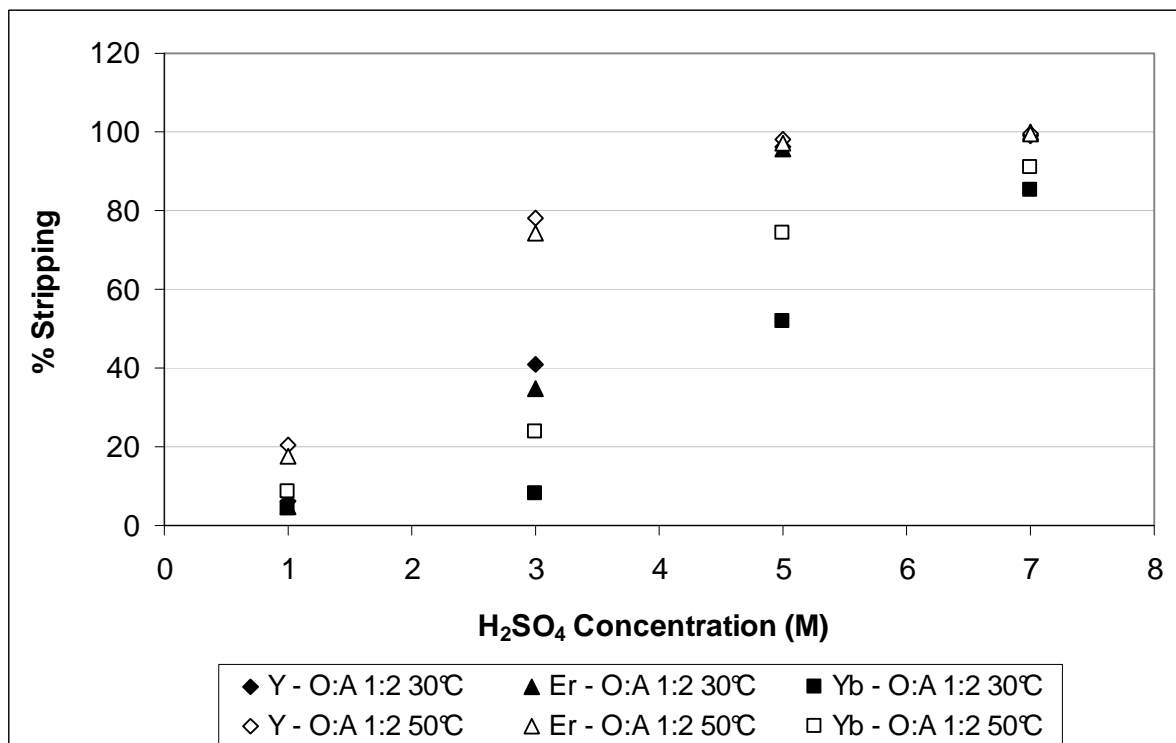
Figure 38: Stripping rare earths from plant organic with H_2SO_4 at O:A 1:2
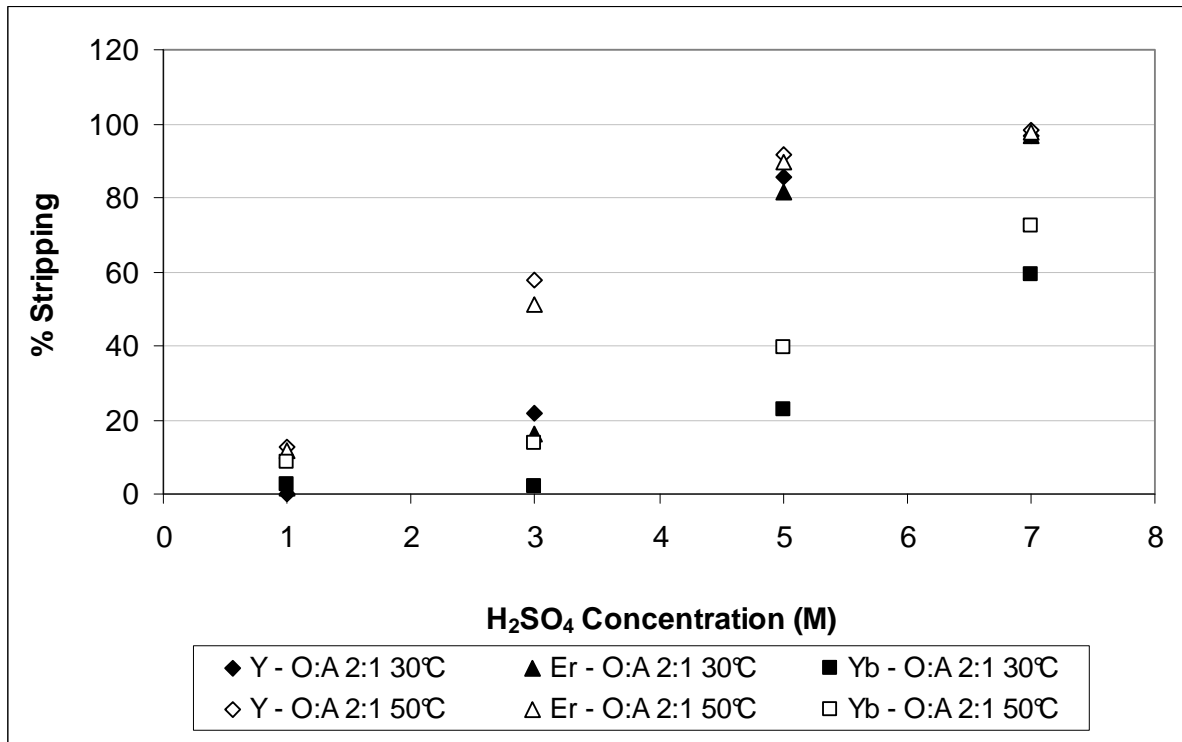
Figure 39: Stripping rare earths from plant organic with H_2SO_4 at O:A 2:1

Significantly lower stripping percentages was achieved for removing iron (see Figure 40) from the organic phase with sulphuric acid than for the rare earths. Higher O:A ratios and a lower temperature reduced iron removal from the organic.
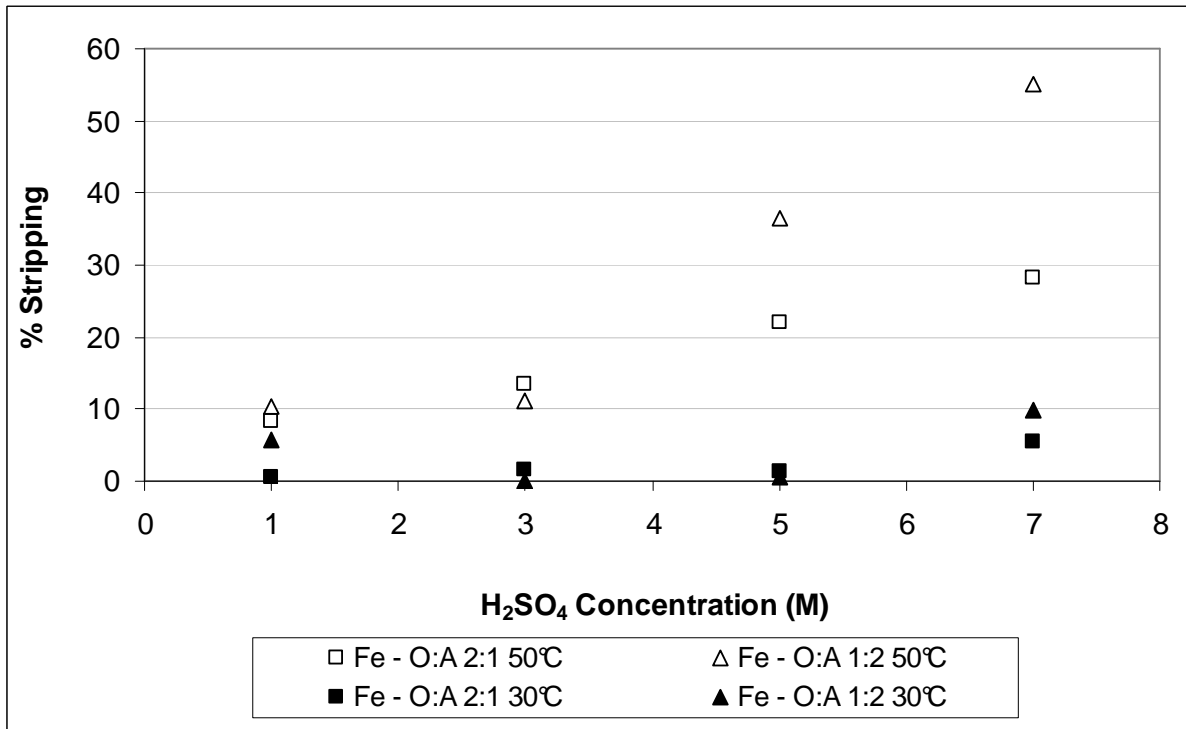
Figure 40: Stripping iron from plant organic with H_2SO_4

6.3.2 Stripping agent concentration: hydrochloric acid

Figures 41 and 42 show the effect of different concentrations of hydrochloric acid on the stripping of the different elements from Skorpion Zinc plant zinc-stripped organic. The plots for yttrium and erbium show a steeper increase in stripping percentage with increase in acid concentration from 3 M to 5 M HCl, but flattens off towards 7 M for O:A equal to 1:2. Stripping percentages of 80% were obtained at 7 M acid concentration for an O:A ratio of 2:1 while more than 90% were achieved for an O:A ratio of 1:2. It can be concluded that equilibrium was reached quicker when the mixture was more aqueous, possibly as a result of the reaction mainly occurring on the phase boundary.

Ytterbium stripping showed low stripping percentages from 1 – 3 M and thereafter increased as the acid concentration was increased to 7 M. Yb stripping doubled when the O:A ratio was reduced from 2:1 to 1:2 and it is expected that the stripping percentages will be even higher at a lower O:A ratio.

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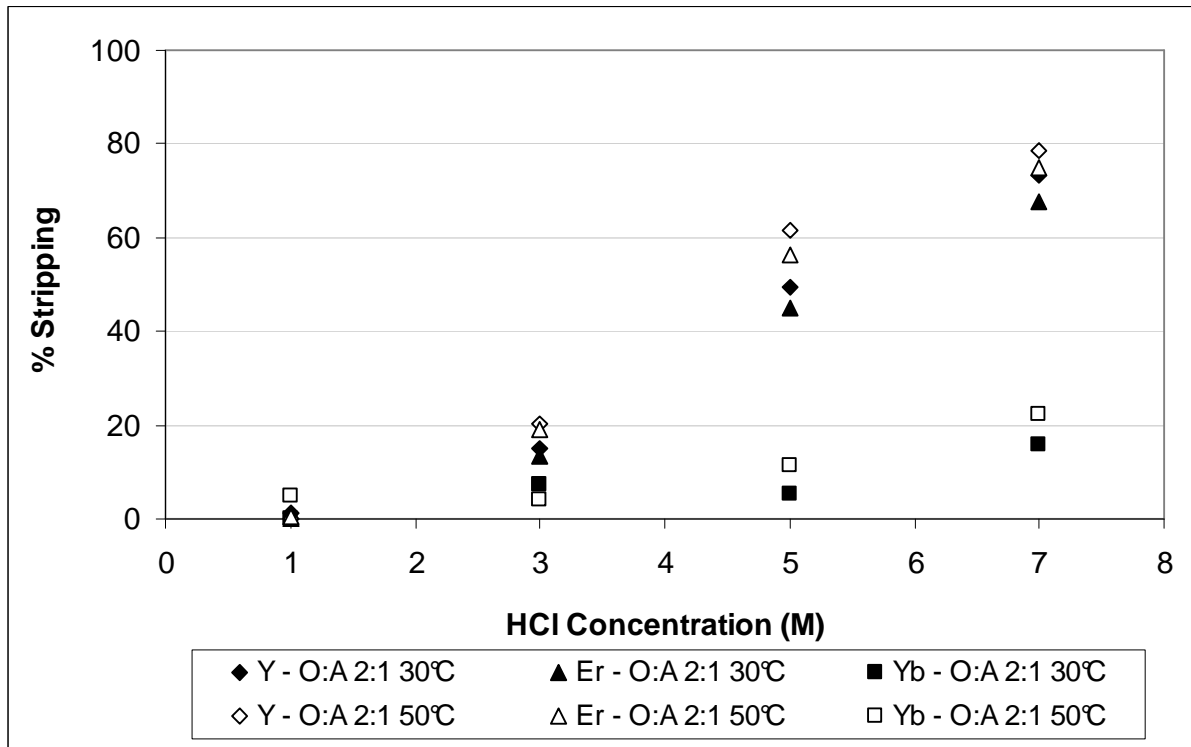
Figure 41: Stripping rare earths from plant organic with HCl at O:A 2:1
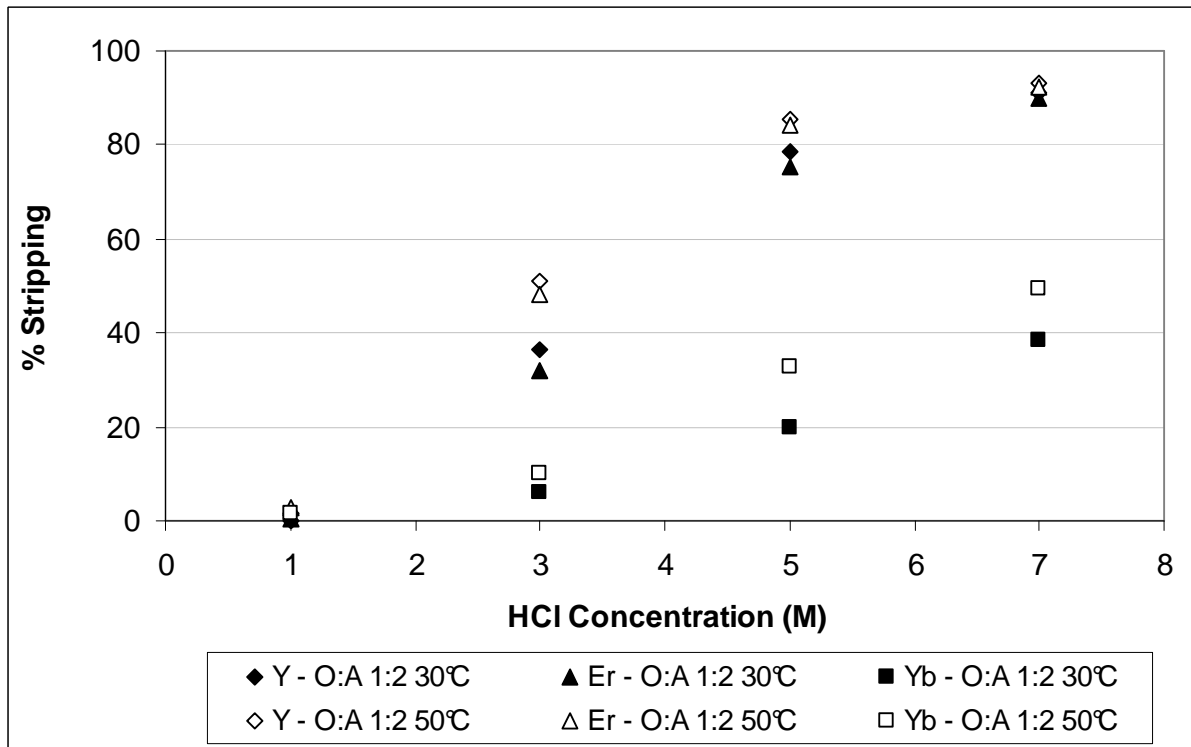
Figure 42: Stripping rare earths from plant organic with HCl at O:A 1:2

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Figure 43 displays the stripping results for plant organic with hydrochloric acid. 85% iron stripping from plant organic was achieved with hydrochloric acid while sulphuric acid could only achieve 55% stripping. Figure 43 indicates that there is an optimum hydrochloric acid concentration of 5 M where the greatest removal of Fe can be accomplished. It also shows that at the optimum concentration, the O:A ratio had considerable effect, with an increase of 20% in stripping from an O:A ratio of 2:1 to 1:2. The peak seen at 5 M HCl and the subsequent decrease can be attributed to the formation of chloro-complexes by D2EHPA, which prevents stripping of the trivalent metal ion as it is locked up in the chloro-complex (Thomas and Burkhart, 1973).
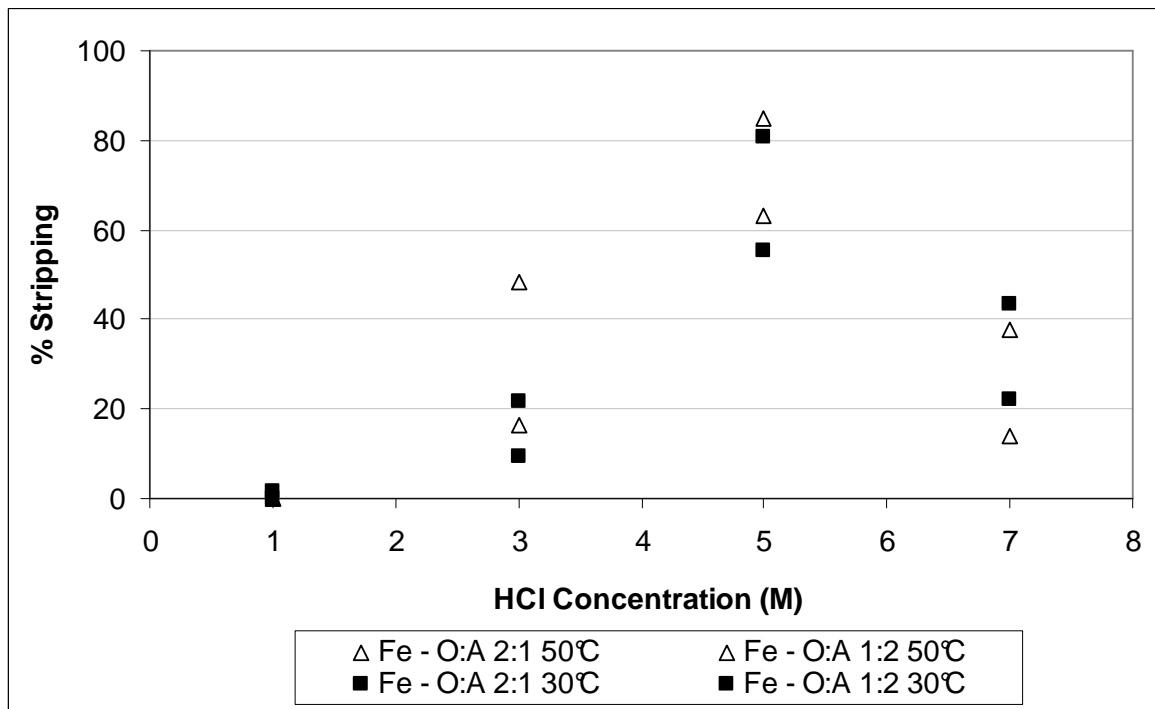
Figure 43: Stripping iron from plant organic with HCl

6.3.3 O:A ratio

The effect that the O:A ratio has on plant organic phase stripping were tested by using three different O:A ratios and keeping the acid concentration constant at 5 M and the temperature at 50°C. All elements under consideration showed a decrease in stripping for an increase in O:A ratio. Similar trends relating to the O:A ratio were seen for sulphuric acid and hydrochloric acid (see Figures 44 and 45, respectively). Ytterbium showed the greatest sensitivity to O:A ratio,

with a reduction in stripping of 30% for an increase in O:A ratio from 1:2 to 2:1. Yttrium and erbium showed a 20% reduction in stripping with an increase in O:A ratio from 1:2 to 4:1 when sulphuric acid was used for stripping, but a much higher reduction of 40% when hydrochloric acid was used. The effect of O:A ratio on iron stripping was similar to Y and Er, only with the absolute stripping percentages being lower for sulphuric acid. The results showed that a stripping operation would require an O:A ratio of less than 1:2.
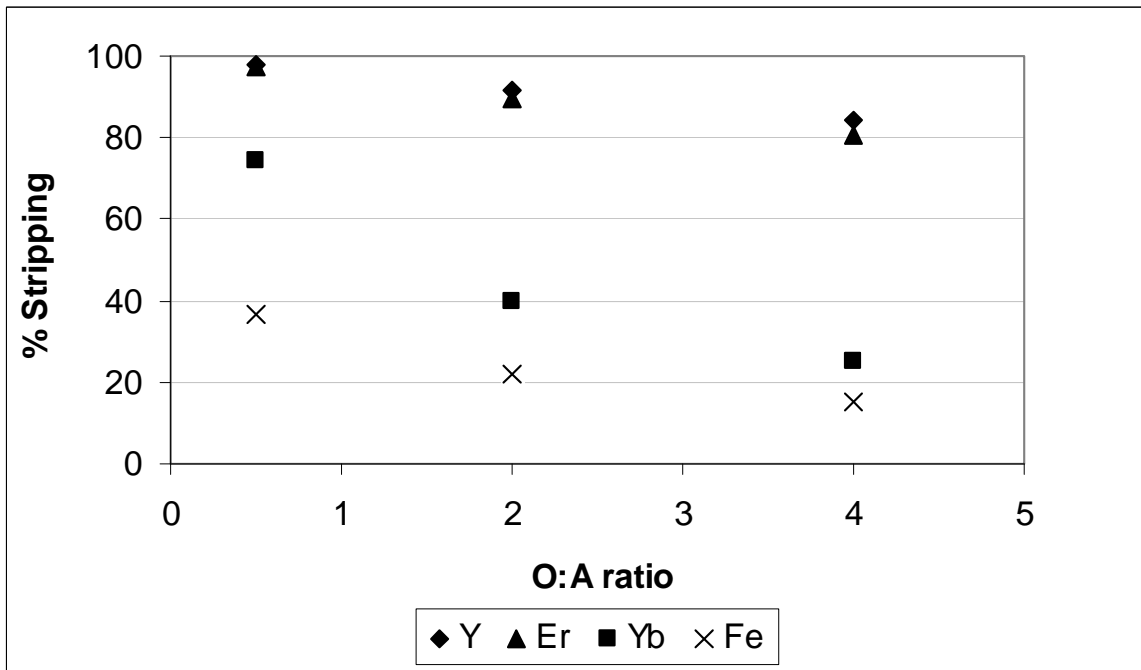
Figure 44: Stripping plant organic with 5 M H$_2$SO$_4$ at T = 50°C
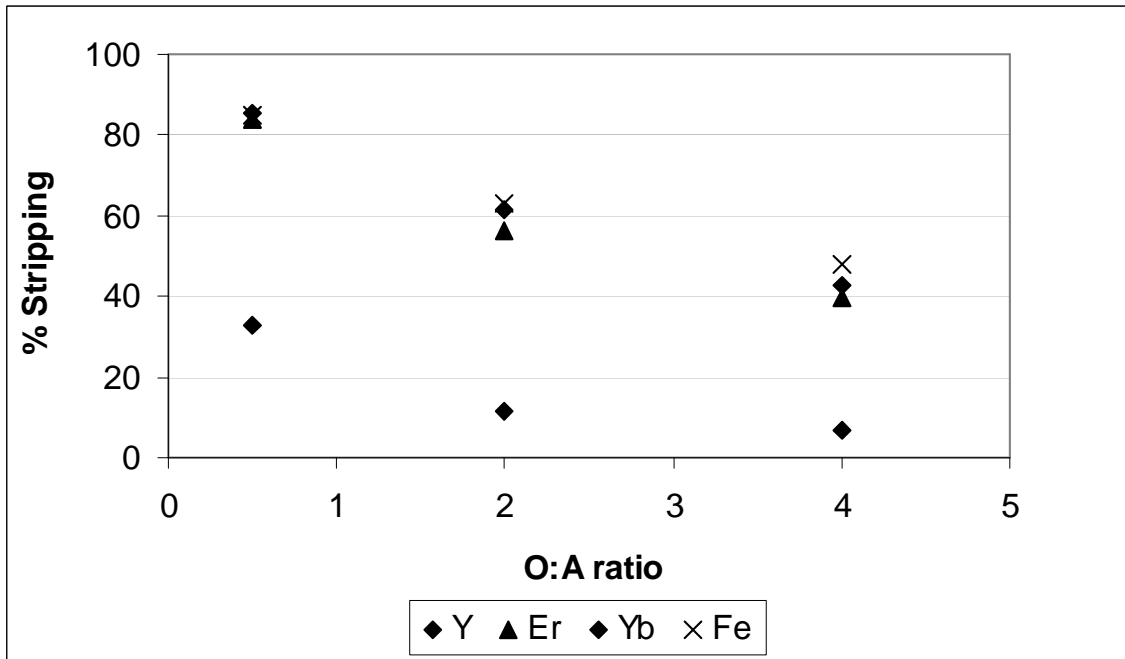
Figure 45: Stripping plant organic with 5 M HCl at T= 50°C

6.4 Statistical regression models for rare earth stripping with H_2SO_4

The experimental data discussed above for synthetic organic were combined and regressed to find statistical models for the prediction of rare earth stripping at different operating conditions. Regression was done via backward elimination (Derksen, 1992), which involved starting with all variables, including linear, 2nd order and cross-product terms and testing them one by one for statistical significance, deleting any that were not significant and re-fitting the model. The process indicated in Figure 46 was followed. The p-value is the probability of observing a certain result or a result more extreme. For example, if the null hypothesis is taken to be: "Temperature does not affect stripping", and a p-value of 0.04 is obtained it means that there is a 4 % probability that temperature does not affect stripping and the null hypothesis is rejected based on a 96 % probability that stripping will be affected by temperature. Variables were considered statistically significant if it had a p-value of less than 0.05, as is commonly used in literature (Bart and Rousselle, 1998).
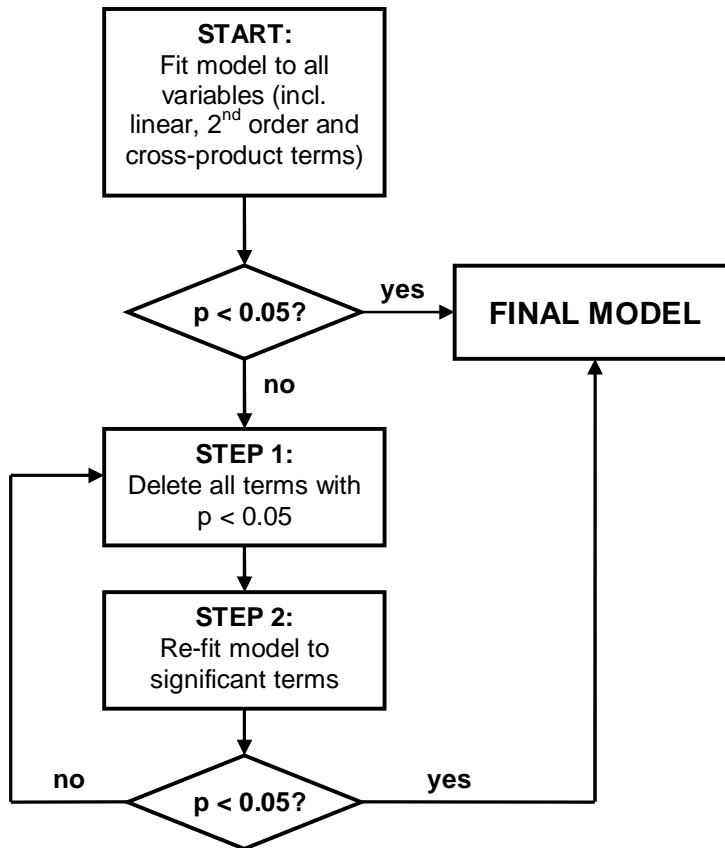
Figure 46: Backward elimination regression process

The ANOVA results for the first fit and for the final model are displayed in Appendix C. After refining the following models were obtained for stripping yttrium, erbium, ytterbium and iron from D2EHPA with sulphuric acid:

$$\%Ystrip(H_2SO_4) = -14.89OA + 0.11T + 45.97C - 0.59OA^2 - 4.71C^2 + 2.54OA \times C - 17.09 \qquad \text{[Equation 17]}$$

$$\%Erstrip(H_2SO_4) = -15.71OA + 0.14T + 42.13C - 0.71OA^2 - 4.03C^2 + 2.56OA \times C - 16.31 \qquad \text{[Equation 18]}$$

$$\%Ybstrip(H_2SO_4) = -5.39OA + 2.08OA^2 + 2.35C^2 + 0.1T \times C - 4.24OA \times C - 7.24 \qquad \text{[Equation 19]}$$

$$\%Festrip(H_2SO_4) = 15.76OA - 4.75C + 2.88OA^2 + 0.01T^2 - 0.54OA \times T + 0.30T \times C - 3.29OA \times C - 4.78$$

$$\text{[Equation 20]}$$

The symbols used are defined as: C for concentration, OA for O:A ratio and T for temperature, OAT the interaction term of O:A ratio and temperature, OAC the interaction term of O:A ratio and concentration and TC the interaction between temperature and concentration. Note that the p-value of the parameter T was greater than 0.05. However, it was included in the model since the plant data (discussed below) showed a stronger dependence on temperature than when synthetic organic was used and the models were to be used to model plant data.

The models show that O:A ratio and concentration are more important parameters for stripping than temperature. Interaction effects between O:A ratio and concentration are also present in all of the models. Since stripping is an interfacial reaction that is both chemically and diffusion controlled, the observed importance of O:A ratio and acid concentration is expected as this will influence the reaction rate on the liquid-liquid interface (Xiong *et al.*, 2004) Table 11 compares stripping values predicted by the models to experimental results achieved when experiments similar to those discussed above were performed on Skorpion Zinc plant zinc-stripped organic.

Table 11: Experimental results compared to predicted percentage stripping with H_2SO_4 for 17 tests

Test no.	O:A ratio	Temp-erature (°C)	H_2SO_4 Conc. (M)	%Y strip exp.	%Y strip pred.	Delta (%)	%Er strip exp.	%Er strip pred.	Delta (%)	%Yb strip exp.	%Yb strip pred.	Delta (%)	%Fe strip exp.	%Fe strip pred.	Delta (%)
1	2	30	1	0	0	0	1	-3	-4	3	2	-1	0.6	9	9
2	2	30	3	22	65	43	16	59	43	2	9	7	1.5	5	4
3	2	30	5	85	92	6	81	89	8	23	36	13	1.2	1	0
4	2	30	7	97	81	-16	97	87	-10	59	82	23	5.5	-4	-9
5	0.5	30	1	6	21	15	5	19	14	4	8	4	5.8	4	-1
6	0.5	30	3	41	78	37	35	74	39	8	29	21	-0.3	10	10
7	0.5	30	5	96	97	1	96	96	0	52	68	16	0.6	16	15
8	0.5	30	7	99	78	-21	100	86	-14	85	126	41	9.8	21	11
9	2	50	1	12	3	-10	12	0	-12	8	4	-5	8.3	5	-4
10	2	50	3	58	67	9	51	62	11	14	15	2	13.5	12	-1
11	2	50	5	92	94	2	90	92	2	40	46	7	22.0	20	-2
12	4	50	5	84	82	-2	80	78	-3	25	18	-7	15.3	-1	-16
13	2	50	7	98	83	-15	98	90	-8	72	96	23	28.1	28	0
14	0.5	50	1	20	23	3	18	22	4	9	10	2	10.4	16	6
15	0.5	50	3	78	80	2	74	77	3	24	35	11	11.0	34	23
16	0.5	50	5	98	99	1	97	99	2	74	78	4	36.4	51	15
17	0.5	50	7	99	81	-19	99	89	-10	91	140	49	55.0	69	14

Statistical models were fitted to data from synthetic organic and then used to predict plant experimental data. The differences between the experimental results and the stripping percentages predicted by the models are plotted in Figure 47. For a temperature of 50°C, concentrations in the range of 1 – 5 M H_2SO_4 and O:A ratios of 4:1 to 1:2, the plant experimental data could be most accurately predicted by the model. These are the tests for which differences of less than 10% are displayed in Figure 47. Predictions at low temperatures (tests 1 to 8) were not reliable, as can be seen by the large differences displayed on the left-hand side of the graph. For ytterbium, and to a lesser extent, for yttrium and erbium, predictions at high concentrations of 7 M (tests 4, 8, 13 and 17) were inaccurate, since the models were based on data obtained in the range of 1 – 5 M acid only. The model for Fe predicted the results for experiments with plant organic with a smaller error than the models for Y, Yb and Er.
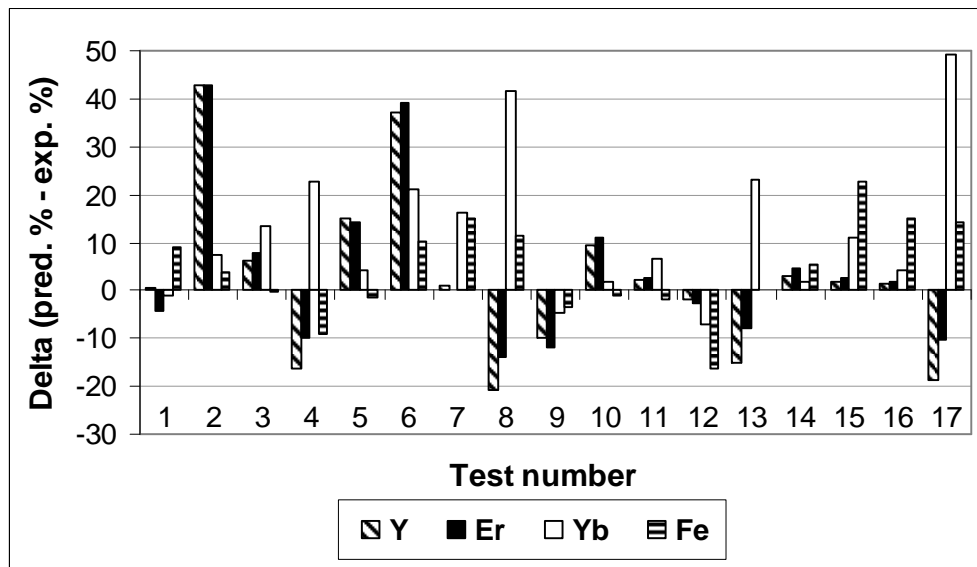
Figure 47: Difference between plant experimental results for H_2SO_4 and model predictions for model fitted to synthetic organic data

Although it has been shown that the plant data can be predicted to within 15% accuracy by the models compiled for synthetic organic, regression was used to fit statistical models to the experimental data for stripping rare earths from Skorpion Zinc plant organic with sulphuric acid. These would be more accurate for the specific (aged) organic phase at Skorpion Zinc mine, while the models given above are valid for 40 % D2EHPA – 60 % kerosene phases in general. Terms with a p-value less than 0.05 were considered statistically significant for the plant experimental data. The ANOVA tables after refining the models can be found in Appendix C.

$$\%Ystrip(\,H_2SO_4\,) = -5.70OA + 8.79 \times 10^{14}T + 44.94C - 0.23TC - 1.10 \times 10^{13}T^2 - 2.48C^2 - 1.65 \times 10^{16}$$

[Equation 21]

$$\%Erstrip(\,H_2SO_4\,) = -5.02OA + 1.34T + 36.66C - 0.16TC - 1.80C^2 - 69.65 \qquad \text{[Equation 22]}$$

$$\%Ybstrip(\,H_2SO_4\,) = 1.70OA + 0.64T + 4.56C + 1.39C^2 - 2.56OAC - 26.46 \qquad \text{[Equation 23]}$$

$$\%Festrip(\,H_2SO_4\,) = 10.15C + 0.25TC + 0.56C^2 + 0.98OAC + 6.52 \qquad \text{[Equation 24]}$$

T^2 was eliminated from some of the models although it had a low p-value indicating that it is a significant parameter, because it caused instability in the predicted values by showing positive bias at high temperatures. Further, the models indicate that C and C^2 are important parameters, occurring in all the models. One or both of the interaction terms OAC and OAT are also present in the models.

6.5   Statistical regression models for rare earth stripping with HCl

The following statistical models (backward elimination with p-values less than 0.05) were obtained for rare earth stripping from synthetically manufactured organic with hydrochloric acid:

$$\%Ystrip(\,HCl\,) = -8.41OA + 0.29T + 28.61C + 1.62OA^2 - 1.20C^2 - 2.38OA \times C - 24.80 \qquad \text{[Equation 25]}$$

$$\%Erstrip(\,HCl\,) = -8.93OA + 0.35T + 25.26C + 2.05OA^2 - 0.64C^2 - 2.76OA \times C - 25.56 \qquad \text{[Equation 26]}$$

$$\%Ybstrip(\,HCl\,) = 5.82OA - 4.06C + 3.01OA^2 + 1.71C^2 - 0.17OA \times T + 0.15T \times C - 4.73OA \times C - 2.87$$

[Equation 27]

$$\%Festrip(\,HCl\,) = -4.51OA + 0.55T + 5.27C + 1.53OA^2 + 2.89C^2 - 2.81OA \times C - 22.40 \qquad \text{[Equation 28]}$$

Similarly to the models for sulphuric acid, the hydrochloric acid models indicate that stripping is dependent on acid concentration and O:A ratio as well as interaction effects between the two. The ANOVA tables after refining the models can be found in Appendix C. Table 12 compares stripping values predicted by the models to experimental results achieved when the experiments discussed above were performed on Skorpion Zinc plant zinc-stripped organic.

Table 12: Experimental results compared to predicted percentage stripping with HCl for 17 tests

Test no.	O:A ratio	Temp-erature (°C)	HCl Conc. (M)	%Y strip exp.	%Y strip pred.	Delta (%)	%Er strip exp.	%Er strip pred.	Delta (%)	%Yb strip exp.	%Yb strip pred.	Delta (%)	%Fe strip exp.	%Fe strip pred.	Delta (%)
1	2	30	1	2.0	-4	-6	-0.9	-6	-5	0.7	3	3	0.0	-6	-6
2	2	30	3	25.6	34	9	20.9	29	8	0.9	-1	-2	7.9	16	8
3	2	30	5	63.2	63	0	58.3	58	0	8.5	9	1	62.7	62	-1
4	2	50	1	2.9	2	-1	1.7	1	-1	0.0	0	0	2.3	5	2
5	2	50	3	35.7	40	4	32.2	35	3	4.8	2	-3	27.1	27	0
6	2	50	5	73.5	69	-5	68.7	65	-4	17.0	18	1	74.9	73	-2
7	0.5	30	1	6.1	6	0	3.5	4	1	0.0	-2	-2	3.0	-1	-4
8	0.5	30	3	56.1	52	-5	50.4	47	-4	7.0	8	1	23.8	30	6
9	0.5	30	5	87.3	87	0	84.3	84	0	31.3	32	1	86.1	84	-2
10	0.5	50	1	6.0	12	6	6.1	11	5	0.0	0	0	1.7	10	8
11	0.5	50	3	66.1	57	-9	60.9	54	-7	12.6	16	3	54.8	41	-14
12	0.5	50	5	91.3	93	2	89.3	91	2	44.6	46	1	91.1	95	4
13	0.25	30	5	91.6	92	0	89.7	89	0	38.0	37	-1	90.4	88	-2
14	4	30	5	40.2	42	1	35.7	37	1	0.0	-1	-1	40.9	43	2
15	0.25	50	5	94.3	98	4	93.0	96	3	55.0	52	-3	94.4	99	5
16	4	50	5	48.9	47	-2	45.2	44	-1	0.0	1	1	56.1	54	-2

The difference between the experimental results for HCl and the stripping percentages predicted by the models are plotted in Figure 48. The models predicted the experimental results with plant organic within 5 – 10% accuracy, which is more accurate than the H_2SO_4 models.
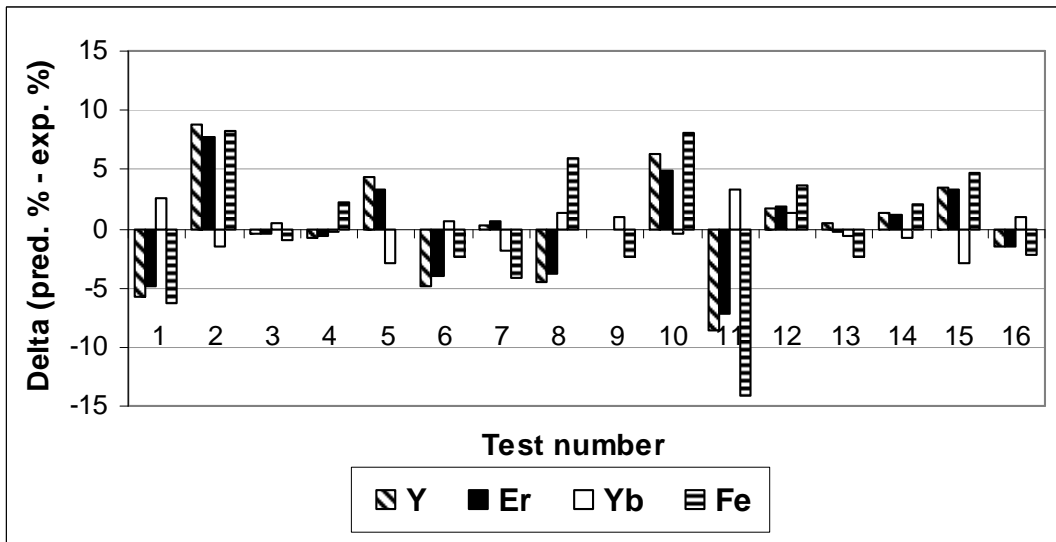
Figure 48: **Difference between plant experimental results for HCl and model predictions for model fitted to synthetic organic data**

Similar to the processing of the data for sulphuric acid as stripping agent, regression (with p-values less than 0.05 considered significant) was used to fit statistical models to the experimental data for stripping rare earths from Skorpion Zinc plant organic with hydrochloric acid. The models are given below and the ANOVA tables after refining the models can be found in Appendix C.

$$\%Ystrip(\,HCl\,) = -10.38OA + 0.30T + 22.20C - 0.97C^2 - 21.39 \qquad \text{[Equation 29]}$$

$$\%Erstrip(\,HCl\,) = -10.90OA + 0.37T + 20.14C - 0.77C^2 - 21.38 \qquad \text{[Equation 30]}$$

$$\%Ybstrip(\,HCl\,) = 0.73C^2 + 0.07TC - 3.06OAC + 2.05OA^2 - 1.83 \qquad \text{[Equation 31]}$$

T^2 was again eliminated from the models although it had a low p-value indicating that it is a significant variable, because it caused instability in the predicted values, for instance showing positive bias at high temperatures. Similarly to the models for sulphuric acid, the models for HCl also indicate that C and C^2 are important variables, occurring in all the models.

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In Figure 43 it was seen that iron shows a distinct optimum when stripped with HCl. The data was therefore modeled in two sections, namely for HCl concentrations of 1 – 5 M and 5 – 7 M. The following models were obtained, with their corresponding curves:

$$\%Festrip(\ HCl:1-5M\ ) = 0.39T + 1.62OA^2 + 3.77C^2 - 3.94OAC - 16.11$$ [Equation 32]

$$\%Festrip(\ HCl:5-7M\ ) = -0.03T - 22.32OA + 2.77OA^2 - 20.87C + 198.54$$ [Equation 33]

6.6 Conclusions

The experimental results showed that rare earths can be removed from a synthetically prepared organic phase by stripping with hydrochloric-, sulphuric- or nitric acid. For yttrium, erbium and ytterbium, the best stripping agent was H_2SO_4, followed by HCl and then HNO_3. Sulphuric acid achieved stripping percentages of 97% for Y and Er at 5 M and 78% for Yb and hydrochloric acid achieved 91% stripping for Y, 89% for Er and 45% for Yb at 5 M. The experiments were repeated using zinc-stripped organic from the plant and similar results were obtained, with the stripping curve flattening off at acid concentrations above 5 M giving 5 M as the optimum operating strength. The behaviour of iron differed from the behaviour of the rare earths in that iron was preferentially stripped off by hydrochloric acid and not H_2SO_4.

The results showed good repeatability, and were not limited by the rare earth concentration, agitation rate or equilibrium time in the range of set points used in the experiments.

Although the relationship between O:A ratio and rare earth concentration was not the same for all of Y, Yb, Er and Fe, stripping of all elements increased as the O:A ratio decreased. Stripping percentages above 90% could be achieved for Y at O:A less than 3 and for Er at O:A less than 2 with sulphuric acid. More than 80% stripping could be attained for Yb with O:A less than 0.5. The O:A ratio trend was the same for sulphuric acid and hydrochloric acid, only with the stripping percentages being higher for the rare earths with H_2SO_4 and for iron with HCl.

Stripping increased with increasing temperature in an S-shaped curve, flattening off at 50°C. However, the increase in stripping achieved when increasing the temperature from 30 to 55°C was only 10% for ytterbium and only 2% for yttrium and erbium, indicating that the reaction is

only slightly endothermic. Increasing the temperature will also reduce the viscosity (Musadaidzwa and Tshiningayamwe, 2009), which would be beneficial for stripping. The effect of O:A ratio is therefore more significant than the effect of temperature on rare earth stripping. After stripping, oxalic acid could be used to recover a REE oxalate precipitate from HCl.

Lastly, statistical models were compiled to fit the experimental data obtained for Y, Yb, Er and Fe when stripped with sulphuric and hydrochloric acid respectively. The models were compiled by elimination of variables based on p-values after regression. All models showed dependence on the acid concentration, squared-concentration and the O:A ratio-concentration product variables. T^2 was eliminated from most of the models since it biased the predicted values. The models were compiled for the experimental data obtained from stripping synthetically prepared organic and then tested on results obtained when stripping the plant organic phase. The statistical models have the value that, for the ranges tested, the stripping percentage for each of the elements can be predicted for different values of O:A ratio, temperature and acid concentration, also accounting for interaction effects.

Chapter 7: Process solutions

7.1 Process solutions considered

From the experimental work it was firstly determined that high concentrations of Y, Er, Yb and Sc have a detrimental effect on the organic phase viscosity, phase separation and zinc loading during solvent extraction and that it influence the current efficiency during zinc electroplating negatively. The experimental work also showed that it is possible to remove the rare earth elements from the organic phase used in solvent extraction effectively by means of sulphuric or hydrochloric acid as stripping agents. Sulphuric acid yielded the best results, but hydrochloric acid also yielded stripping percentages of above 80% on a laboratory scale. The detrimental effect of REE on solvent extraction and electroplating of zinc therefore justifies the implementation of a REE removal process. This chapter discusses a number of removal process options which can be implemented on a plant scale and selects the best preliminary practical and financial process.

The following three processes were considered as options to remove rare earths and iron from the organic phase in the Skorpion Zinc solvent extraction plant:

7.1.1 Sulphuric acid stripping mixer-settler

A sulphuric acid mixer-settler section would use sulphuric acid in the conventional mixer-settler set-up to strip off rare earths from the organic phase, since the experimental work showed that the best stripping percentages are achieved with H_2SO_4. The process (see Figure 49) involves a mixer box where between 20 and 40 m^3/h of organic is mixed with 5 M sulphuric acid in a ratio of 2:1. After mixing the emulsion is agitated to increase residence time for the stripping reaction where after phases are allowed to separate in a settler. An after-settler would also be required to ensure that the waste sulphuric acid stream is free of organic and can be pumped to the leaching section. The "dirty" sulphuric acid stream can either be bled directly to the leaching process upstream, or can be treated with oxalic acid to remove the rare earths as a solid oxalate product.
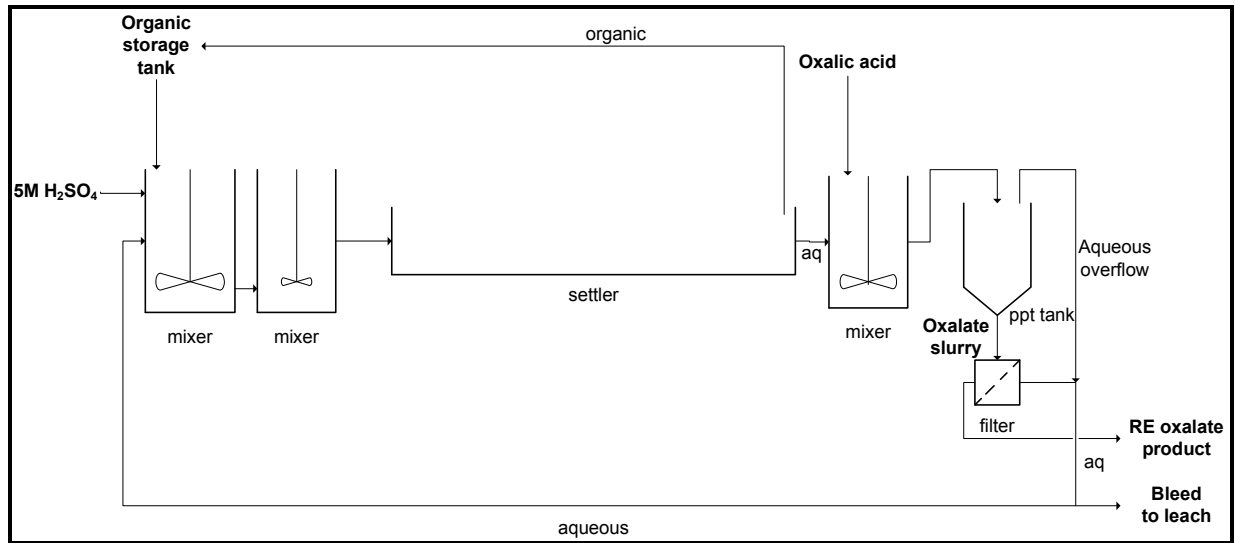
Figure 49: Schematic of sulphuric acid mixer-settler process

Instead of a conventional mixer-settler setup as discussed above, a stripping column (see Figure 50) can also be used for the rare earth stripping process. The zinc-stripped organic will be moving counter-currently to the aqueous sulphuric acid phase through the column and each stage of the column will provide contact between the two phases so that the organic phase will be stripped of rare earths when exiting the top of the column.

Different column designs are available for the process, of which pulsed columns appear to be the most popular (Bateman, 2010). However, solvent extraction columns for metals processing are a relatively new technology and mass transfer characteristics have to be determined for the specific system on a pilot scale to ensure success of the plant-scale project. After the stripping column, the downstream process will be the same as for the conventional mixer-settler, either ending as a bleed stream to the leach plant or going through oxalic acid precipitation.
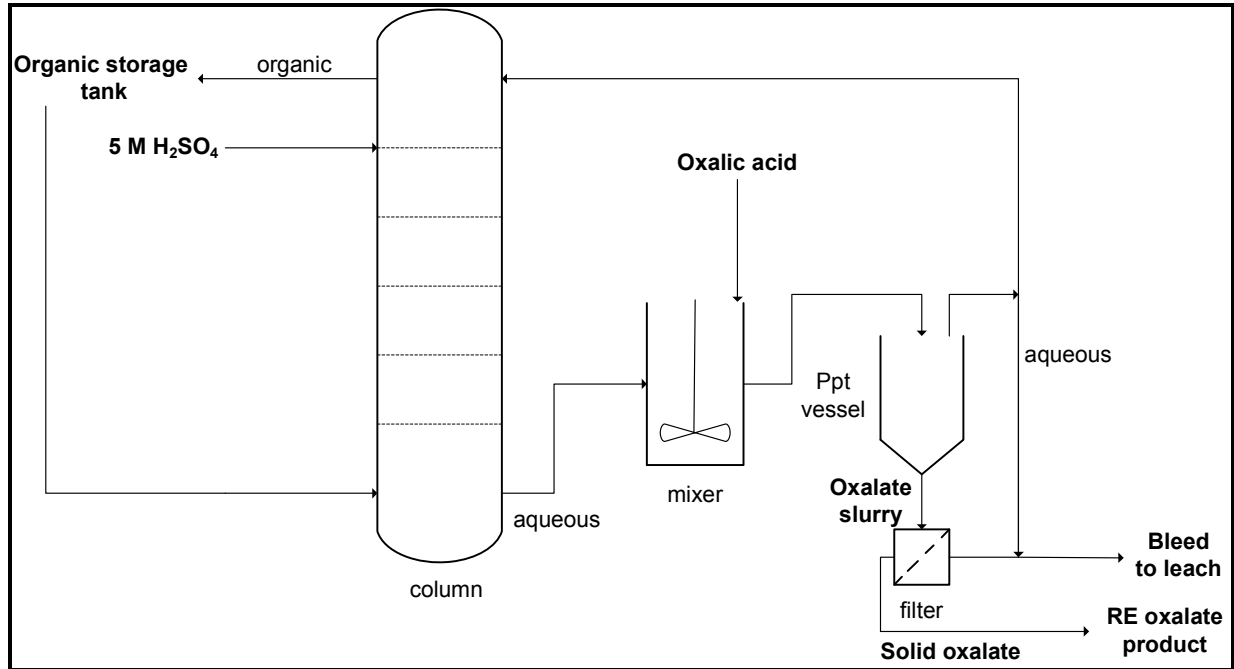
Figure 50: Schematic of sulphuric acid stripping column process

Advantages

1. Since Skorpion Zinc mine has a sulphuric acid plant with high capacity as part of its process, strong sulphuric acid is available.

2. Experimental tests on a bench scale showed sulphuric acid to be the best stripping agent for removing rare earths from the D2EHPA-kerosene organic phase, giving stripping percentages of up to 90%.

3. The waste sulphuric acid stream containing the stripped off rare earth elements can be used in the leaching section for zinc leaching provided that the rare earths will precipitate out during the neutralisation process. From the plant samples analysed it seems that the rare earths do precipitate during the neutralisation process with limestone.

4. A less-viscous organic phase with a higher capacity for zinc loading will be produced with a lower concentration of rare earths and this can be sustained in the long term.

Disadvantages

1. High capital expenditure will be necessary to build a new sulphuric acid stripping section.

2. The mixer-settler process will require a large amount of ground space which is not available in the current established process.

3. Columns for solvent extraction and stripping are a relatively new technology and have not been used for processing small streams to strip rare earths off organic, although they have found application in nickel treatment (Bateman, 2010).

4. Pilot plant tests are required for pulsed columns to establish that the planned design will provide sufficient mass transfer for a plant-scale process to work. Pilot plant tests involve extra capital expenditure and time.

From the discussion above a sulphuric acid mixer settler section will remove rare earths and the associated problems from the organic, although it would be at a significant capital cost. However, a mixer-settler is practically not feasible due to limited available ground space. A sulphuric acid stripping column will overcome the practical problem of limited ground space, but the technology is relatively new for this specific application and pilot plant tests will be necessary before designing a plant-scale process, which will involve additional capital expenditure. Based on the time and expenditure necessary to do the pilot plant construction and test work, a stripping column is also not a feasible option.

7.1.2 Expand/improve available HCl stripping section

Iron is currently removed from the zinc-stripped organic phase at Skorpion Zinc with the use of HCl in a conventional mixer-settler process (see Figure 51). In this way, 280 m^3 per day of the total organic inventory of 3000 m^3 can be treated. An HCl regeneration plant is available to recover the spent HCl and produce clean HCl of the desired strength. The regeneration process works as follows: the chlorides in the spent HCl is replenished with the addition of salt (NaCl), where after the spent HCl is mixed with sulphuric acid at 120°C to produce HCl gas. The Fe in spent HCl is precipitated as sulphates in the reactor and is sent to the leach plant via a bleed stream. The gaseous HCl is absorbed in water to give 5 M HCl that can be used to strip iron and rare earths from the organic phase (in the mixer-settler, MS011). However, the HCl plant and stripping process is not functioning at optimum, achieving only 20% stripping of iron on average and approximately 3% stripping of rare earth elements.

The experimental results have shown that HCl of a concentration of 183 g/l (5 M) at a low O:A ratio is necessary to achieve optimum stripping of iron and rare earths such as yttrium, erbium

and ytterbium. The HCl plant therefore has to produce aqueous HCl of the correct strength, as well as operate at sufficient capacity to deliver high enough HCl flow rates so that the stripping section can be operated at a low O:A ratio.

HCl plant performance is very sensitive to plant down-time. Whenever equipment fails, the volume of organic regenerated per day is reduced and the plant takes upwards of 12 hours to stabilise after start-up.
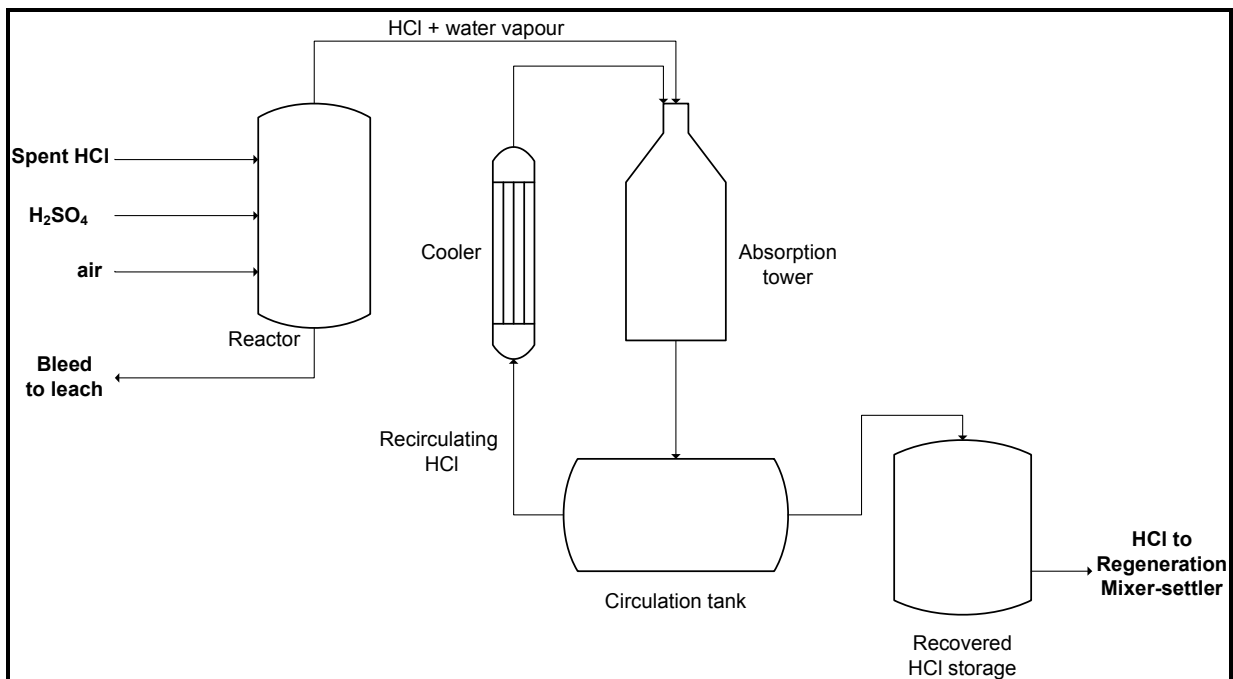
Figure 51: Simplified schematic of HCl regeneration plant

Advantages

1. The HCl plant already exists on site and is running.
2. By focusing on detecting leaks and equipment failures before final failure, the down-time on the HCl regeneration plant can be reduced, which will ensure that the maximum possible organic flow is treated in a day.
3. A precipitation section can be added to the HCl plant where rare earths can be precipitated by oxalic acid and the solids collected for sale.

Disadvantages

1. Due to the high corrosivity of HCl, the plant is no longer able to perform as at commissioning.
2. Capital expenditure will be required to upgrade the HCl plant to handle higher capacities so that a larger volume of organic can be treated daily.
3. Although HCl gives very good Fe stripping, sulphuric acid achieves better rare earth stripping and the regeneration unit with HCl cannot be converted to a sulphuric acid unit since it would not strip off Fe efficiently.

7.1.3 Replace organic inventory

The high concentration of rare earths has accumulated on the organic over four years. If the organic inventory could be fully or partially replaced with fresh organic, the solvent extraction plant will again be able to run for three to four years without rare-earth related problems. Table 13 gives a cost summary for replacement of the organic inventory.

Table 13: Organic inventory replacement costs

Days required:	**5** days			
Organic volume replaced:	**1415** m^3			
Guaranteed solution time	**7** months			
COST				
D2EHPA concentration required	**39%**	**40%**	**41%**	**42%**
Kerosene tankers required:	4.7	4.7	4.6	4.5 per day
Isotainers D2EHPA required:	110	113	116	119 per day
Cost of tankers (N$)	1,353,987	1,331,790	1,309,594	1,287,397 per day
Cost of D2EHPA (N$)	3,425,223	3,513,049	3,600,875	3,688,701 per day
Total cost of tankers (N$)	6,769,934	6,658,951	6,547,969	6,436,986
Total cost of D2EHPA (N$)	17,126,113	17,565,244	18,004,375	18,443,506
TOTAL COST (N$)	23,896,047	24,224,195	24,552,344	24,880,492

Advantages

1. After replacement the problem will immediately be solved.
2. No changes in the process or additional equipment are required.

Disadvantages

1. Very high expenditure required.
2. Only a short term solution which cannot be justified for the high cost since the rare earth element concentration will be at the current levels again within four years and the improved performance of the fresh organic phase will not increase zinc production to the effect of N$24 million over four years.

7.2 Feasible process solutions

7.2.1 Expand/improve available HCl stripping section

As mentioned, the HCl plant is currently not performing as it should, and is only able to operate at 60% of the design capacity. In order to ensure that the plant capacity can be increased, the following equipment will be necessary: spare reactor piping and instrumentation, one 14-block cooling tower, one 7-block heater, one larger bleed to leach pump and the absorption column packing has to be inspected and replaced if necessary. This additional equipment will ensure that the plant can run at 100% of its design capacity and treat 960 m^3 of organic per day to remove Fe and REE.

The HCl plant refurbishment project is estimated to cost N$ 2 500 434 (see Table 14). This includes installation of a second 14-block cooling tower, 7-block heater and instrumentation and piping costs needed to get the second HCl reactor operational. It also includes replacement of one of the bleed to leach pumps with a larger pump. Note that prices were obtained from current suppliers and contractors of Skorpion Zinc.

Table 14: Cost summary

	Reactor	Cooling tower	Heat exchanger	Fe-salts bleed pump
Lead time	**3 months**	**12 months**	**12 months**	**1 month**
Unit parts	-	840 125.00	309 589.00	97 500.00
Piping	187 083.46	136 596.16	53 652.54	-
Instrumentation	333 000.00	99 000.00	99 000.00	-
Sub-total	**520 083.46**	**1 075 721.16**	**462 241.54**	**97 500.00**
Construction (1%)	5200.83	10757.21	4622.42	975.00
Contingency (15 %)	78012.52	161358.17	69336.23	14625.00
Total per unit	**603 296.82**	**1 247 836.55**	**536 200.19**	**113 100.00**
TOTAL				**2 500 433.55**

The benefits of increasing the HCl plant capacity are that rare earth and iron concentrations on the organic in SX will be decreased, reducing organic phase viscosity, phase disengagement times and zinc transfer, thereby increasing extraction efficiency and process stability.

7.2.2 Replace organic inventory

Replacing the organic inventory is a practically feasible option but it is not financially feasible at a cost of more than N$ 24 000 000.

7.3 Proposed process solution

Refurbishment of the HCl plant will provide a long term solution, eliminating the need to replace the organic inventory to reduce the rare earth concentration, which was estimated to cost N$ 24 880 000. With increased focus, HCl plant run time can also be improved to sustain continuous rare earth and iron stripping. It is therefore recommended that the HCl plant is refurbished and optimized to improve rare earth stripping.

7.4 Conclusions

It can be concluded that the current process that uses HCl to strip off iron and rare earths is the best practically and financially feasible process at the moment. Value can be gained from the

rare earths if a financially feasible precipitation section can be established. To determine the feasibility of the precipitation process, the following is therefore recommended:

1. Precipitate rare earths with oxalic acid on a laboratory scale and determine the quality of product that can be produced.
2. Find a buyer for the product and negotiate the selling price of the product.
3. Do a detailed cost evaluation for construction and commissioning of a precipitation section.
4. Find a supplier for oxalic acid and negotiate the oxalic acid price.
5. Determine whether the process will be financially feasible.
6. Determine what the effect of excess oxalic acid remaining in the bleed to leach stream will be on the zinc leaching process.

Chapter 8: Conclusions and recommendations

8.1 Conclusions

Firstly, the effect of the rare earths on zinc electrowinning was investigated. An increase of 100 mg/l Y in the electrolyte was found to decrease the current efficiency by 6%. The elemental order of decreasing current efficiency was found to be: Y > Yb > Er > Sc. However, the mechanism by which REE reduces current efficiency is not known.

Secondly, the effect of the rare earth concentration on zinc solvent extraction was determined. The organic viscosity increased from 20 mPa.s to 40 mPa.s for synthetic PLS and from 20 mPa.s to 80 mPa.s for plant PLS for an increase from 3100 to 6250 mg/l in the total organic rare earth and iron concentration. For the same increase in REE and Fe, the phase disengagement time increased by 600 seconds and zinc loading decreased by 1 – 3 g/l. Phase disengagement was affected by the zinc loading at low viscosities and by the REE loading at high viscosity.

High REE concentrations therefore negatively affect zinc solvent extraction and electrowinning operations, therefore justifying the need to develop a REE removal process. The stripping of low concentrations of rare earth elements from 40% D2EHPA diluted in kerosene to produce a clean organic for zinc extraction was investigated. Bench-scale experiments were used to determine the optimum stripping agent, stripping agent concentration, organic-aqueous ratio and temperature.

For the rare earths, the best stripping agent was found to be H_2SO_4, followed by HCl and then HNO_3, while iron was preferentially stripped by HCl. The stripping curve for Y and Er increased steeply initially and then flattened out from at acid concentrations from 5 to 7 M, possibly indicating that the hydrogen ion concentration is the limiting factor below 5 M and that sufficient hydrogen ions are available at high acid concentrations. More than 80% stripping of yttrium and erbium could be achieved with an optimum hydrochloric acid concentration of 5 M and more than 90% REE (specifically Y, Er, Yb) stripping from the organic phase with 5 M sulphuric acid

with one stripping stage. Iron stripping with HCl showed an optimum at 5 M acid, which may be explained by the formation of organic chloro-complexes at higher chloride concentrations.

Rare earth and iron stripping were improved by reducing the organic-to-aqueous ratio to as low as 0.5 and increasing the temperature. Stripping increased with increasing temperature in an S-shaped curve, flattening off at 50°C. The effect of O:A ratio on rare earth stripping is more significant than the effect of temperature. The interfacial reaction kinetics for stripping supports the findings that O:A ratio are significant. The results showed good repeatability, and were not limited by the rare earth concentration, agitation rate (for the equipment used) or equilibrium time in the range of set points used in the experiments.

Statistical models were compiled to fit the experimental data obtained for Y, Yb, Er and Fe when stripped with sulphuric and hydrochloric acid, respectively. The models were compiled by elimination of variables based on p-values after regression. All models showed dependence on C, C^2 and OAC. Interaction effects between the O:A ratio and temperature and stripping agent concentration were therefore seen to be significant. The models were compiled for the experimental data obtained from stripping synthetically prepared organic and then tested on results obtained when stripping the plant organic phase. The statistical models have the value that, for the ranges tested, the stripping percentage for each of the elements can be predicted for different values of O:A ratio, temperature and acid concentration, also accounting for interaction effects.

The test work showed that REE can be stripped from the plant organic and that optimum conditions would be at 5 M H_2SO_4 at an O:A ratio of 1:2 and a temeprature of 50°C. The following three process solutions were discussed for implementation on a plant scale for the removal of rare earths from the organic phase during zinc solvent extraction: sulphuric acid stripping mixer settler or stripping column, improvement of available HCl stripping section and replacement of the organic inventory. A process to possibly obtain value from the rare earths as by-product was also referred to.

It is concluded that the current process that uses HCl to strip off iron and rare earths is the best practically and financially feasible process. Value can be gained from the rare earths if a financially feasible precipitation section can be established. To determine the feasibility of the process, it is recommended that the quality of precipitate that can be produced is determined

and a buyer found. The capital cost required can then be estimated and an oxalic acid supplier established. A financial feasibility calculation should then be done. The effect that residual oxalic acid in the HCl bleed to leach will have on the leach process should also be investigated.

8.2 Recommendations

Considering the accumulating rare earth concentrations at Skorpion Zinc mine, it is recommended that the available HCl plant is used to strip the rare earths from the organic phase. Focus should be placed on increasing the HCl plant runtime and improving the plant equipment to achieve and sustain maximum capacity.

The possibility of implementing a process for the precipitation of the rare earths stripped from the organic as oxalates or oxides should be further investigated. The following is recommended:

1. Precipitate rare earths with oxalic acid on a lab scale and determine the quality of product that can be produced.
2. Find a buyer for the product and negotiate the selling price of the product.
3. Do a detailed cost evaluation for construction and commissioning of a precipitation section.
4. Find a supplier for oxalic acid and negotiate the oxalic acid price.
5. Determine whether the process will be financially feasible.
6. Determine what the effect of excess oxalic acid remaining in the bleed to leach stream will be on the zinc leaching process, especially focusing on the effect that the organic molecule of oxalic acid will have on leach efficiencies and total suspended solids in solution.

From a research perspective it is recommended that the following aspects in zinc plating, extraction and rare earth stripping are further investigated:

Firstly, it would be useful to know what reaction mechanism causes rare earths to reduce zinc current efficiency. It is proposed that cathodic zinc is firstly analysed for the lanthanides to determine whether any co-plating takes place. Then it would also be necessary to study Pourbaix diagrams for zinc electrolyte including rare earth elements. The mechanism and effect

of rare earth hydride formation might also warrant investigation. Cyclic voltammetry will provide better insight into the reaction peaks and how the reaction peaks differ when zinc is plated from pure electrolyte or when it is plated from electrolyte containing rare earth elements.

Secondly, it would be valuable to know exactly where the cut-off concentration is where zinc loading is considered to be "high loading" and results in complex aggregation. This could be done by measuring the viscosity of the organic phase with different zinc loadings and plotting a graph of viscosity against zinc loading. A large range of zinc concentrations as well as a sufficient number of data points would be necessary to determine the transition point. The contribution of rare earths to complex aggregation should also be investigated. Once the transition point has been determined with zinc loading from rare earth-free leach liquor, different rare earth concentrations can be added to zinc concentrations below the transition point and the viscosity measured to determine whether the rare earth elements shift the transition point.

Thirdly, further research is required to determine exactly why a difference in stripping is seen between different acids, apart from the difference in hydrogen ion contribution. Specifically of interest here is the difference between HCl and HNO_3 and also why HCl produces the best results for iron but not for the rare earths. This will require analysis of the kinetics by establishing the mechanisms and rate equation for each system. The mechanisms might explain the differences between the chloride, nitrate and sulphate systems better. If no conclusions can be derived from the mechanisms, analysis of the ionic bonding on a molecular level will be required.

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Appendix A: Experimental design

Synthetic organic preparation factorial design

Test	REE concentration	Temperature
1	-1	-1
2	-1	+1
3	0	-1
4	0	+1
5	+1	-1
6	+1	+1

A: Optimum stripping agent type and concentration with O:A and temperature interactions

Test	Stripping agent	O:A	T (°c)	C (mol/l)	Test	Stripping agent	O:A	T (°c)	C (mol/l)
1	HCl	2:1	30	1	25	H_2SO_4	2:1	30	1
2	HCl	2:1	30	3	26	H_2SO_4	2:1	30	3
3	HCl	2:1	30	5	27	H_2SO_4	2:1	30	5
4	HCl	2:1	50	1	28	H_2SO_4	2:1	50	1
5	HCl	2:1	50	3	29	H_2SO_4	2:1	50	3
6	HCl	2:1	50	5	30	H_2SO_4	2:1	50	5
7	HCl	1:2	30	1	31	H_2SO_4	1:2	30	1
8	HCl	1:2	30	3	32	H_2SO_4	1:2	30	3
9	HCl	1:2	30	5	33	H_2SO_4	1:2	30	5
10	HCl	1:2	50	1	34	H_2SO_4	1:2	50	1
11	HCl	1:2	50	3	35	H_2SO_4	1:2	50	3
12	HCl	1:2	50	5	36	H_2SO_4	1:2	50	5
13	HNO_3	2:1	30	1	37	NaOH	2:1	30	20%
14	HNO_3	2:1	30	3	38	NaOH	2:1	30	25%
15	HNO_3	2:1	30	5	39	NaOH	2:1	30	30%
16	HNO_3	2:1	50	1	40	NaOH	2:1	50	20%
17	HNO_3	2:1	50	3	41	NaOH	2:1	50	25%
18	HNO_3	2:1	50	5	42	NaOH	2:1	50	30%
19	HNO_3	1:2	30	1	43	NaOH	1:2	30	20%
20	HNO_3	1:2	30	3	44	NaOH	1:2	30	25%
21	HNO_3	1:2	30	5	45	NaOH	1:2	30	30%
22	HNO_3	1:2	50	1	46	NaOH	1:2	50	20%
23	HNO_3	1:2	50	3	47	NaOH	1:2	50	25%
24	HNO_3	1:2	50	5	48	NaOH	1:2	50	30%

Constants:

Equilibrium time = 12 min

No stripping steps = 1

Organic: synthetic solution of 60% kerosene, 40% D2EPHA and spiked with 1100 mg/l Y, 450 mg/l Yb, 110 mg/l Er, 300 mg/l Fe (avg) 1000 mg/l Zn, 65 mg/l Sc

B: Optimum stripping agent concentration

Test	Synthetic organic composition	Stripping agent	Stripping agent concentration	O:A	T (°C)
1			1 M	2:1	30
2			3 M	2:1	30
3			5 M	2:1	30
4			7 M	2:1	30
5			1 M	1:2	30
6			3 M	1:2	30
7			5 M	1:2	30
8			7 M	1:2	30
9	Plant zinc-stripped organic	H_2SO_4	1 M	2:1	50
10			3 M	2:1	50
11			5 M	2:1	50
12			5 M	4:1	50
13			7 M	2:1	50
14			1 M	1:2	50
15			3 M	1:2	50
16			5 M	1:2	50
17			7 M	1:2	50
17			1 M	2:1	30
18			3 M	2:1	30
19			5 M	2:1	30
20			7 M	2:1	30
21			1 M	1:2	30
22			3 M	1:2	30
23			5 M	1:2	30
24			7 M	1:2	30
25	Plant zinc-stripped organic	HCl	1 M	2:1	50
26			3 M	2:1	50
27			5 M	2:1	50
28			5 M	4:1	50
29			7 M	2:1	50
30			1 M	1:2	50
31			3 M	1:2	50
32			5 M	1:2	50
33			7 M	1:2	50

Constants:
Equilibrium time = 12 min
Agitation rate = 500 rpm

C: Results validation: Agitation rate and equilibrium time

Test	Agitation rate (rpm)	Equilibrium time (min)
1	400	12
2	500	12
3	600	12
4	500	3
5	500	6
6	500	9

Constants:
Stripping agent = H_2SO_4
Acid concentration = 5M
Organic composition = avg REE
O:A ratio = 2:1
Temperature = 45 °C

Results validation: Effect of rare earth concentration

Test	Synthetic organic composition		H_2SO_4 concentration	O:A
1		1100 mg/l Y, 450 mg/l Yb, 110 mg/l Er, 300 mg/l Fe, 1000 mg/l Zn, 65 mg/l Sc	2 M	2:1
2	REE avg:		4 M	2:1
3			6 M	2:1
4			7 M	2:1
5		1500 mg/l Y, 600 mg/l Yb, 140 mg/l Er, 400 mg/l Fe, 1000 mg/l Zn, 65 mg/l Sc	3 M	2:1
6	REE high:		5 M	2:1
7			3 M	1:2
8			5 M	1:2
9		700 mg/l Y, 300 mg/l Yb, 80 mg/l Er, 200 mg/l Fe, 1000 mg/l Zn, 65 mg/l Sc	3 M	2:1
10	REE low:		5 M	2:1
11			3 M	1:2
12			5 M	1:2

Constants:

Equilibrium time = 12 min

Agitation rate = 500 rpm

Temperature = 50 °C

D: Optimum O:A and temperature

Test	Stripping agent	Synthetic organic composition	O:A	T (°C)
1			1:4	30
2			1:3	30
3			1:2	30
4			1:1	30
5		REE avg:	2:1	30
6		1100 mg/l Y,	3:1	30
7		450 mg/l Yb,	4:1	30
8	5M H_2SO_4	110 mg/l Er,	6:1	30
9		300 mg/l Fe	1:4	50
10		(avg)	1:3	50
11		1000 mg/l Zn,	1:2	50
12		65 mg/l Sc	1:1	50
13			2:1	50
14			3:1	50
15			4:1	50
16			6:1	50
17		REE avg:	1:4	30
18		1100 mg/l Y,	1:2	30
19		450 mg/l Yb,	2:1	30
20	5M HCl	110 mg/l Er,	4:1	30
21		300 mg/l Fe	1:4	50
22		(avg) 1000 mg/l	1:2	50
23		Zn, 65 mg/l Sc	2:1	50
24			4:1	50
25			1:2	30
26		REE avg:	1:2	40
27		1100 mg/l Y,	1:2	45
28		450 mg/l Yb,	1:2	50
29	5M H_2SO_4	110 mg/l Er,	1:2	55
30		300 mg/l Fe	2:1	30
31		(avg)	2:1	40
32		1000 mg/l Zn,	2:1	45
33		65 mg/l Sc	2:1	50
34			2:1	55

Constants:
Equilibrium time = 12 min
Acid concentration = 5 M

Appendix B: Experimental results

Mini-cell tests

Cell	Y conc	V (start)	V(end)	Current	Time	Mass	CE
				A	h	g	%
1	0	3.01	2.95	0.05	28.8	1.69	96.1
2	400	2.97	2.94	0.05	28.8	1.27	72.2
3	0	2.96	2.95	0.05	28.8	1.69	96.1
4	800	3.03	2.92	0.05	28.8	0.92	52.3

Cell	Y conc	V (start)	V(end)	Current	Time	Mass	CE
				A	h	g	%
1	0	2.91	2.89	0.05	26.1	1.53	96.2
2	100	2.91	2.92	0.05	26.1	1.44	90.5
3	0	2.96	3.05	0.05	26.1	1.55	97.4
4	200	2.94	2.94	0.05	26.1	1.28	80.5
5	300	2.94	2.98	0.05	26.1	1.25	78.6

Cell	Element spiked	V (start)	V(end)	Current	Time	Mass	CE
				A	h	g	%
1	Blank	3.05	2.95	0.05	25.6	1.52	97.3
2	Y	3.01	2.92	0.05	25.6	1.33	85.2
3	Sc	3.03	2.97	0.05	25.6	0.93	59.6
4	Er	2.98	2.96	0.05	25.6	1.15	73.6
5	Yb	3.01	2.94	0.05	25.6	1.27	81.3

O:A ratio and temperature – synthetic organic

Sample id	Stripping agent	O:A	T	Sc mg/l	Stripping %	Fe mg/l	Stripping %	Y mg/l	Stripping %	Er mg/l	Stripping %	Yb mg/l	Stripping %
A0				80		303		1256		115		540	
C1	H_2SO_4	0.25	30	84	-5	237	22	13.7	98.9	1.72	98.5	109	79.8
C2	H_2SO_4	0.33	30	83	-3.75	256	16	19	98.5	2.38	97.9	133	75.4
A33	H_2SO_4	0.50	30	76	5	239	21	26	97.9	2.97	97.4	156	71.1
C3	H_2SO_4	1	30	89	-11.25	294	3	61	95.1	7.21	93.7	289	46.5
A27	H_2SO_4	2	30	66	17.5	277	9	97	92.3	12	89.6	339	37.2
C4	H_2SO_4	3	30	88	-10	319	-5	167	86.7	20	82.6	434	19.6
C5	H_2SO_4	4	30	87	-8.75	318	-5	222	82.3	25.5	77.8	471	12.8
C6	H_2SO_4	0.25	50	89	-11.25	105	65	10	99.2	1.14	99.0	68	87.4
C7	H_2SO_4	0.33	50	88	-10	113	63	14	98.9	1.52	98.7	87	83.9
A36	H_2SO_4	0.5	50	80	0	131	57	39	96.9	3.84	96.7	118	78.1
C8	H_2SO_4	1	50	89	-11.25	204	33	42	96.7	4.9	95.7	208	61.5
A30	H_2SO_4	2	50	77	3.75	214	29	71	94.3	8.3	92.8	257	52.4
C9	H_2SO_4	3	50	89	-11.25	289	5	134	89.3	15.5	86.5	390	27.8
C10	H_2SO_4	4	50	85	-6.25	299	1	208	83.4	24.5	78.7	433	19.8
C11	H_2SO_4	6	50	84	-5	317	-5	443	64.7	50	56.5	520	3.7
C12	HCl	0.25	30	89	-11.25	29	90	106	91.6	11.8	89.7	335	38.0
A9	HCl	0.5	30	76	5	42	86	160	87.3	18	84.3	371	31.3
A3	HCl	2	30	77	3.75	113	63	462	63.2	48	58.3	494	8.5
C13	HCl	4	30	89	-11.25	179	41	751	40.2	74	35.7	571	-5.7
C14	HCl	0.25	50	90	-12.5	17	94	72	94.3	8	93.0	243	55.0
A12	HCl	0.5	50	78	2.5	27	91	109	91.3	12.3	89.3	299	44.6
A6	HCl	2	50	78	2.5	76	75	333	73.5	36	68.7	448	17.0
C15	HCl	4	50	85	-6.25	133	56	642	48.9	63	45.2	548	-1.5
A33	H_2SO_4	0.5	30	76	5	239	21	26	97.9	2.97	97.4	156	71.1
C16	H_2SO_4	0.5	40	88	-10	221	27	28	97.8	3.3	97.1	159	70.6
C17	H_2SO_4	0.5	45	85	-6.25	189	38	23	98.2	2.78	97.6	137	74.6
A36	H_2SO_4	0.5	50	80	0	131	57	39	96.9	3.84	96.7	118	78.1
C18	H_2SO_4	0.5	55	87	-8.75	133	56	21	98.3	2.34	98.0	113	79.1
A27	H_2SO_4	2	30	66	17.5	277	9	97	92.3	12	89.6	339	37.2
C19	H_2SO_4	2	40	88	-10	291	4	98	92.2	11.5	90.0	338	37.4
C20	H_2SO_4	2	45	87	-8.75	269	11	90	92.8	9.6	91.7	325	39.8
A30	H_2SO_4	2	50	77	3.75	214	29	71	94.3	8.3	92.8	257	52.4
C21	H_2SO_4	2	55	87	-8.75	234	23	71	94.3	8.7	92.4	269	50.2
				Sc		Fe		Y		Er		Yb	

Agitation rate and equilibrium time

Sample ID	O:A	Temp	Agitation rate (rpm)	Eq time (min)	Fe mg/l	% Stripping	Y mg/l	% Stripping	Er mg/l	% Stripping	Yb mg/l	% Stripping
B0	blank				327		2075		220		854	
D1	2:1	45	400	12	312	4.6	245	88.2	29.6	86.5	606	29.0
D2	2:1	45	500	12	307	6.1	229	89.0	28.6	87.0	604	29.3
D3	2:1	45	600	12	301	8.0	233	88.8	28	87.3	609	28.7
D4	2:1	45	500	3	330	-0.9	674	67.5	84	61.8	733	14.2
D5	2:1	45	500	6	331	-1.2	288	86.1	38	82.7	670	21.5
D6	2:1	45	500	9	316	3.4	239	88.5	30	86.4	618	27.6

Plant organic stripped with H_2SO_4

Sample ID	Stripping agent	O:A	T	C	Fe mg/l	%Fe strip	Y mg/l	%Y strip	Er mg/l	%Er strip	Yb mg/l	%Yb strip
BO1	blank				327		2075		220		854	
B1	H_2SO_4	2	30	1	325	0.6	2075	0.0	217	1.4	831	2.7
B2	H_2SO_4	2	30	3	322	1.5	1619	22.0	184	16.4	835	2.2
B3	H_2SO_4	2	30	5	323	1.2	301	85.5	41	81.4	660	22.7
B4	H_2SO_4	2	30	7	309	5.5	65	96.9	7.16	96.7	350	59.0
B5	H_2SO_4	0.5	30	1	308	5.8	1945	6.3	209	5.0	818	4.2
B6	H_2SO_4	0.5	30	3	328	-0.3	1224	41.0	144	34.5	786	8.0
B7	H_2SO_4	0.5	30	5	325	0.6	80	96.1	9.16	95.8	411	51.9
B8	H_2SO_4	0.5	30	7	295	9.8	15.9	99.2	0.05	100.0	128	85.0
B9	H_2SO_4	2	50	1	300	8.3	1816	12.5	194	11.8	782	8.4
B10	H_2SO_4	2	50	3	283	13.5	879	57.6	108	50.9	737	13.7
B11	H_2SO_4	2	50	5	255	22.0	175	91.6	22.8	89.6	516	39.6
B12	H_2SO_4	4	50	5	277	15.3	329	84.1	43	80.5	640	25.1
B13	H_2SO_4	2	50	7	235	28.1	42	98.0	5.4	97.5	236	72.4
B14	H_2SO_4	0.5	50	1	293	10.4	1654	20.3	181	17.7	781	8.5
B15	H_2SO_4	0.5	50	3	291	11.0	450	78.3	57	74.1	650	23.9
B16	H_2SO_4	0.5	50	5	208	36.4	44	97.9	5.81	97.4	221	74.1
B17	H_2SO_4	0.5	50	7	147	55.0	10.5	99.5	1.22	99.4	76	91.1
					Fe		Y		Er		Yb	

Plant organic stripped with HCl

Sample ID	Stripping agent	O:A	T	C	Fe mg/l	% Fe Stripping	Y mg/l	% Y Stripping	Er mg/l	% Er Stripping	Yb mg/l	% Yb Stripping
BO1					327		2075	1750	220	183	854	750
B17	HCl	2	30	1	327	0.0	2049	1.3	220	0.0	854	0.0
B18	HCl	2	30	3	296	9.5	1761	15.1	191	13.2	793	7.1
B19	HCl	2	30	5	146	55.4	1046	49.6	121	45.0	810	5.2
B20	HCl	2	30	7	255	22.0	551	73.4	71	67.7	718	15.9
B21	HCl	0.5	30	1	322	1.5	2071	0.2	219	0.5	863	-1.1
B22	HCl	0.5	30	3	256	21.7	1322	36.3	150	31.8	803	6.0
B23	HCl	0.5	30	5	63	80.7	446	78.5	54	75.5	686	19.7
B24	HCl	0.5	30	7	185	43.4	182	91.2	22.4	89.8	524	38.6
B25	HCl	2	50	1	327	0.0	2077	-0.1	219	0.5	814	4.7
B26	HCl	2	50	3	274	16.2	1657	20.1	178	19.1	820	4.0
B27	HCl	2	50	5	121	63.0	801	61.4	96	56.4	757	11.4
B28	HCl	4	50	5	171	47.7	1190	42.7	133	39.5	798	6.6
B29	HCl	2	50	7	282	13.8	449	78.4	55	75.0	664	22.2
B30	HCl	0.5	50	1	329	-0.6	2044	1.5	214	2.7	840	1.6
B31	HCl	0.5	50	3	169	48.3	1019	50.9	114	48.2	767	10.2
B32	HCl	0.5	50	5	50	84.7	301	85.5	35	84.1	575	32.7
B33	HCl	0.5	50	7	204	37.6	145	93.0	17.3	92.1	432	49.4
					Fe		Y		Er		Yb	

Appendix C: Anova tables

C.1 Models for REE stripping from synthetic organic with sulphuric acid

STEP 1: FIRST FITTING

Yttrium					

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.98
Standard Error	4.13
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	9	24214.16	2690.46	157.81	6.33E-16
Residual	19	323.92	17.05		
Total	28	24538.08			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-21.38	28.29	-0.76	0.46	-80.59	37.82
O:A	-14.47	3.95	-3.66	0.00	-22.74	-6.20
T	0.19	1.41	0.13	0.89	-2.75	3.13
C	47.11	4.41	10.67	1.83E-09	37.87	56.35
OA^2	-0.56	0.36	-1.57	0.13	-1.30	0.19
T^2	0.00	0.02	0.04	0.97	-0.04	0.04
C^2	-4.71	0.59	-7.97	1.77E-07	-5.95	-3.47
OAT	-0.01	0.07	-0.18	0.86	-0.16	0.13
TC	-0.03	0.06	-0.52	0.61	-0.14	0.09
OAC	2.53	0.69	3.66	0.00	1.08	3.98

Erbium					

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.98
Standard Error	3.88
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	9	25489.56	2832.17	187.92	1.24E-16
Residual	19	286.35	15.07		
Total	28	25775.91			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-22.97	26.60	-0.86	0.40	-78.63	32.70
O:A	-15.75	3.71	-4.24	0.00	-23.52	-7.98
T	0.32	1.32	0.24	0.81	-2.44	3.09
C	43.64	4.15	10.52	2.33E-09	34.95	52.32
OA^2	-0.69	0.33	-2.08	0.05	-1.39	0.00
T^2	0.00	0.02	-0.02	0.99	-0.03	0.03
C^2	-4.03	0.56	-7.25	7E-07	-5.19	-2.86
OAT	0.00	0.06	0.01	0.99	-0.13	0.14
TC	-0.04	0.05	-0.74	0.47	-0.15	0.07
OAC	2.56	0.65	3.94	0.00	1.20	3.92

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.98
Standard Error	4.31
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	9	22855.75	2539.53	136.60	2.43E-15
Residual	19	353.24	18.59		
Total	28	23208.99			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	28.73	29.54	0.97	0.34	-33.09	90.56
O:A	-3.84	4.13	-0.93	0.36	-12.48	4.79
T	-1.23	1.47	-0.84	0.41	-4.30	1.84
C	0.03	4.61	0.01	1.00	-9.62	9.68
OA^2	2.17	0.37	5.84	1.27E-05	1.39	2.94
T^2	0.02	0.02	0.92	0.37	-0.02	0.05
C^2	2.43	0.62	3.95	8.66E-04	1.14	3.73
OAT	-0.05	0.07	-0.64	0.53	-0.20	0.10
TC	0.09	0.06	1.49	0.15	-0.03	0.21
OAC	-4.23	0.72	-5.86	1.2E-05	-5.75	-2.72

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.97
R Square	0.94
Adjusted R Square	0.91
Standard Error	6.01
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	9	10078.33	1119.81	31.01	1.68E-09
Residual	19	686.21	36.12		
Total	28	10764.54			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	19.93	41.17	0.48	0.63	-66.24	106.10
O:A	15.48	5.75	2.69	0.01	3.45	27.52
T	-1.08	2.05	-0.53	0.60	-5.37	3.20
C	-8.23	6.42	-1.28	0.22	-21.68	5.21
OA^2	2.85	0.52	5.50	2.61E-05	1.76	3.93
T^2	0.02	0.03	0.79	0.44	-0.03	0.07
C^2	0.57	0.86	0.67	0.51	-1.23	2.37
OAT	-0.54	0.10	-5.36	3.58E-05	-0.74	-0.33
TC	0.30	0.08	3.77	0.00	0.13	0.47
OAC	-3.29	1.01	-3.27	0.00	-5.39	-1.18

STEP 2…N: FINAL FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.98
Standard Error	3.87
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	6	24208.55	4034.76	269.37	1.95E-19
Residual	22	329.52	14.98		
Total	28	24538.08			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-17.09	6.46	-2.65	0.01	-30.48	-3.70
O:A	-14.89	2.92	-5.10	4.14E-05	-20.95	-8.83
T	0.11	0.08	1.47	0.16	-0.05	0.27
C	45.97	3.61	12.72	1.28E-11	38.48	53.47
OA^2	-0.59	0.31	-1.93	0.07	-1.22	0.04
C^2	-4.71	0.55	-8.52	2.04E-08	-5.86	-3.57
OAC	2.54	0.65	3.92	7.40E-04	1.19	3.88

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.99
Standard Error	3.66
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	6	25480.93	4246.82	316.73	3.37E-20
Residual	22	294.98	13.41		
Total	28	25775.91			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-16.31	6.11	-2.67	0.01	-28.98	-3.65
O:A	-15.71	2.76	-5.69	1.02E-05	-21.44	-9.98
T	0.14	0.07	2.01	0.06	0.00	0.29
C	42.13	3.42	12.32	2.38E-11	35.04	49.22
OA^2	-0.71	0.29	-2.44	0.02	-1.30	-0.11
C^2	-4.03	0.52	-7.71	1.08E-07	-5.12	-2.95
OAC	2.56	0.61	4.18	0.00	1.29	3.84

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Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.98
Standard Error	4.06
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	5	22829.28	4565.86	276.56	9.62E-20
Residual	23	379.72	16.51		
Total	28	23208.99			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	7.24	3.49	2.07	0.05	0.02	14.47
O:A	-5.39	3.02	-1.79	0.09	-11.63	0.85
OA^2	2.08	0.32	6.52	1.2E-06	1.42	2.73
C^2	2.35	0.19	12.27	1.43E-11	1.95	2.75
TC	0.10	0.02	5.59	1.08E-05	0.06	0.14
OAC	-4.24	0.66	-6.40	1.57E-06	-5.61	-2.87

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.97
R Square	0.93
Adjusted R Square	0.91
Standard Error	5.82
Observations	29

ANOVA

	df	SS	MS	F	Significance F
Regression	7	10053.02	1436.15	42.39	5.52E-11
Residual	21	711.52	33.88		
Total	28	10764.54			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-4.78	9.71	-0.49	0.63	-24.98	15.42
O:A	15.76	5.55	2.84	0.01	4.21	27.30
C	-4.75	3.48	-1.36	0.19	-11.98	2.49
OA^2	2.88	0.50	5.76	1.01E-05	1.84	3.92
T^2	0.01	0.00	1.56	0.13	0.00	0.02
OAT	-0.54	0.10	-5.67	1.24E-05	-0.74	-0.34
TC	0.30	0.08	3.92	0.00	0.14	0.47
OAC	-3.29	0.97	-3.38	0.00	-5.32	-1.26

C.2 Models for REE stripping from synthetic organic with hydrochloric acid

STEP 1: FIRST FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.82
Standard Error	6.37
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	9	16802.29	1866.92	51.70	5.35E-05
Residual	7	284.36	40.62		
Total	16	17086.66			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-13.54	12.65	-1.07	0.32	-43.46	16.38
O:A	-10.80	7.63	-1.41	0.20	-28.84	7.25
T	0.00	0.00	65535.00	#NUM!	0.00	0.00
C	26.51	7.36	3.60	0.01	9.10	43.91
OA^2	1.62	1.51	1.07	0.32	-1.95	5.19
T^2	0.00	0.00	0.05	0.96	-0.01	0.01
C^2	-1.20	0.96	-1.25	0.25	-3.48	1.07
OAT	0.06	0.13	0.44	0.67	-0.26	0.38
TC	0.05	0.10	0.54	0.61	-0.18	0.28
OAC	-2.38	1.30	-1.83	0.11	-5.46	0.70

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.83
Standard Error	5.40
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	9	16660.77	1851.20	71.40	2.072E-05
Residual	7	204.19	29.17		
Total	16	16864.96			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-14.63	10.72	-1.36	0.21	-39.98	10.73
O:A	-11.33	6.47	-1.75	0.12	-26.62	3.97
T	0.00	0.00	65535.00	#NUM!	0.00	0.00
C	23.87	6.24	3.83	0.01	9.12	38.62
OA^2	2.05	1.28	1.60	0.15	-0.98	5.08
T^2	0.00	0.00	0.40	0.70	-0.01	0.01
C^2	-0.64	0.81	-0.79	0.46	-2.57	1.28
OAT	0.06	0.11	0.53	0.61	-0.21	0.33
TC	0.03	0.08	0.42	0.69	-0.16	0.23
OAC	-2.76	1.10	-2.50	0.04	-5.37	-0.15

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.00
R Square	0.99
Adjusted R Square	0.84
Standard Error	2.64
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	9	4943.96	549.33	88.83	1.09E-05
Residual	7	48.70	6.96		
Total	16	4992.66			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-3.74	5.24	-0.71	0.50	-16.12	8.64
O:A	6.01	3.16	1.90	0.10	-1.45	13.48
T	0.00	0.00	65535.00	#NUM!	0.00	0.00
C	-3.75	3.05	-1.23	0.26	-10.95	3.46
OA^2	3.01	0.63	4.81	0.00	1.53	4.48
T^2	0.00	0.00	0.25	0.81	0.00	0.01
C^2	1.71	0.40	4.31	0.00	0.77	2.66
OAT	-0.18	0.06	-3.16	0.02	-0.31	-0.04
TC	0.15	0.04	3.65	0.01	0.05	0.24
OAC	-4.73	0.54	-8.77	0.00	-6.00	-3.45

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.81
Standard Error	8.15
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	9	18938.82	2104.31	35.61	0.000159
Residual	7	465.42	66.49		
Total	16	19404.25			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-6.15	16.19	-0.38	0.72	-44.43	32.13
O:A	-7.12	9.76	-0.73	0.49	-30.21	15.96
T	0.00	0.00	65535.00	#NUM!	0.00	0.00
C	3.13	9.42	0.33	0.75	-19.14	25.40
OA^2	1.53	1.93	0.79	0.45	-3.04	6.10
T^2	0.00	0.01	0.52	0.62	-0.01	0.02
C^2	2.89	1.23	2.35	0.05	-0.01	5.80
OAT	0.07	0.17	0.38	0.71	-0.34	0.47
TC	0.05	0.12	0.43	0.68	-0.24	0.35
OAC	-2.81	1.67	-1.69	0.14	-6.75	1.13

STEP 2…N: FINAL FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.97
Standard Error	5.85
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	6	16778.56	2796.43	81.69	2.46E-07
Residual	9	308.09	34.23		
Total	15	17086.66			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-24.80	10.43	-2.38	0.04	-48.40	-1.19
O:A	-8.41	4.97	-1.69	0.12	-19.66	2.83
T	0.29	0.15	2.00	0.08	-0.04	0.62
C	28.61	5.73	4.99	0.00	15.64	41.58
OA^2	1.62	1.39	1.17	0.27	-1.52	4.76
C^2	-1.20	0.88	-1.36	0.21	-3.20	0.79
OAC	-2.38	1.20	-1.99	0.08	-5.09	0.32

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.99
Adjusted R Square	0.98
Standard Error	4.94
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	6	16644.93	2774.15	113.47	5.79E-08
Residual	9	220.03	24.45		
Total	15	16864.96			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-25.56	8.82	-2.90	0.02	-45.51	-5.62
O:A	-8.93	4.20	-2.12	0.06	-18.43	0.58
T	0.35	0.12	2.79	0.02	0.07	0.62
C	25.26	4.84	5.21	0.00	14.30	36.22
OA^2	2.05	1.17	1.75	0.11	-0.60	4.70
C^2	-0.64	0.75	-0.86	0.41	-2.33	1.04
OAC	-2.76	1.01	-2.73	0.02	-5.05	-0.48

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.00
R Square	0.99
Adjusted R Square	0.98
Standard Error	2.48
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	7	4943.53	706.22	115.00	2.16E-07
Residual	8	49.13	6.14		
Total	15	4992.66			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-2.87	3.66	-0.79	0.45	-11.31	5.56
O:A	5.82	2.87	2.02	0.08	-0.81	12.44
C	-4.06	2.61	-1.55	0.16	-10.08	1.96
OA^2	3.01	0.59	5.12	0.00	1.65	4.36
C^2	1.71	0.37	4.59	0.00	0.85	2.58
OAT	-0.17	0.05	-3.49	0.01	-0.28	-0.06
TC	0.15	0.02	6.46	0.00	0.10	0.21
OAC	-4.73	0.51	-9.34	0.00	-5.90	-3.56

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.97
Adjusted R Square	0.96
Standard Error	7.39
Observations	16

ANOVA

	df	SS	MS	F	Significance F
Regression	6	18912.76	3152.13	57.72	1.12E-06
Residual	9	491.48	54.61		
Total	15	19404.25			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-22.40	13.18	-1.70	0.12	-52.21	7.41
O:A	-4.51	6.28	-0.72	0.49	-18.71	9.70
T	0.55	0.18	2.96	0.02	0.13	0.96
C	5.27	7.24	0.73	0.49	-11.12	21.65
OA^2	1.53	1.75	0.88	0.40	-2.43	5.50
C^2	2.89	1.11	2.60	0.03	0.37	5.41
OAC	-2.81	1.51	-1.86	0.10	-6.23	0.61

C.3 Models for REE stripping from plant organic with sulphuric acid

STEP 1: FIRST FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.97
Adjusted R Square	0.94
Standard Error	9.67
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	22424.55	2491.62	26.67	0.000132
Residual	7	653.90	93.41		
Total	16	23078.45			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-3.43E+16	1.76E+16	-1.94	0.09	-7.6E+16	7.42E+15
O:A	-30.12	15.75	-1.91	0.10	-67.36	7.12
T	1.83E+15	9.41E+14	1.94	0.09	-3.96E+14	4.05E+15
C	46.48	7.95	5.85	0.00	27.69	65.27
OAT	0.28	0.35	0.80	0.45	-0.55	1.11
TC	-0.29	0.12	-2.37	0.05	-0.59	0.00
OAC	2.48	1.66	1.50	0.18	-1.44	6.39
OA^2	0.04	2.46	0.02	0.99	-5.78	5.86
T^2	-2.29E+13	1.18E+13	-1.94	0.09	-5.07E+13	4.95E+12
C^2	-2.64	0.66	-4.03	0.00	-4.19	-1.09

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.92
Standard Error	11.08
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	22839.36	2537.71	20.68	0.000306
Residual	7	859.08	122.73		
Total	16	23698.44			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-3.96E+16	2.02E+16	-1.96	0.09	-8.74E+16	8.24E+15
O:A	-31.93	18.05	-1.77	0.12	-74.61	10.76
T	2.11E+15	1.08E+15	1.96	0.09	-4.39E+14	4.66E+15
C	44.72	9.11	4.91	0.00	23.19	66.26
OAT	0.31	0.40	0.78	0.46	-0.64	1.26
TC	-0.30	0.14	-2.13	0.07	-0.64	0.03
OAC	2.37	1.90	1.25	0.25	-2.12	6.86
OA^2	0.15	2.82	0.05	0.96	-6.52	6.82
T^2	-2.64E+13	1.35E+13	-1.96	0.09	-5.83E+13	5.49E+12
C^2	-2.30	0.75	-3.06	0.02	-4.08	-0.52

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.97
Adjusted R Square	0.93
Standard Error	8.48
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	14982.60	1664.73	23.13	0.0002115
Residual	7	503.80	71.97		
Total	16	15486.40			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-1.27E+16	1.55E+16	-0.82	0.44	-4.93E+16	2.39E+16
O:A	-9.69	13.82	-0.70	0.51	-42.37	23.00
T	6.77E+14	8.26E+14	0.82	0.44	-1.28E+15	2.63E+15
C	5.12	6.97	0.73	0.49	-11.38	21.61
OAT	0.09	0.31	0.29	0.78	-0.64	0.81
TC	0.01	0.11	0.05	0.96	-0.25	0.26
OAC	-2.36	1.45	-1.63	0.15	-5.80	1.07
OA^2	1.65	2.16	0.77	0.47	-3.45	6.76
T^2	-8.47E+12	1.03E+13	-0.82	0.44	-3.29E+13	1.59E+13
C^2	1.31	0.58	2.27	0.06	-0.06	2.67

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.91
Standard Error	4.40
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	3400.40	377.82	19.54	0.0003676
Residual	7	135.32	19.33		
Total	16	3535.72			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	1.63E+16	8.02E+15	2.03	0.08	-2.70E+15	3.53E+16
O:A	17.31	7.16	2.42	0.05	0.37	34.25
T	-8.68E+14	4.28E+14	-2.03	0.08	-1.88E+15	1.44E+14
C	-13.43	3.61	-3.72	0.01	-21.98	-4.89
OAT	-0.41	0.16	-2.57	0.04	-0.78	-0.03
TC	0.31	0.06	5.43	0.00	0.17	0.44
OAC	-2.25	0.75	-2.98	0.02	-4.03	-0.47
OA^2	2.11	1.12	1.88	0.10	-0.54	4.76
T^2	1.08E+13	5.35E+12	2.03	0.08	-1.80E+12	2.35E+13
C^2	0.82	0.30	2.76	0.03	0.12	1.53

STEP 2…N: FINAL FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.93
Standard Error	9.80
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	6	22117.10	3686.18	38.34	2.454E-06
Residual	10	961.36	96.14		
Total	16	23078.45			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-1.65E+16	1.44E+16	-1.14	0.28	-4.86E+16	1.57E+16
O:A	-5.70	2.63	-2.17	0.06	-11.56	0.17
T	8.79E+14	7.69E+14	1.14	0.28	-8.36E+14	2.59E+15
C	44.94	7.90	5.69	0.00	27.34	62.53
TC	-0.23	0.12	-1.89	0.09	-0.49	0.04
T^2	-1.10E+13	9.62E+12	-1.14	0.28	-3.24E+13	1.04E+13
C^2	-2.48	0.64	-3.85	0.00	-3.91	-1.04

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.97
R Square	0.94
Adjusted R Square	0.91
Standard Error	11.25
Observations	17.00

ANOVA

	df	SS	MS	F	Significance F
Regression	5	22306.81	4461.36	35.26	2.06E-06
Residual	11	1391.63	126.51		
Total	16	23698.44			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-69.65	25.00	-2.79	0.02	-124.67	-14.64
O:A	-5.02	2.88	-1.74	0.11	-11.37	1.32
T	1.34	0.58	2.33	0.04	0.07	2.61
C	36.66	7.62	4.81	0.00	19.89	53.43
TC	-0.16	0.13	-1.28	0.23	-0.44	0.12
C^2	-1.80	0.69	-2.60	0.02	-3.33	-0.28

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.94
Standard Error	7.76
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	5	14823.68	2964.74	49.21	3.7E-07
Residual	11	662.72	60.25		
Total	16	15486.40			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-26.46	11.92	-2.22	0.05	-52.70	-0.23
O:A	1.70	5.29	0.32	0.75	-9.95	13.34
T	0.64	0.19	3.35	0.01	0.22	1.06
C^2	1.39	0.48	2.91	0.01	0.34	2.44
OAC	-2.56	1.11	-2.30	0.04	-5.01	-0.11
C	4.56	4.22	1.08	0.30	-4.73	13.84

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.96
R Square	0.91
Adjusted R Square	0.89
Standard Error	5.03
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	4	3232.44	808.11	31.97	2.58E-06
Residual	12	303.28	25.27		
Total	16	3535.72			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	6.52	4.28	1.52	0.15	-2.80	15.83
C^2	0.56	0.31	1.80	0.10	-0.12	1.23
OAC	-0.98	0.27	-3.62	0.00	-1.57	-0.39
C	-10.15	2.84	-3.58	0.00	-16.33	-3.97
TC	0.25	0.03	9.38	7.13E-07	0.19	0.31

C.4 Models for REE stripping from plant organic with hydrochloric acid

STEP 1: FIRST FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.95
Standard Error	7.54
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	18472.10	2052.46	36.08	4.801E-05
Residual	7	398.25	56.89		
Total	16	18870.35			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-2.74E+16	1.38E+16	-1.99	0.09	-6.00E+16	5.14E+15
O:A	-21.92	12.29	-1.78	0.12	-50.98	7.14
T	1.46E+15	7.34E+14	1.99	0.09	-2.74E+14	3.20E+15
C	29.12	6.20	4.70	0.00	14.46	4.38E+01
OAT	0.18	0.27	0.65	0.54	-0.47	0.82
TC	-0.07	0.10	-0.74	0.49	-0.30	0.16
OAC	-0.35	1.29	-0.27	0.79	-3.41	2.71
OA^2	1.06	1.92	0.55	0.60	-3.48	5.60
T^2	-1.83E+13	9.18E+12	-1.99	0.09	-4.00E+13	3.42E+12
C^2	-1.31	5.12E-01	-2.56	0.04	-2.52	-0.10

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.95
Standard Error	7.26
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	17507.08	1945.23	36.92	0.00
Residual	7	368.80	52.69		
Total	16	17875.88			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-2.42E+16	1.32E+16	-1.82	0.11	-5.55E+16	7.16E+15
O:A	-20.64	11.83	-1.75	0.12	-48.60	7.33
T	1.29E+15	7.07E+14	1.82	0.11	-3.82E+14	2.96E+15
C	26.68	5.97	4.47	0.00	12.57	40.79
OAT	0.15	0.26	0.56	0.59	-0.47	0.77
TC	-0.06	0.09	-0.65	0.53	-0.28	0.16
OAC	-0.88	1.24	-0.71	0.50	-3.82	2.06
OA^2	1.62	1.85	0.88	0.41	-2.75	5.99
T^2	-1.61E+13	8.83E+12	-1.82	0.11	-3.70E+13	4.77E+12
C^2	-1.05	0.49	-2.13	0.07	-2.22	0.11

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1.00
R Square	0.99
Adjusted R Square	0.98
Standard Error	2.17
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	3279.17	364.35	77.58	3.532E-06
Residual	7	32.87	4.70		
Total	16	3312.04			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	1.01E+16	3.96E+15	2.56	0.04	7.80E+14	1.95E+16
O:A	9.02	3.53	2.56	0.04	0.67	17.37
T	-5.40E+14	2.11E+14	-2.56	0.04	-1.04E+15	-4.16E+13
C	-0.46	1.78	-0.26	0.81	-4.67	3.76
OAT	-0.21	0.08	-2.65	0.03	-0.39	-0.02
TC	0.10	0.03	3.53	0.01	0.03	0.16
OAC	-3.62886138	0.371357	-9.77	0.00	-4.506982	-2.750741
OA^2	2.91	0.55	5.28	0.00	1.61	4.22
T^2	6.76E+12	2.64E+12	2.56	0.04	5.20E+11	1.30E+13
C^2	0.72	0.15	4.87	0.00	0.37	1.06

Iron

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.89
R Square	0.79
Adjusted R Square	0.52
Standard Error	19.38
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	9	10001.01	1111.22	2.96	0.0832832
Residual	7	2628.40	375.49		
Total	16	12629.40			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-3.22E+16	3.20E+16	-1.01	0.35	-1.08E+17	4.34E+16
C	39.30	14.82	2.65	0.03	4.27	74.34
O:A	0.33	27.67	0.01	0.99	-65.11	65.77
T	1.72E+15	1.70E+15	1.01	0.35	-2.31E+15	5.75E+15
TC	0.05	0.25	0.20	0.85	-0.54	0.64
OAC	-3.88	3.32	-1.17	0.28	-11.73	3.97
OAT	-0.42	0.70	-0.60	0.57	-2.08	1.24
OA^2	7.05	5.30	1.33	0.22	-5.47	19.58
T^2	-2.15E+13	2.13E+13	-1.01	0.35	-7.18E+13	2.89E+13
C^2	-3.57	1.31	-2.71	0.03	-6.67	-0.46

STEP 2…N: FINAL FITTING

Yttrium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.95
Standard Error	8.03
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	4	18096.61	4524.15	70.17	3.21E-08
Residual	12	773.74	64.48		
Total	16	18870.35			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-21.39	10.16	-2.10	0.06	-43.53	0.75
O:A	-10.38	2.05	-5.06	0.00	-14.86	-5.91
T	0.30	0.20	1.54	0.15	-0.13	0.74
C	22.20	4.04	5.49	0.00	13.39	31.00
C^2	-0.97	0.49	-1.96	0.07	-2.05	0.11

Erbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.96
Adjusted R Square	0.94
Standard Error	8.03
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	4	17102.41	4275.60	66.33	4.42E-08
Residual	12	773.47	64.46		
Total	16	17875.88			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-21.38	10.16	-2.10	0.06	-43.51	0.76
O:A	-10.90	2.05	-5.31	0.00	-15.37	-6.43
T	0.37	0.20	1.87	0.09	-0.06	0.80
C	20.14	4.04	4.99	0.00	11.34	28.95
C^2	-0.77	0.49	-1.57	0.14	-1.85	0.30

Ytterbium

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.97
Adjusted R Square	0.96
Standard Error	2.71
Observations	17

ANOVA

	df	SS	MS	F	Significance F
Regression	4	3223.88	805.97	109.70	0.00
Residual	12	88.16	7.35		
Total	16	3312.04			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-1.83	1.36	-1.35	0.20	-4.79	1.13
OA^2	2.05	0.43	4.71	0.00	1.10	2.99
C^2	0.73	0.09	8.32	0.00	0.54	0.92
OAC	-3.06	0.34	-9.07	0.00	-3.80	-2.33
TC	0.07	0.01	5.49	0.00	0.04	0.10

Iron (for HCl concentrations of 1 - 5 M)

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98
R Square	0.97
Adjusted R Square	0.95
Standard Error	7.16
Observations	13

ANOVA

	df	SS	MS	F	Significance F
Regression	4	11612.44	2903.11	56.61	6.6E-06
Residual	8	410.28	51.28		
Total	12	12022.72			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-16.11	8.64	-1.87	0.10	-36.03	3.81
T	0.39	0.21	1.89	0.10	-0.09	0.86
C^2	3.77	0.36	10.33	0.00	2.92	4.61
OAC	-3.94	1.55	-2.54	0.03	-7.51	-0.37
OA^2	1.62	1.67	0.97	0.36	-2.24	5.48

Iron (for HCl concentrations of 5 - 7 M)

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99
R Square	0.98
Adjusted R Square	0.96
Standard Error	4.68
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	4	4556.89	1139.22	51.92	0.001058
Residual	4	87.77	21.94		
Total	8	4644.66			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	198.54	12.52	15.86	0.00	163.77	233.31
C	-20.87	1.66	-12.60	0.00	-25.47	-16.27
O:A	-22.32	4.80	-4.65	0.01	-35.64	-9.00
T	-0.03	0.17	-0.18	0.86	-0.49	0.43
OA^2	2.77	1.17	2.37	0.08	-0.48	6.02