PURIFICATION OF COAL FLY ASH LEACH SOLUTION BY SOLVENT EXTRACTION

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Materials and Metallurgy in Engineering.

30 May 2016

DECLARATION

I declare that this research report is my own unaided work. It is being submitted to the Degree of Master of Materials and Metallurgy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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ABSTRACT

The solvent extraction of iron and titanium from solution generated by the two-step sulphuric acid leaching of coal fly ash by Primene JMT was investigated.

The influence of hydrogen ion concentration, Primene JMT concentration, aqueous to organic volume phase ratio and temperature on the extraction of iron and titanium was determined by the use of Design of Experiments.

Hydrogen ion concentration and the interaction between the aqueous to organic volume phase ratio with Primene JMT concentration had a significant effect on the extraction of iron while temperature did not.

Hydrogen ion concentration and temperature did not have a significant effect on the extraction of titanium, while the interaction between Primene JMT concentration and aqueous to organic volume phase ratio had a significant effect.

Extraction improvement tests showed that at a hydrogen ion concentration of 0.28M, 88% iron and 99% extraction of titanium from coal-fly ash leach solution could be achieved.

Construction of a McCabe-Thiele diagram showed that a four-stage solvent extraction system with Primene JMT could reduce the iron and titanium concentration in the coal fly ash leach solutions to below 0.05g/L.

DEDICATION

To Ruvimbo and Ngoni, your patience and understanding is greatly appreciated.

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LIST OF SYMBOLS AND ABBREVIATIONS

A/O	Aqueous to organic
CFA	Coal Fly Ash
[Extractant]	Concentration of extractant
DAL	Direct Acid Leach
ICP-OES	Inductively Coupled Optical Emission Spectrometry
kg	Kilogramme
IR	Infra-Red (spectroscopy)
M	Molar (concentration)
mol	Mole
Rpm	Revolutions per minute
SX	Solvent Extraction
Wt	Weight
Temp	Temperature

1 INTRODUCTION

1.1 Background

Aluminium is the most widely used non-ferrous metal globally. Bauxite, a naturally occurring alumina ore is the chief source of aluminium. South Africa has no known exploitable high-grade bauxite ore deposits, despite this, it operates some of the world’s largest aluminium smelters. In 2009, South Africa produced 809 000 metric tonnes of aluminium at two smelters in Richards Bay. Feedstock to these smelters was alumina imported mainly from Guinea (Yager, 2009). The identification and exploitation of a local source of alumina has the potential to reduce import dependency and strengthen the local economy by the development of a new industry based on the production of alumina. Coal fly ash (CFA) is one potential resource found abundantly in South Africa that could be exploited to produce alumina.

CFA is the incombustible residue that remains from the burning of coal in electrical power generating stations. South Africa produces 20 million tonnes of CFA annually while global quantities are estimated to be over 300 billion tonnes (Babajide et al., 2010). The disposal of such a large CFA tonnage is an environmental concern because of the large dumping sites required and the subsequent leaching of heavy metals from the CFA dumps.

Kendal Power Station in the Mpumalanga province of South Africa is an example of a generator of electrical power and producer of CFA. An analysis of the major constituents of the CFA produced by the Kendal Power Station is: 56wt% SiO_2; 31wt% Al_2O_3; 5wt% CaO; 3wt% FeO and 2wt% TiO_2. The significant proportion of alumina (Al_2O_3) in the CFA makes its exploitation attractive as an alternative to the processing of bauxite for alumina production.

Alumina is traditionally produced by the leaching of bauxite ore using sodium hydroxide in pressure leaching vessels. Seeding the produced purified aluminate leach solution with fine alumina particles results in the formation of a precipitate comprised of pure alumina particles. The leaching of bauxite ore with sodium hydroxide is possible only because of the low silica content in the ore; if the silica content were high, the alumina produced would be contaminated by silica. In the case of CFA, leaching with sodium hydroxide is not possible owing to its high silica content (40-60 wt%) that will co-dissolve with the alumina and contaminate the alumina product. Other lixiviants that do not dissolve silica in the CFA are therefore preferred. Sulphuric acid is a prime candidate for the dissolution of CFA due to its low cost and availability.

Historically, two methods of leaching CFA with sulphuric acid have been investigated these are: direct and indirect leaching. Direct leaching of CFA is the acid attack of CFA without thermal pre-treatment of the CFA (Li et al., 2007) while indirect leaching involves the thermal pre-treatment of dry CFA followed by acid leaching (Gabler and Stoll, 1982).

Current research at the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, has shown that a leaching method which incorporates a combination of direct and indirect leaching has the potential of producing a leach solution with higher aluminium content compared to either direct or indirect leaching alone (Shemi, 2013). This process is known as the two-step acid leaching of CFA.

Although the use of sulphuric acid to leach CFA has the advantage of not dissolving silica, it has the disadvantage of dissolving impurity metals present in the CFA. The major impurity metals in CFA are calcium, titanium and iron.

Alumina produced from unpurified CFA leach solution will contain undesirable levels of iron and titanium. Besides increasing the electrical cost of producing aluminium in the Hall-Heroult electrolysis process, they give undesirable effects to the aluminium product. Iron reduces ductility while titanium reduces electrical conductivity; this reduces the usefulness of aluminium for those applications where ductile strength or electrical conductivity is important (Jentoftsen, 2000). Therefore these metals must be removed before alumina can be recovered by crystallisation.

Of the major impurity metals, calcium is relatively simple to remove. Below 75°C and at sulphuric acid concentrations above 3molal, calcium sulphate and gypsum all have solubility's less than 0.1mol per kg of sulphuric acid (Azimi et al., 2007). This low solubility can be exploited in the removal of calcium from CFA leach solutions. Iron and titanium on the other hand are difficult to remove and are therefore, the subject of this work.

One method that is able to remove impurity metals from CFA leach solutions is solvent extraction (SX). In SX, an organic solvent known as an extractant is used to remove from an aqueous solution, one or more targeted metals. The resulting metal organic compound is soluble in an organic diluent such as kerosene, while it is insoluble in the aqueous solution. The most effective extractants that remove impurity metals from CFA leach solutions are high molecular weight amines. These have been shown to be capable of selectively removing titanium and iron from leach solutions (Matjie et al., 2005; Alguacil & Amer., 1986; Mahi & Bailey. 1985).

Primene JMT (a primary amine) and Alamine 336 (a tertiary amine) have been selected as extractants for this work due to their commercial availability and selectivity towards iron and titanium over aluminium. Alamine 336 has been found to be effective in removing iron from chloride acidic solutions (Mahi and Bailey, 1985). Primene JMT has been found to be effective in acidic sulphate conditions produced from indirect leaching of CFA (Matjie et al., 2005).

1.2 Motivation and rationale

CFA is a growing environmental problem in South Africa. In recent years the major power supplier in South Africa, Eskom, a government parastatal responsible for electricity generation, under pressure to satisfy growing demand for power, has reopened two old power stations and is currently constructing two new coal fired power stations (Eberhard, 2013). Consequently, it is anticipated that there will be additional generation and dumping of CFA as more coal fired power stations come online. This is in addition to the CFA dumps already in existence. There is therefore, increased incentive to invest into technology to recover alumina and other valuable materials from CFA.

The use of a two-step acid leaching process to dissolve CFA (Shemi, 2013) has the potential to increase the amount of aluminium leached into solution compared to the traditional direct and indirect leaching methods. This will result in improved alumina recoveries and consequently increased viability of extracting alumina from CFA.

In the first step of the two-step acid leaching process, CFA is dissolved by 6M sulphuric acid to make a CFA solution and a residue. In the second step, the residue produced in the first step is then sintered and leached again with 6M sulphuric acid to make a second residue and CFA leach solution. The two solutions are then mixed to make a CFA leach solution that contains the total dissolved aluminium. The addition of 6M sulphuric acid in both steps implies that the CFA produced has a higher acid concentration than all other CFA solutions that have been investigated to date. The successful production of high purity alumina requires the prior removal of iron and titanium from this solution. Past researchers (Seeley et al., 1981; Alguacil et al.; 1987; Matjie et al., 2005) managed to remove impurity metals at pH values of 1.5, 0.05 and 2 respectively. The high acid concentration presents a challenge for the purification of CFA solution from the two-step leaching process because the efficient removal of impurity metals may not be possible at a high acid concentration. Subsequently, large volumes of neutralising agents to reduce the acid concentration may be required; this introduces foreign cations, which could impede the purification process. This report therefore, seeks to determine if iron and titanium can be removed from CFA leach solutions at high acid concentration by adjusting selected process factors. In the event that neutralisation is required, this work will also determine if removal of these metals is still possible after the addition of neutralising reagents.

1.3 Research Objectives

- To investigate the influence of selected factors on the solvent extraction of iron and titanium from a two-step acid CFA leach solution.
- To determine the feasibility of purifying a two-step acid CFA leach solution by solvent extraction at high sulphuric acid concentration.
- To determine the number of solvent extraction stages that will reduce the impurity content of CFA leach solution to acceptable levels.

1.4 Research Questions

- What is the influence of hydrogen ion concentration, extractant concentration, aqueous to organic (A/O) phase ratio and temperature on the solvent extraction of iron and titanium from a two-step acid CFA leach solution? Are there any interactions amongst these factors?

- How many extraction stages are required to purify the CFA leach solution to metal concentration levels below 1mg/L?
- Can the extractant be successfully recycled without degrading?
- Is there significant co-extraction of aluminium in the removal of iron and titanium by SX from the CFA leach solution?

2 LITERATURE REVIEW

2.1 Introduction

Aluminium is a metal that is of great industrial importance. It is chosen over copper in the transmission of electrical power over large distances due to its superior electrical conductivity and lower density. Aluminium can be alloyed with other elements to make lightweight alloys that are used in the construction of automobiles and aircraft. Aluminium compounds such as aluminium sulphate are used in water treatment works and in the paper making industries (Karimi and Gheadi, 2007).

High purity aluminium is produced from the electrolysis of alumina in the Hall-Heroult process. The purity of alumina acceptable for the electrolysis plant is: 98.8wt% Al_2O_3, 0.1 wt% CaO+MgO, $Na_2O+K_2O< 0.1$wt% SiO_2, < 0.04wt% Fe_2O_3 and < 0.005wt% TiO_2 (Hudson, 1987). Alumina feedstock is traditionally obtained from the Bayer process that uses sodium hydroxide to pressure leach bauxite ore that has low silica content. It is necessary to have low silica content because sodium hydroxide can easily dissolve silica and the resulting dissolved silica is difficult to remove from the leach solution. A comparison of the alumina content between bauxite and CFA shows that bauxite has a higher recoverable alumina grade at 41wt.% compared to CFA, which has an average of 30wt.%. However, the global bauxite reserves in 2004 stood at 25 000 Mt with a bauxite mining rate of 159Mt per year. This represents an estimated reserve life of 157 years (Luo & Soria, 2007). Unfortunately, none of these reserves are in South Africa, the continued depletion of this resource could result in an increase in the price of imported alumina and threaten the viability of the aluminium production industry in South Africa. The exploitation of a local alumina resource such as CFA could significantly introduce another easily available, reliable and cost competitive alumina feedstock supply.

Disposal of fly ash in the vicinity of power generation plants is an environmental problem. Besides the large footprint, the accumulation of heavy metals in ground water leached from the CFA dump attracts attention from environmental regulatory authorities, which leads to possible sanctions. Furthermore, communities in the environs of dry CFA dumps are exposed to CFA dust that causes respiratory tract illnesses such as silicosis and bronchitis (Haynes, 2009).

The recovery of alumina from CFA represents an opportunity to ameliorate the environmental impact of CFA dumps and to strengthen the aluminium smelting industry in South Africa.

2.2 Sulphuric acid leaching

The first step in the process route for the production of alumina from CFA requires leaching by a mineral acid (Zimmels and Seidel, 1998). Sulphuric acid leaching dissolves the major metal oxides in the CFA according to the following equations:

$$Al_2O_3 + 3\,H_2SO_4 \rightleftharpoons Al_2(SO_4)_3 + 3H_2O \qquad (2.1)$$

$$2FeO + 3H_2SO_4 + ½O_2 \rightleftharpoons Fe_2(SO_4)_3 + 3H_2O \qquad (2.2)$$

$$CaO + H_2SO_4 \rightleftharpoons CaSO_4 + H_2O \qquad (2.3)$$

$$TiO_2 + 2H_2SO_4 \rightleftharpoons TiO(SO_4)_2 + 2H_2O \qquad (2.4)$$

The aluminium in solution can be recovered directly at this stage by crystallisation, but the product is not of the required purity owing to the presence of impurities that include Ti^{4+}, Fe^{3+}, Ca^{2+} and K^{+} (Matjie et al., 2005). The solution must therefore be purified by removal of these impurities prior to crystallisation (Nayak & Chitta, 2009).

2.3 Recovery of pure alumina

It is possible to directly recover aluminium from leach solutions by solvent extraction, precipitation or crystallisation. This recovery involves directly extracting aluminium from leach solution and subsequently calcining to produce alumina. The success of these process routes hinge upon the ability of each method to be highly selective and avoid co-recovery of contaminant metals.

2.3.1 Direct recovery of alumina by precipitation

Precipitation is the formation from solution, of a solid product as the result of dilution or of the addition of a reagent to the solution (Jackson, 1986). It has been postulated by Charlot (1983) that Ti^{4+}, Fe^{3+} and Al^{3+} ions in aqueous solution can be selectively precipitated as metal hydroxides at pH values of 2, 3 and 3.5 respectively:

$$TiO^{2+} + 2OH^- \rightleftharpoons TiO(OH)_2 \qquad (2.5)$$

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3 \qquad (2.6)$$

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3 \qquad (2.7)$$

Precipitation of metals from CFA leach solution with the composition: 12g/l Al, 0.8g/l Ti and 2g/l Fe using sodium hydroxide at different pH values was investigated by Matjie et al. (2005). The calcined precipitate obtained at pH 2 had the composition: 0.7wt% TiO_2. The calcined precipitate obtained at pH 3 had composition 2.8wt% Fe_2O_3. The calcined precipitate at pH 3.5 had composition: 78.5wt% Al_2O_3. It was concluded that selective precipitation failed to produce pure metal hydroxides of Ti^{4+}, Fe^{3+}, and Al^{3+} at the expected pH values.

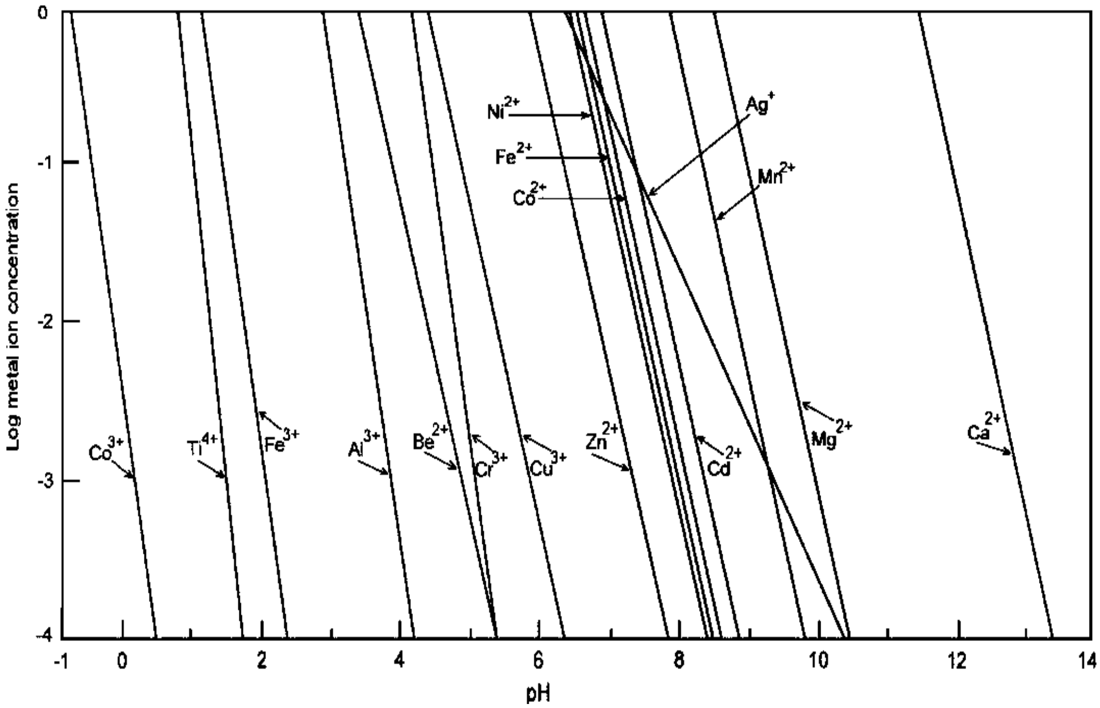


Figure 2.1 Metal hydroxide precipitation diagram (Gupta, 2003)

An inspection of the metal hydroxide precipitate diagram, Figure 2.1, confirms this conclusion as observed with the equilibrium conditions for the existence of hydroxides of titanium, aluminium and iron that lie close to each other, thus selective precipitation of these metals is difficult due to co-precipitation.

2.3.2 Recovery of alumina by crystallisation

Crystallisation is the formation of solid crystals from solution by exceeding the saturation solubility of a solute in a solvent. Mullin & Zacek (1980) investigated the crystallisation of aluminium sulphate by potassium sulphate. It was reported that the solubility of Al_2SO_4 at 20°C was 36.2g anhydrous salt/100g water, that of K_2SO_4 was 10.9g/100g water and that of the double salt $K_2SO_4.AlSO_4.24H_20$ as 5.9g hydrous salt /100g water. Hence, an equimolar reaction under supersaturated conditions should crystallise potash alum:

$$Al_2SO_4 + K_2SO_4 + 24H_2O \rightleftharpoons K_2SO_4.AlSO_4.24H_20 \qquad (2.8)$$

The kinetics of the crystallisation increased with temperature and super saturation of the synthetic solutions. Matjie et al. (2005) used this technique with $(NH_4)_2SO_4$ in a CFA leach solution with the following major species in solution: $CaSO_4$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, H_2SO_4 and $TiSO_4$. The addition of ammonium sulphate produced white crystals of $Al(NH_4)(SO_4)_2.20H_2O$ at a pH of 1.5 :

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 + 40\ H_20 \rightleftharpoons 2Al(NH_4)(SO_4)_2.20H_2O \quad (2.9)$$

After calcination of the crystals, white alumina was formed giving a product with 97wt% Al_2O_3, 0.59wt% CaO, 0.8wt% SiO_2 and 0.4wt % MgO with iron and titanium oxides making up the balance of 1.21wt%.

Crystallisation on its own would be an effective method of recovering alumina. Unfortunately, impurities such as Ca^{2+}, Si^{4+}, Fe^{3+}, Ti^{4+} and Mg^{2+} tend to co-crystallize with the aluminium. The purity of the resulting calcined alumina is thus, lowered to below specification levels for use in the alumina electrolysis plant. Thus, crystallisation on its own as a method of alumina recovery is not adequate.

2.3.3 Recovery of alumina by Solvent Extraction

Solvent extraction (SX) is a separation technique by which a solute is transferred from one liquid phase to another immiscible or partially miscible liquid phase. In hydrometallurgy, the aqueous phase contains the metal which is to be concentrated into the organic phase. There are three basic stages in solvent extraction: extraction, scrubbing and stripping. During extraction, the aqueous phase is brought into contact with the organic phase by thorough mixing. The products of the extraction stage are the organic solvent loaded with the desired metal and the aqueous raffinate. The loaded solvent may be sent for scrubbing by an aqueous phase to remove contaminating impurities. The scrubbed organic solvent can then be stripped to remove the desired solute (Hudson, 1981).

Many researchers have examined the direct extraction of aluminium by solvent extraction. Preston (1985), investigated the ability of carboxylic acids in a xylene diluent to recover aluminium and other metals from nitrate solutions. Tsakaridis and Agatzini-Leonardou (2005) also examined extraction of aluminium from sulphate solutions using Cyanex 272 a phosphinic acid. While both reports indicated that it is possible to extract aluminium from the respective leach solutions, the desired purity of aluminium could only be achieved by the prior removal of iron that is also strongly extracted by these solvents. The recovery of alumina directly from aluminium containing acidic solutions is therefore not possible due to contamination by impurity metals. The solutions must be purified by removal of these impurity metals prior to extraction of alumina.

2.4 Removal of impurity metals by solvent extraction

Different extractants have been extensively tested to remove iron and titanium from acidic solutions. Organo-phosphates such as bis-(2-ethyl-hexl) phosphoric acid (D2EHPA) and tributyl phosphoric acid (TBP) are popular because of their commercial availability and low price.

Da Silva et al. (2008), showed that D2EPHA in n-dodecane was able to extract iron and titanium from sulphuric acid solution with the possibility of recycling the reagents used. However, the selective removal of iron and titanium from aluminium containing leach solutions was not satisfactory with D2EHPA due to the co-extraction of aluminium (Mohapatra et al., 2007; Matjie et al., 2005). Moreover, organo-phosphate extractants are also difficult to strip, requiring expensive stripping agents such as fluorine and hydrogen peroxide to improve stripping kinetics (Seyfi, 2008; Da Silva, 2008). Hence, the use of organo-phosphates to purify aluminium rich acidic solutions is not favourable.

Although amines are more expensive, they have been shown to be superior at removing iron from acidic sulphate leach solutions than other extractants such as carboxylic acids and organo-phosphates in terms of selectivity, extraction yield and stripping (Li et al., 2011). Primary amines in particular have shown excellent performance in extracting impurity metals from CFA sulphate solutions. Seeley et al. (1981) used Primene JMT in toluene to purify CFA leach solutions. Alguacil et al. (1987), used the primary amine Primene 81R, to extract iron(III) from aluminium sulphate solutions which contained various metal impurities such as Ca, Mg and Ti. Extraction of iron was successful with sulphuric acid concentrations of up to 0.1M. At hydrogen ion concentrations greater than 0.1M the extraction of iron reduced significantly. Hence, pH adjustment must be exercised for the effective use of Primene 81R to remove iron from aluminium sulphate acidic solutions.

Li et al. (2011) examined the removal of iron from industrial grade aluminium sulphate using the primary amine N-1923 and managed to reduce the iron concentration to less than 50mg/L at pH above 1.2. Matjie et al. (2005) used the primary amine Primene JMT to remove iron and titanium from CFA in acidic sulphate leach solution. An alumina product with purity > 99.4% was produced after crystallisation and calcination from the purified solution.

2.5 Principles of solvent extraction

Ritcey and Ashbrook (1984) describe SX as being based on the equilibrium:

$$M_{(aq)} + E_{(org)} \rightleftharpoons ME_{(org)} \quad (2.10)$$

M is a metal in the aqueous phase that is to be extracted from the bulk solution. The metal M is then transferred to the organic phase by reacting it with an organic extractant E to form a complex $ME_{(org)}$. This is known as extraction and it requires that equilibrium lies to the right. The majority of unwanted anions and cations must remain in the aqueous phase. This implies that the organic solvent should be selective for the targeted metal. After extraction, the metal must be transferred back to another aqueous phase by shifting the equilibrium to the left; this process is known as stripping.

In commercial applications, the metal in the aqueous feed and the extractant in the organic phase are usually fed into the first contactor in the extraction stage as shown in Figure 2.2.

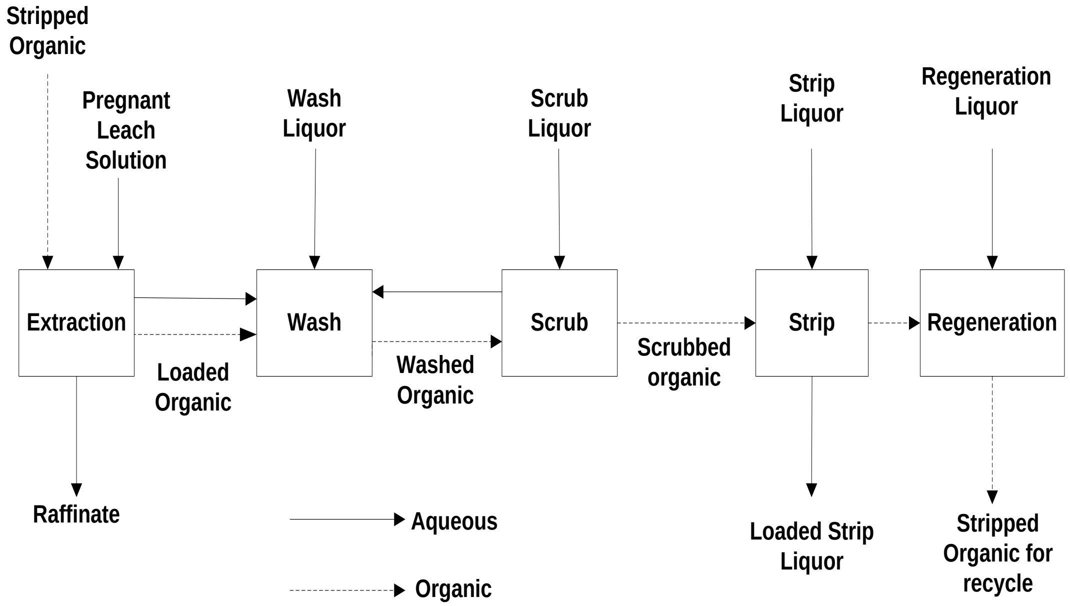


Figure 2.2 Generalised solvent extraction circuit (Sole, 2008)

In this contactor, after mixing, settling and separation of the phases, the metal of interest will be in the organic phase and the metal depleted aqueous phase now known as the raffinate is either discarded as waste or is treated for other metals of which can be of commercial value.

Washing is necessary for those cases where there is considerable entrainment of the organic phase into the aqueous phase or vice versa. In the latter case, the wash liquor is contacted with the loaded organic phase and any aqueous phase droplets present are collected into the raffinate or in the spent wash liquor.

During extraction, there is usually co-extraction of unwanted impurities and these are usually removed from the loaded organic phase by a suitable aqueous solution. This is known as scrubbing and the resulting raffinate is usually recycled to the leaching tank or feed SX tank.

The loaded organic phase from the scrubbing stage is then sent for stripping by a suitable aqueous reagent producing a concentrated aqueous phase known as the loaded strip liquor.

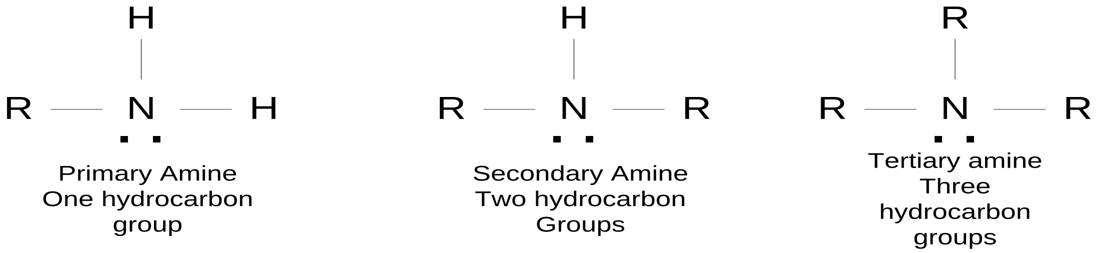
Regeneration is often required to convert the now modified organic phase back to a state suitable for reuse. For example, for those SX systems that involve stripping by acid, the extractant may by protonated rendering it unsuitable for recycle and deprotonation will be required by addition of an alkali.

2.6 Chemistry of Solvent Extraction

The successful application of SX as a technique to remove targeted metal ions in CFA leach solutions is influenced by the chemical properties of the organic phase for that particular SX system. This section will discuss these chemical characteristics of the reagents that make up the organic phase.

2.6.1 Amine Extractants

Amines are classified according to the number of long chain alkyl (denoted by R) groups attached to the nitrogen atom. Figure 2.3 shows the primary, secondary and tertiary amines with 1, 2 and 3 long chain alkyl groups respectively. Quaternary amines have 3 long chain alkyl groups and an additional methyl group which makes the whole structure ionic.



Primary Amine
One hydrocarbon
group

Secondary Amine
Two hydrocarbon
Groups

Tertiary amine
Three
hydrocarbon
groups

$[R_3NCH_3^+]Cl^-$

Quaternary amine

Figure 2.3 Structure of alkyl amines. (Dudley et al., 2009)

Primary, secondary and tertiary amines require that they be converted to an amine salt prior to acting as anion exchangers. For example, tertiary amines behave as follows when they react with an acid:

$$R_3N_{(org)} + H^+ + B^- \rightleftharpoons R_3NH^+B^-{}_{(org)}$$

The equilibrium constant is given by $K = \frac{[R_3NH^+B^-]}{[R_3N][H^+][B^-]}$ (2.16)

The value of K is an indication of the extent to which the amine salt is formed. Extraction of a metal M^{2+}, with anion B^- can proceed as follows:

$$MB_4^{2-}{}_{(aq)} + 2\,(R_3NH^+B^-)_{(org)} \rightleftharpoons (R_3NH^+)_2.MB_4^{2-}{}_{(org)} + 2B^-_{(aq)} \quad (2.17)$$

The equilibrium constant would be: $K_f = \frac{[(R_3NH^+)_2\ MB_4^{2-}][B^-]^2}{[R_3NH^+B^-]^2[MB_4^{2-}]}$

By definition the metal distribution coefficient is defined as: $D = \frac{[M]_{(org)}}{[M]_{(aq)}}$

Where $[M]_{(org)}$ and $[M]_{(aq)}$ represent the total metal analytical concentrations in the equilibrated organic and aqueous phases respectively.

Hence $K_f = \frac{D[B^-]^2}{[R_3NH^+B^-]^2}$ but we know that from 2.16:

$$[R_3NH^+B^-] = K[R_3N][H^+][B^-]$$

Hence $K_f = \frac{D}{(K[R_3N][H^+])^2}$

Combining K^2 and K_f gives $K_1 = K^2.K_f$ then

$K_1[R_3N]^2[H^+]^2 = D$

Taking logarithms $\log K_1 + 2\log[R_3N] + 2\log[H^+] = \log D$ hence:

$$\log D = \log K_1 + 2\log[R_3N] - 2pH \qquad (2.18)$$

Equation (2.18) establishes the general dependence of the metal distribution between the organic (R_3N, R_2NH or RNH_2) and aqueous phases with pH and extractant concentration. In general, more metal is transferred to the organic phase from the aqueous phase at higher extractant concentration. At low pH, equation (2.18) predicts that metal transfer to the organic phase will be high; this is contradicted by research work that has shown that a high hydrogen ion concentration hinders metal extraction (Alguacil et al., 1987; Li et al., 2011). This work seeks to corroborate this evidence and determine if the adjustment of other process factors improves metal transfer at low pH.

The primary amine Primene JMT and tertiary amine Alamine 336 have been selected for this work because of their ability to extract iron from acidic solutions (Chou & Lin, 1986; Mahi & Bailey, 1984). They are readily available and cheap, this is important in the development of an economically viable process route of extracting alumina from CFA.

Alamine 336

In acidic chloride solutions Alamine 336, a tertiary amine, is firstly converted to an amine salt:

$R_3N_{(org)} + HCl \rightleftharpoons (R_3NH^+)Cl^-$ (2.19)

Iron(III) in chloride media exists as the following ion:

$Fe^{3+} + 4Cl^- \rightleftharpoons FeCl_4^-$ (2.20)

Anionic exchange is thought to occur as follows:

$R_3NH^+Cl^- + FeCl^-_4 \rightleftharpoons R_3NH.\ FeCl_4 + Cl^-$ (2.21)

Mahi and Bailey (1984) successfully extracted iron from aluminium containing acidic chloride solutions using Alamine 336. Extractions from solutions containing iron concentrations of up to 9g/L were performed successfully at hydrogen ion concentrations of up to 3M.

To date, there has been very little research on the extraction of iron and titanium from aluminium rich acid sulphate leach solutions with Alamine 336. Because Mahi and Bailey (1984) could extract from acidic aqueous solutions with very high concentrations of iron(III), then Alamine 336 is a prime candidate for use in test-work to extract iron(III) from acidic sulphate solutions such as those found in the two-step acid CFA leach solutions.

Primene JMT

Neutral and anionic mechanisms are thought to be both at play for the extraction of iron by Primene JMT in acidic sulphate solutions. Liu et al. (1992) showed that the primary amine system formed followed a neutral mechanism characterised by the following reactions:

$$Fe^{3+} + H_2O + SO_4^{2-} \rightleftharpoons Fe(OH)SO_4 + H^+ \qquad (2.24)$$

$$2RNH_2 + 2H^+ + SO_4^{2-} \rightleftharpoons (RNH_3)_2SO_4 \qquad (2.25)$$

$$Fe + H_2O + SO_4^{2-} + 2(RNH_3)_2SO_4 \rightleftharpoons Fe(OH)SO_4.[(RNH_3)_2SO_4]_2 + H^+ \qquad (2.26)$$

These reactions show that the extraction of iron(III) by Primene JMT is closely influenced by the iron(III) species in solution, which in turn is influenced by the prevailing pH.

2.6.2 Diluents

Most extractants tend to have a high viscosity; they are therefore unsuitable for use without alteration due to the poor phase separation of the organic and aqueous solutions after mixing. The addition of aliphatic or aromatic hydrocarbons to the extractant helps to reduce the viscosity of the extractant. These diluents have demonstrated their ability to solvate metal complexes formed. Furthermore, diluents also act as a diluting medium since extractants are sold at high concentrations and if used as is, would result in the unnecessary recycling of unreacted extractant.

Some of the desirable properties of a diluent are:

- Low volatility and high flashpoint to avoid the risk of fire.
- Insolubility in the aqueous phase.

- Ability to dissolve the extracted metal into the organic phase, this minimises problems of third phase formation.
- It must be cheap and readily available because it forms the major component of the organic phase.

Aromatic diluents allow for higher organic loading and have less third phase formation problems; however, they tend to be carcinogenetic as well as exhibiting high flammability and volatilization. An aromatic diluent has more solvating power and is expected to have a faster phase disengagement time, this allows for the use of smaller settling vessels thereby reducing the cost of capital equipment.

Amine systems have used both aliphatic and aromatic diluents depending on the required solvating power required for a particular system. Aliphatic diluents that are used on an industrial scale for amines are kerosene's; the shellsol range of hydrocarbon solvents has been used successfully in many SX systems (Sole et al., 2005).

2.6.3 Modifiers

The formation of an undesirable third phase in SX occurs when the diluent fails to solvate the metal-extractant complex into the organic phase. This third phase is usually of intermediate density between the density of the aqueous phase and the density of the organic phase. An alcohol, for example isodecanol, is added to the diluent to enhance its dissolving power. These alcohols are known as modifiers. The choice of the diluent/modifier pair has a direct influence on the phase disengagement time that in turn affects the following important design factors:

- Size of contactor: the contactor size is a function of kinetics of the diluent/modifier choice.

- Settler area: directly affects the solvent inventory for extraction, scrubbing and stripping stages.
- Equilibrium: influences the efficiency of the system that determines the number of stages for each of stripping, scrubbing and extraction. The more the number of stages, the higher the capital costs.

Isodecanol is the most commonly used modifier for amine systems and has been used extensively with Alamine 336 in uranium extraction (Sole, 2008).

2.6.4 Stripping and Recycling

The successful operation of a SX plant is partly dependant on the ability of the organic extractant to be recycled without significantly affecting its extractive strength. After each successive extraction, the extracted metal must be removed from the organic phase by a suitable aqueous reagent thus, preparing the extractant for reuse. The removal of extracted metal from the loaded organic phase is known as stripping. The stripping operation often affects the ability of the extractant to perform in the next extraction cycle.

In primary amine systems, basic or acidic reagents can carry out stripping. The stripping of iron by sulphuric acid is a reversal of equilibrium conditions in favour of extraction as observed in equation (2.27):

$$4(RNH_3)_2SO_4.(Fe(OH)SO_4)_2+H_2SO_4 \rightleftharpoons 4(RNH_3\,)_2SO_4+Fe_2(SO_4)_3+2H_2O \quad (2.27)$$

The advantage of sulphuric acid stripping is that it does not introduce new ions into the SX system for a sulphuric acid SX system. Alguacil et al. (1987) investigated the stripping of iron(III) from Primene 81R in kerosene diluent modified by decanol using both acids and bases. The technique implemented was to recontact the stripped organic phase with fresh aqueous iron(III) solution and determine whether the same iron loading could be obtained successively. It was discovered that sulphuric acid stripping led to a progressive decrease in iron loading with each successive recycle. This was attributed to the formation of $5(RNH_3^+)_2SO_4.3(RNH_3HSO_4)$, an amine bisulphate during stripping that is considered unable to extract iron. The amine bisulphate therefore requires regeneration, which is deprotonation by a base. Regeneration was found to be best with ammonium hydroxide compared to sodium hydroxide and ammonium carbonate.

The use of basic reagents to strip iron from the loaded organic phase was found to result in better organic loadings by the recycled extractant compared to acidic reagents. However, the use of a basic solution leads to the precipitation of iron (III) hydroxide that required an additional filtration stage. This is a disadvantage compared to acid stripping because additional equipment is required for effective filtration leading to higher process costs.

2.7 Factors influencing solvent extraction of impurity metals

In addition to identifying appropriate reagents for the removal of impurity metals from CFA liquor, it is also important to have an understanding of how various process parameters influence the amount of impurity metal extracted. This is important from a SX process optimisation and capital cost perspective. Those parameters that do not exert great influence on metal extraction do not need optimisation, but those that do, must be managed well. Acceptable levels of impurity metal extractions may only be possible under certain variable values which may produce an unwanted by-product or that need extra plant and equipment.

2.7.1 Temperature

Generally, the rate of extraction of metals by organic solvents is rapid at room temperature and there is no significant benefit in using higher temperatures in trying to reach equilibrium conditions in a shorter period. The advantage of using a higher temperature in SX plants is that phase separation times are reduced. This is important because rapid phase separation allows for increased throughput; in addition, the settler size can be considerably reduced, thus lowering capital costs. However, there is a limit on the extent to which temperature can be increased. There is increased risk of fire as the SX operating temperature approaches the flashpoints of either the diluent or extractant (Ritcey & Ashbrook, 1984). Furthermore, there is increased volatilisation of the organic phase and this constitutes an environmental and health hazard. Volatilisation also increases working costs since the lost organic reagent must be replaced periodically (Rederberg et al., 2004).

2.7.2 Hydrogen ion concentration

The hydrogen ion concentration of the CFA leach solution to be purified is an important process variable. This is because optimum extraction of targeted metal often occurs in a narrow pH range and as a result, adjustment of pH is often necessary to achieve optimum extraction. Sulphuric acid is dibasic in nature and dissociates in water with the following equilibria:

$$H_2SO_4 + H_2O \rightleftharpoons HSO^-_4 + H_3O^+ \qquad K_2 = 1 \times 10^3 \qquad (2.28)$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO^{2-}_4 \qquad K_3 = 1.27 \times 10^{-2} \qquad (2.29)$$

K_2 is very large and this implies that in sulphuric acid solution there will be predominately bisulphate (HSO^-_4) and hydrogen ions compared to the sulphate ion. Furthermore, K_3 is small which means that the bisulphate formed does not easily dissociate (Lide & Fredericks, 1995). Consequently, at high sulphuric acid concentrations, there exists a high concentration of both hydrogen ions and bisulphate ions. Both, these ions have considerable influence on the extraction of impurity metals.

During sulphuric acid leaching of CFA, all the FeO (iron(II)) is oxidsed to iron(III) as illustrated by equation (2.2) (Zimmels and Seidel, 1998). Li et al. 2011, showed that iron(III) is only extracted in its hydrolysed form:

$$Fe^{3+} + H_2O + SO_4^{2-} \rightleftharpoons Fe(OH)SO_4^{2-} + H^+ \tag{2.30}$$

Reaction 2.30 shows that an increase in hydrogen ion concentration does not favour the formation of the hydrolysed iron(III) complex but rather its dissociation. Hence, less iron(III) is available in extractable form at higher hydrogen ion concentrations. Figure 2.4 is an illustration of the speciation of the iron(III) complex in acidic sulphate media at 2 ×10 -3M iron(III) concentration.

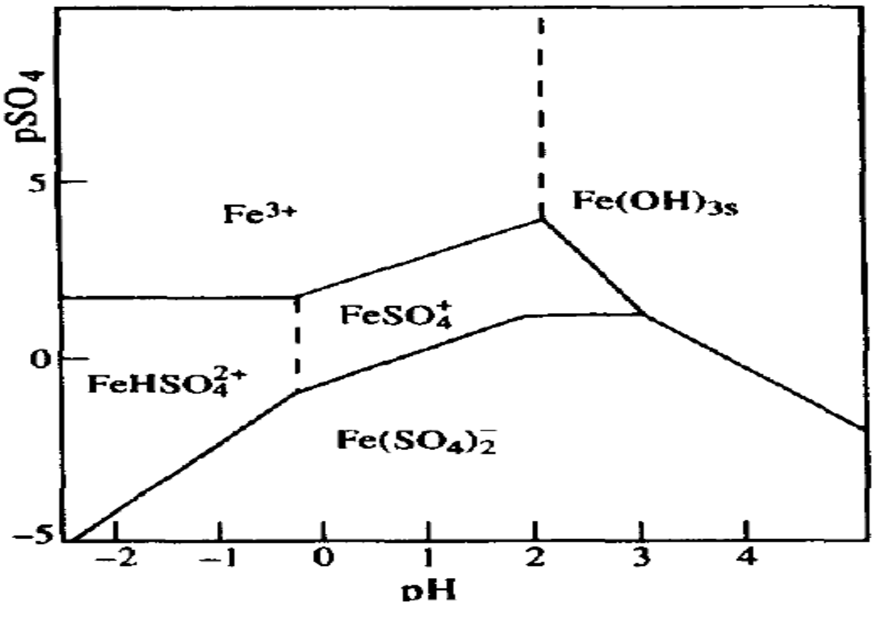


Figure 2.4 Iron(III)-sulphate-pH diagram (Gil et al., 1994)

As the acid concentration increases, iron(III) species in solution such as $FeSO_4^+$ and $Fe(SO)_2^-$ are converted to $FeHSO_4^{2+}$.

The formation $FeHSO_4^{2+}$ is explained by the increase in the bisulphate and hydrogen ion concentration as the sulphuric acid concentration increases (reaction 2.28). The bisulphate and hydrogen ions react with Fe^{3+}, $FeSO_4^+$ and $Fe(SO)_2^-$ to form $FeHSO_4^{2+}$.

Infra-Red spectroscopy investigations by Li et al. (2011) on the composition of the iron(III) extracted species by a primary amine indicated only the existence of $SO^{2-}{}_4$ and no trace of the $HSO^-{}_4$ in the extracted organic species.

It is therefore, concluded that at high acid concentrations, extraction of iron(III) is expected to be low owing to the increased concentration of $FeHSO_4^{2+}$ which is not extracted by amine extractants (Li et al., 2011).

Alguacil et al. (1987) showed that with the primary amine Primene 81R, the bisulphate amine complex $5(R_3NH_3)_2SO_4.3RNH_3{\cdot}HSO_4$ is formed at 25°C at sulphuric acid concentrations greater than 0.1M. This amine complex is thought to be unable to extract iron(III), therefore high acid concentrations result in reduced iron (III) extraction because the amine extractant is not in a form that extracts iron(III).

Figure 2.5 illustrates the speciation of titanium in sulphuric acid as reported by Sole (1999). Titanium hydroxide is observed to exist at all acid concentrations as $Ti(OH)_3HSO_4$, $Ti(OH)_2^{2+}$, $Ti(OH)_2HSO_4^+$ or $Ti(OH)_3^+$.

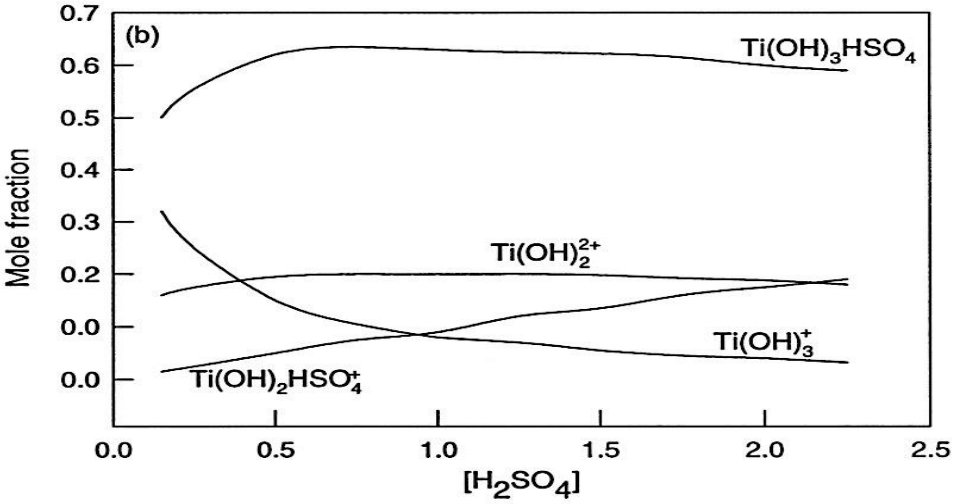


Figure 2.5 Distribution of titanium species in sulphuric acid (Sole, 1999).

The bisulphate complex $Ti(OH)_3HSO_4$ is the dominant species at all sulphuric acid concentrations. An amine system that extracts iron well will therefore be able to extract the $Ti(OH)_3HSO_4$ species.

2.7.3 Extractant Concentration

An increase in extractant concentration results in the increase of the distribution ratio for a particular extracted metal. This is illustrated by equation (2.18) and illustrated graphically in Figure 2.6 below.

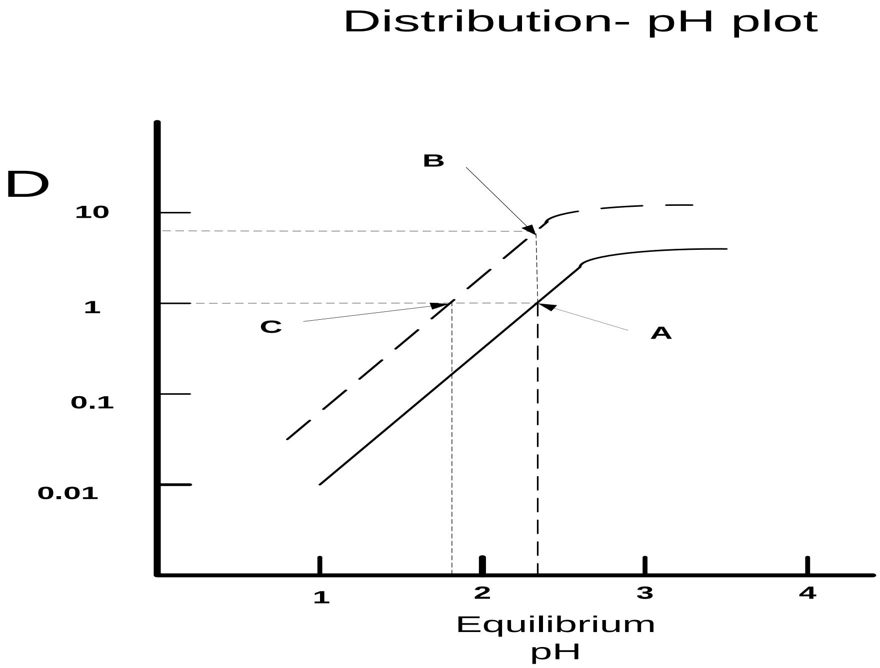


Figure 2.6 Effect of extractant concentration on distribution ratio with change in pH. (Ritcey & Ashbrook, 1984).

The solid curve represents a system in which there is 50% extraction (D=1) at a pH of 2.3. This is denoted as $pH_{0.5}$ and is represented by point A. Increasing the extractant concentration results in an increase in the metal extracted into the organic phase, but the amount of metal in solution has not increased at this pH and therefore the distribution ratio increases as shown to point B. This implies a shift of the curve as represented by the dotted line to lower pH values. Alguacil and Amer (1986) studied the dependence of initial amine concentration on the extraction of iron(III) from sulphate solutions. At 3% by volume Primene 81R, a metal loading of 2.9g/l was obtained in the organic phase. At an amine concentration of 10% by volume, the loading of the iron(III) increased to 11g/l. This increase in metal loading is explained by the fact that a higher extractant concentration in the organic phase implies that a larger number of extracting amine molecules per unit organic volume are available to come into contact with the target metal in the aqueous phase.

2.7.4 A/O phase ratio

In a SX system, the efficiency of the extraction step is typically expressed by the use of an equilibrium curve. The relationship between the concentration of metal extracted into the organic phase $[M]_{(org)}$ with the concentration of metal remaining in the raffinate $[M]_{(aq)}$ at various A/O volume phase ratios is an equilibrium curve commonly known as a extraction isotherm. This extraction isotherm is obtained experimentally with the same experimental conditions for each plotted point at different A/O volume phase ratios as illustrated in curves I to III in Figure 2.7.

Ritcey & Ashbrook (1984) describe curve I as one that has a high extraction efficiency, curve II is described as normal and curve III as an s-shaped type that cannot obtain low metal tenor in the raffinate. They also point out that all of these three curves reach a limiting metal loading in the organic phase.

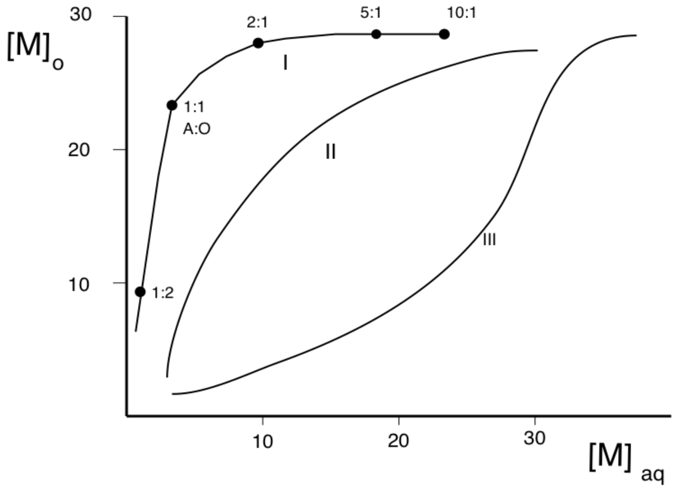


Figure 2.7 Effect of A/O ratio on metal extraction (Ritcey & Ashbrook, 1984)

As the A/O ratio increases (more aqueous volume) more of target metal is loaded into the organic phase until a limit is reached, this is the maximum loading capacity of a solvent under the prevailing experimental conditions. Rictcey & Ashbrook (1984) further point out that this limit is reached when, free extractant has been depleted or the metal-extractant species can no longer dissolve into the organic phase.

2.8 Construction of the McCabe-Thiele diagram

For a working counter current solvent extraction system, a plot of the organic versus the aqueou phase solute metal concentrations throughout the column is known as the operating line. If such an operating line of a continuous counter current SX system is added to an equilibrium isotherm then the diagram becomes a McCabe-Thiele diagram as shown in Figure 2.8 (Habashi, 1980).

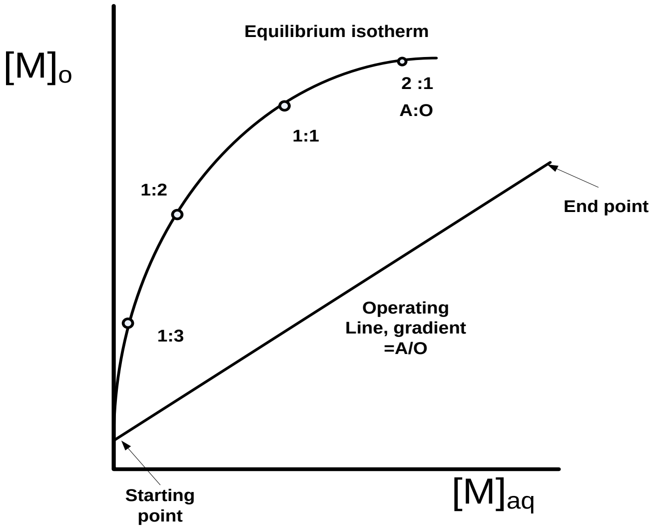


Figure 2.8 Generalised McCabe-Thiele diagram (Habashi, 1980)

The starting point of operating line represents the metal assay of the raffinate and stripped organic while the end-point represents the metal concentration of aqueous feed and loaded organic.

The McCabe-Thiele diagram is routinely used to determine the theoretical number of stages that particular extraction efficiency requires. This has implications for the capital cost of the contacting equipment. The more the number of stages required the higher the capital and working costs.

2.9 Summary

Alumina is the primary feedstock in the smelting process for the production of aluminium. The substitution of imported alumina with locally produced alumina in South Africa has the potential to stimulate the growth of a new alumina production industry which brings with it economic benefits. The minimum alumina content in the large volume of CFA available in South Africa is 30%. This substantial content of alumina has made it important to investigate the possibility of commercial extraction of alumina from CFA.

This chapter has shown that a critical step in the extraction of alumina from CFA is the dissolution of alumina from CFA by a suitable lixiviant. The metals extraction group at the University of the Witwatersrand has developed a two-step sulphuric acid leaching process that has shown potential to dissolve a greater proportion of alumina into solution than traditional dissolution methods (Shemi, 2013). In the recovery of alumina from this novel two-step leaching process route by crystallisation, the difficulty now rises because of the co-crystallisation of the dissolved impurity metals iron and titanium found in the CFA leach solution. These two metals need to be removed by purification before smelter grade alumina can be produced.

Literature has identified SX as one of the appropriate methods to purify CFA leach solutions by the removal of these two dissolved metals. Two amine extractants namely Alamine 336 and Primene JMT have been identified as promising candidates to remove iron and titanium.

In assessing the effectiveness of a particular solvent to remove iron and titanium from CFA leach solution, the influence of experimental factors must be examined. Amongst the factors that affect metal extraction from CFA leach solutions by SX, the following have been chosen for investigation: temperature, extractant concentration, A/O phase ratio and hydrogen ion concentration.

Furthermore, for the purposes of gathering design information for a potential SX system, batch test work must be completed. This work will generate data for the construction of a McCabe-Thiele diagram that can be used to predict the number of mixing and settling stages for a potential industrial SX operation.

3 MATERIALS AND METHODS

This section gives a description of the nature and source of materials, preparation of reagents, experimental equipment, experimental conditions, experimental procedures and analytical methods used in experimental work.

3.1 Materials

3.1.1 Coal Fly Ash Liquor

CFA from Kendall Power Station was used to generate the leach liquor used in the test work. Figure 3.1 shows the process route used to generate the CFA leach liquor (Shemi, 2013).

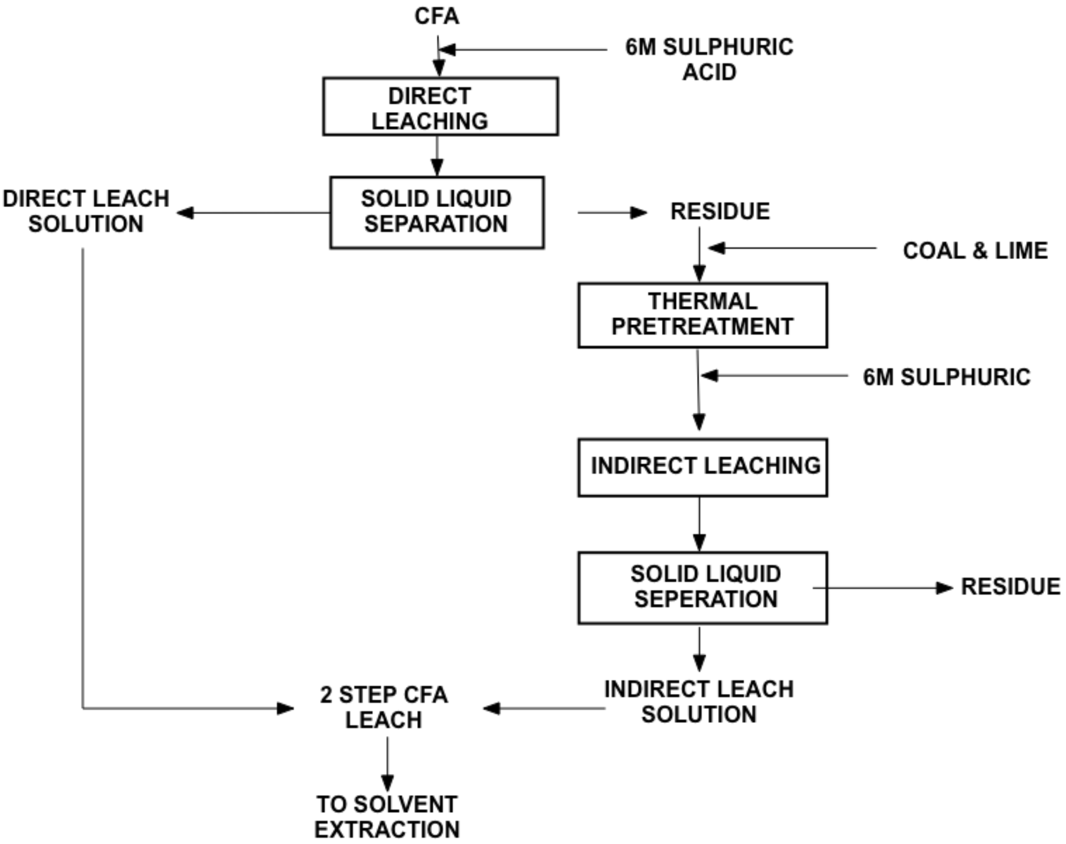


Figure 3.1 Two-step CFA leaching (Shemi, 2013)

The first step in the preparation of the two-step CFA leach solution was the leaching of CFA by 6M sulphuric acid. 1.8L of a 6M solution of sulphuric acid was added into a flask that contained 100g of CFA in a temperature controlled water bath. The temperature of the bath was adjusted to 70ºC and the mixture was shaken at 150 rpm for 6 hours. The product of this direct leaching was a mixture of a residue and direct leach solution. Filter paper was used to separate the residue from the direct leach solution; washing was done to ensure all the aluminium was collected in solution. The residue was then mixed with calcium oxide at 5:4 ratio by mass and then sintered at 1200ºC for 6 hours. The sinter ash produced was then leached with 6M sulphuric acid at 70ºC at a stirring speed of 150 rpm. This secondary leaching process is known as indirect leaching. The indirect leach solution produced was then mixed with the direct leach solution to produce a single solution that would undergo purification experiments. The final analytical composition of the diluted mixed leach liquor is shown in Table 3.1.

Table 3.1 Composition of CFA leach liquor

Source	[Al] (mg/L)	[Fe] (mg/L)	[Ti] (mg/L)	$[H^+]$ (M)
Mixed Leach Solution	9982	2074	464	10.47

The pH of this solution was measured to be -1.02 and this indicates the presence of a high concentration of hydrogen ions. The choice of a 6M sulphuric acid solution in the 2 step leaching process is because of the need to maximise the dissolution of aluminium from the CFA. Shemi (2013), showed that the aluminium dissolved from Kendall power station CFA increased from 15.7% to 16.5% as the acid concentration increased from 2M to 6M. At 8M acid concentration, 14.8% aluminium was dissolved and therefore 6M was chosen as the best acid concentration for alumina dissolution. The fact that the hydrogen ion concentation in the CFA leach solution was measured at a concentration higher than 6M suggests that the second proton during the dissociation of sulphuric acid is being released as shown in equations (2.28) and (2.29). The white calcium sulphate particles observed in the CFA leach solution suggest that sulphate is being produced. The production of sulphate is only possible with the release of the hydrogen ion as shown in equation (2.29). This then results in an increase in the hydrogen ion concnetration in leach solution.

3.1.2 Extractants

Primene JMT was obtained from Rohm and Haas and was used as received. Its composition was 80% alkyl amine. Alamine 336 was obtained from Cognis and was used as received. It was supplied as 100% alkyl amine.

3.1.3 Diluent

Extractants are supplied at high concentrations. In order to reduce the concentration of the extractant to match the concentration of the targeted metal, a diluent is added. In addition, diluents also help to dissolve the metal into the organic phase by solvation. In this work, the diluent used was Shellsol D70 supplied by Shell Chemicals. It comprises mainly of aliphatic hydrocarbon chains with less than 22% aromatics.

3.1.4 Modifier

In SX, conditions exist when the target metal extracted from the aqueous phase fails to dissolve completely in the organic phase. This condition is characterised by the formation of a third phase that is of intermediate density between the aqueous and organic phases. Modifiers, usually alcohols are used to enhance the dissolution of the metal from this intermediate phase into the organic phase. In this work, isodecanol a long chain carbon alcohol was used as a modifier. It was used as received from ChemQuest with a purity of 99%.

3.1.5 Aqueous Reagents

Analytical grade sulphuric acid was supplied at a concentration of 98% by Merck Chemicals South Africa. Merck supplied ammonium hydroxide as 25% ammonia solution. Merck also supplied sodium hydroxide as pure pellets.

3.1.6 Preparation of the organic phase

The extractant concentration was made up on a volume basis (V/V). An extractant concentration of 5% on a volume basis indicates that of the total volume of the organic phase, 5% is the extractant and the remaining 95% is made of the diluent and or modifier.

A 100mL-measuring cylinder was used to measure out the required aliquots of the solvent, diluent, and modifier as shown in Table 3.2.

Table 3.2 Volumes used in preparation of the organic phase

Extractant type	[Extractant] % (v/v)	Extractant volume (mL)	Diluent volume (mL)	Modifier volume (mL)
Primene JMT	15	4.5	25.5	0
	10	3	27	0
	5	1.5	28.5	0
Alamine 336	15	4.5	22.5	3
	10	3	24	3
	5	1.5	25.5	3

The aliquots were then stored in 100mL bottles for mixing with the aqueous phase when required.

In the early stages of the experimental work, it was discovered that Alamine 336 exhibited third phase formation; as a result, isodecanol, a modifier was added to enhance dissolution of the extracted metal into the organic phase. The amount added to make up the organic was 10% by volume (v/v) as indicated in Table 3.2.

3.1.7 Preparation of the aqueous phase

The prepared two-step CFA leach liquor had a hydrogen ion concentration of 10.47M. In this work, SX experimental work with CFA leach solutions that had hydrogen ion concentrations lower than 10.47M was conducted. Therefore, there was a need to reduce the hydrogen ion concentration. Adjustment of hydrogen ion concentration was first attempted by ammonium hydroxide. This was unsuccessful on account of the precipitation of an alum sulphate. The ammonium hydroxide reacted with the sulphuric acid to form ammonium sulphate, which would then react with aluminium sulphate to form an alum sulphate (Matjie et al., 2005):

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 + 40H_2O \rightarrow 2\ Al(NH_4)(SO_4)_2.20H_2O \qquad (3.1)$$

A 15M sodium hydroxide solution was used instead to adjust the hydrogen ion concentration of the two-step CFA leach liquor to make solutions of 0.28M, 0.46M, 1M, 4.67M and 7.57M hydrogen ion concentration.

3.1.8 A/O phase mixing ratios

Table 3.3 shows the phase volumes used in preparing the different A/O phase ratios to be used for the SX experiments.

Table 3.3 Volumes used for different A/O phase ratios

Ratio	Aqueous volume (mL)	Organic volume (mL)
1:2	15	30
1.5:1	45	30
1:1	30	30
2:1	60	30
3:1	90	30

3.2 Methods

3.2.1 Experimental set-up

Each experiment consisted of mixing the selected organic and aqueous phases and mixing them in 250mL or 500mL pyrex volumetric flasks placed in a 40 litre Merck reciprocal shaking bath, model 207 as shown in Figure 3.2.

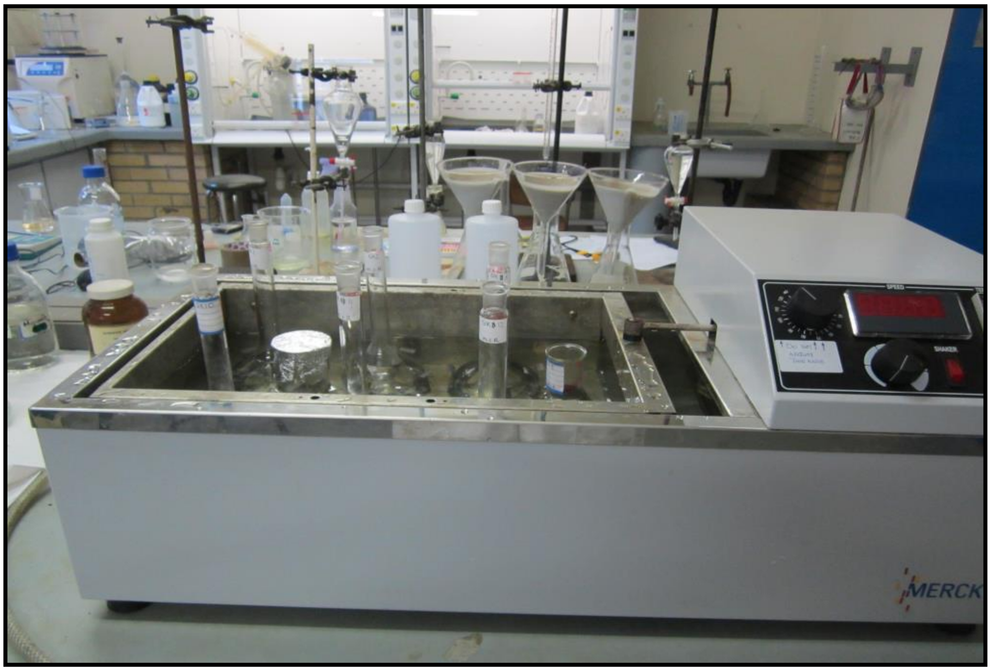


Figure 3.2 Shaking bath

The extraction of iron by primary amines has been shown to have a fast rate of reaction, the extraction has been shown to have reached equilibrium in experimental shaking tests within 10 minutes (Li et al., 2011; Schrötterová and Nekovář, 1999). It was therefore decided to use a shaking time of 15 minutes at a shaking speed of 150rpm.

After shaking for 15 minutes the flasks were removed from the bath and the contents poured into separating funnels. A separation of the organic and aqueous phases was then allowed to occur. After the separation, the aqueous phase was sent for metal content analysis while the organic phase was sent for metal removal by stripping with a base.

3.2.2 Analytical Techniques

The measurement of hydrogen ion concentration was by pH measurement using a Metrohm model 827 laboratory meter that has a range from -8 to +22. Metal assay was done only on the aqueous phase by inductively coupled plasma optical emission spectrometry (IES- OES).

3.2.3 Design of Experiments

In Design of Experiments (DOE), a controllable variable that influences the response is defined as a factor. If a factor level is changed from one value to another value, the average change in response is known as an effect (Mason et al., 2003). DOE is a statistical technique that allows for the simultaneous study of these factors and is more efficient compared to the one factor at a time method that fails to take into consideration interactions amongst the factors. From the factors selected for investigation, the major objective of DOE is to identify the main factors that affect extraction as well as any interaction amongst these factors. Identification of significant factors was achieved by the implementation of a full factorial DOE methodology that gives a quantitative description of the individual and collective effects of each factor on extraction. The combined effect of the factors on extraction was then made using an empirical statistical model. Design Expert® 6 (Design Expert® is a registered trademark of Stat-Ease Incorporated, Minneapolis, USA) statistical software was used to determine the main and interactive effects of the factors selected. The influence of hydrogen ion concentration, extractant concentration, A/O volume phase ratio and temperature on the solvent extraction of iron and titanium from a two-step CFA leach solution was investigated with the use of DOE.

The agitation rate was an important factor that influences how quickly equilibrium between the organic and aqueous phase is attained. The mixing equipment most commonly used for large-scale SX continuous contacting are mixer-settler units that make use of impellers for agitation (Lloyd, 2004). High impeller speeds allow for rapid mass transfer but have the disadvantage of causing increased entrainment of the organic phase into the aqueous phase (Sole, 2008). In this work a shaking bath was used for mixing, the effects of impeller speed and impellor design cannot be investigated with this shaking bath. Therefore agitation as a factor was not investigated and one shaking speed and shaking time was selected as described in section

Factor levels

Implementation of DOE methodology requires the manipulation of factors to establish their influence on the response. The studied factor levels were coded using the following formula (Box et al., 1978):

$$\text{Coded value} = \frac{\text{Actual Value} - \text{Mean}}{0.5 \times (\text{Highest level} - \text{lowest level})} \qquad (3.2)$$

The coding of the factors is given in Table 3.5.

Table 3.5 Controlled factor levels and thier coded values used in DOE

Factor	Code	-1	0 (Centre point)	+1
Temperature	A	25°C	47°C	70°C
[Extractant]	B	5%	10%	15%
$[H^+]$	C	4.67M	7.57M	10.47M
A:O ratio	D	1:1	2:1	3:1

The maximum temperature selected for this work was 70°C. This temperature was chosen because it is safer to work below the lowest flash point of the organic reagents in use, for this work, the diluent shellsol D70 has the lowest flashpoint of 80°C, working 10°C below this temperature was considered adequate for the prevention of fire.

Fresh two-step coal fly ash leach solution had a hydrogen ion concentration of 10.47M; this is therefore the maximum hydrogen ion concentration used in this design. The low factor level value of hydrogen ion concentration of 4.67M was chosen because this concentration is still considered as high, in addition there are no metal hydroxides that will have precipitated at 4.67M hydrogen ion concentration in this solution

Full Factorial Design

A two level full factorial design was implemented experimentally. The chosen design does not use replicates but centre points for error estimation. The experiments were performed in random order (order generated by Design Expert® 6) as indicated in the first column of Table 3.6 to even out any experimental error that can be caused by external noise factors.

Table 3.6 Two level factorial experimental design with centre points

Standard order	Experiment run order	A	B	C	D
14	1	+1	-1	+1	+1
13	2	-1	-1	+1	+1
12	3	+1	+1	-1	+1
3	4	-1	+1	-1	-1
18	5	0	0	0	0
17	6	0	0	0	0
8	7	+1	+1	+1	-1
6	8	+1	-1	+1	-1
20	9	0	0	0	0
5	10	-1	-1	+1	-1
11	11	-1	+1	-1	+1
15	12	-1	+1	+1	-1
1	13	-1	-1	-1	-1
9	14	-1	-1	-1	+1
10	15	+1	-1	-1	+1
19	16	0	0	0	0
7	17	-1	+1	+1	-1
2	18	+1	-1	-1	-1
4	19	+1	+1	-1	-1
16	20	+1	+1	+1	+1

A: Temperature; B: [Extractant]; C: [H^+]; D: A/O ratio.

3.2.4 Preliminary Investigation

A preliminary investigation was conducted as a screening test to establish whether both Alamine 336 and Primene JMT gave significant extraction of the targeted metals. The choice of experimental conditions was based on previous work done on iron extraction using Alamine 336 and Primene JMT. Mahi and Bailey (1985) showed that iron could be effectively extracted by Alamine 336 at 15% v/v extractant concentration, 1:1 A/O phase ratio at acid concentrations less than 3M in the aqueous phase. Li et al. (2011) showed that primary amine could extract more than 50% of iron at 8.3% v/v extractant concentration, A/O ratio of 2:1 only at acid concentrations less than 0.25M. The important experimental factor to control was the acid concentration since CFA leach liquor was produced at an acid concentration of 10.47M (Table 3.1).

Table 3.4 Preliminary investigation factor levels

Experiment	Extractant	$[H^+]$ (M)	[Extractant]	A:O	Temp (ºC)
1	Alamine 336	1	15%	1:1	70
2	Alamine 336	4.67	15%	1:1	70
3	Primene JMT	4.67	15%	1:1	70
4	Primene JMT	1	15%	1:1	70

Table 3.4 lists the experimental conditions of the four preliminary experiments that were selected. The motivation for selecting an acid concentration greater than 1M is to avoid the possibility of precipitating hydroxides. In addition, the maximum acid concentration was 4.67M. The basis of this choice was that if either Alamine 336 or Primene JMT showed a significant improvement in metal extraction from 1M to 4.67M, then further investigation of that extractant would be warranted. This is because manipulation of other experimental factors could result in acceptable metal extraction as the acid concentration increased to the highly acidic CFA leach solution produced by the two step CFA leach method.

4 RESULTS AND DISCUSSION

The ability of an extractant to selectively remove targeted impurity metals is an important consideration in the design of a SX system. The aim of the preliminary investigation was to establish which is the superior extractant in terms of extraction efficiency between Primene JMT and Alamine 336. Thereafter, a full factorial design was implemented with the extractant of choice to determine the influence of the following factors: hydrogen ion concentration, extractant concentration, temperature and A/O volume phase ratio. This design, firstly acts as a screening test in identifying which of the factors are significant, secondly it then gives a quantitative description of the effect of each of the significant factors, individually and collectively on the extraction of selected impurity metals. The quantitative description is a statistical effects model that is developed from the results of the full factorial experiments given in this section.

Extraction improvement tests were then done to establish if better extraction of targeted impurity metals could be obtained by manipulating those factors that were determined to be significant.

A McCabe-Thiele diagram was constructed using those conditions that were obtained from the extraction improvement tests. The diagram was used to calculate the number of theoretical stages that a potential SX extraction system would need to purify a two-step coal fly ash leach solution.

4.1 Preliminary Investigation

An ideal extractant for the purification of the two-step CFA leach solution is one that is selective for iron and titanium over aluminium. The results of the extraction of iron, titanium and aluminium with Alamine 336 and Primene JMT under different experimental conditions are given in Table 4.1 below. All experiments were done at 70°C with a 1:1 A/O phase ratio and 15% extractant concentration.

Table 4.1 Preliminary investigation results

			Extraction %		
Experiment	Extractant	$[H^+]$ (M)	Al	Fe	Ti
1	Alamine 336	4.67	2.38	4.12	21
2	Alamine 336	1	3.3	2.15	0
3	Primene JMT	4.67	3.8	36.85	99
4	Primene JMT	1	2.36	82	99

With the CFA leach solution at a hydrogen ion concentration of 4.67M, Alamine 336 was able to extract 21% of the titanium and 4.12% of the iron. There was 2.38% co-extraction of aluminium. Adjustment of the hydrogen ion concentration to 1M resulted in no titanium being extracted and 2.15% extraction of iron with 3.3% aluminium co-extraction.

With the CFA leach solution at a hydrogen ion concentration of 4.67M, Primene JMT was able to extract 99% of the titanium and 36.9% of the iron. There was 3.8% co-extraction of aluminium. Adjustment of the hydrogen ion concentration to 1M resulted in a 99% extraction of titanium, 82% extraction of iron and 2.4% co-extraction of aluminium. A comparison of these two extractants indicated that at both 4.67M and 1M hydrogen ion concentrations, Primene JMT was able to extract significantly more iron and titanium than Alamine 336. Furthermore, Alamine 336 exhibited third phase formation and required isodecanol, a modifier to dissolve the third phase that formed.

Based on these observations, it was concluded that Primene JMT was the superior extractant in the hydrogen ion concentration range 4.68M to 1M. On this basis further investigation of Alamine 336 as a purification extractant for two-step CFA leach solution was discontinued.

4.2 Identification of main factors affecting solvent extraction

Statistical analysis of the experimental results was done using Design Expert®. For a factorial design, Design Expert® 6 allows for the selection of significant factors from half normal probability plots. On a normal probability plot, those effects that lie on or near the best-fit line are insignificant but those that lie far from the line cannot be explained by noise and are considered significant. Design Expert® 6 then develops a model using the selected significant factors chosen from the normal probability plot.

For the entertained linear model, Design Expert® 6 then checks for significance of the model, significance of curvature in the model and significance of goodness of fit in the model using analysis of variance (ANOVA). Statistical significance is determined by using of the F-test, the F-test checks if the probability (Prob > F) falls within the 95% confidence interval. A value of Prob > F that is less than 0.05 indicates significance.

In the instance where curvature is detected, then a central composite design can be implemented with the experimental data to fit a quadratic model rather than a linear model that will better model the effect of the factors on the response. Design Expert® then uses ANOVA to check for significance of each of the linear and quadratic model terms, those terms that are insignificant are removed so as to improve the model.

Any entertained model must be checked for adequacy for it to be valid. In this work, probability residual plots were used to check for adequacy. A residual is the difference between the actual extraction percentage and the predicted extraction percentage of a particular run in the experiment. The residual plot will validate the model only if the plot indicates a normal distribution; this is observed as a best-fit line passing through the residues (Montgomery D.C, 2001). The coefficient of determination (R^2) will be used to assess how close these residues are to the best-fit line. A value closer to 1 shows a good fit of the residues on the best-fit line.

4.2.1 Identification of main factors affecting the extraction of iron

Table 4.2 shows the experimental results for the extraction of iron and titanium by Primene JMT. For sections 4.3.1 and 4.3.2, reference can be made to Appendix A that lists the raw experimental data for the extraction tests.

Table 4.2 Full Factorial design results for the extraction of iron

Standard run order	Factor				Fe extraction %	Ti extraction %
	A	B	C	D		
1	-1	-1	-1	-1	18.18	99.82
2	1	-1	-1	-1	12.62	99.85
3	-1	1	-1	-1	33.80	99.90
4	1	1	-1	-1	33.80	99.91
5	-1	-1	1	-1	5.31	99.87
6	1	-1	1	-1	12.56	99.73
7	-1	1	1	-1	24.64	99.40
8	1	1	1	-1	24.15	98.89
9	-1	-1	-1	1	13.64	38.82
10	1	-1	-1	1	10.61	40.29
11	-1	1	-1	1	14.14	99.79
12	1	1	-1	1	9.66	99.78
13	-1	-1	1	1	2.89	50.40
14	1	-1	1	1	3.86	46.96
15	-1	1	1	1	10.15	98.91
16	1	1	1	1	11.59	98.91
17	0	0	0	0	14.00	99.66
18	0	0	0	0	14.49	99.86
19	0	0	0	0	11.11	99.49
20	0	0	0	0	8.70	99.60

A: Temperature; B: [Extractant]; C: [H^+]; D: A/O ratio.

Design Expert® 6 used the data in Table 4.2 to plot Figure 4.1, a half normal probability plot to determine the significant factors.

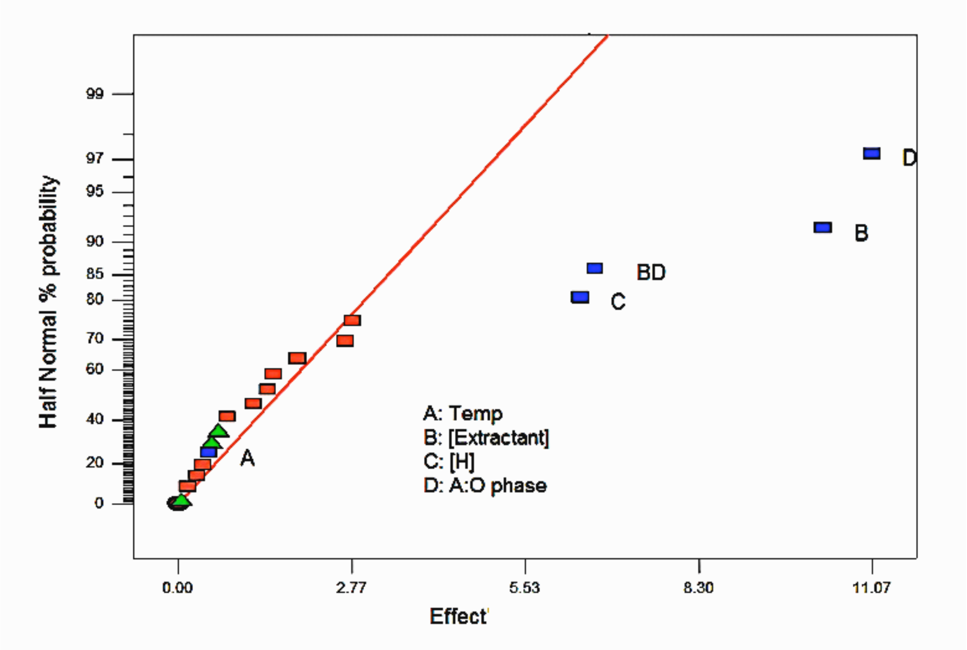


Figure 4.1 Half Normal probability plot of the average effects on iron extraction.

The extractant concentration (B), the A/O to phase ratio (D), the hydrogen ion concentration (C) and the interaction between extractant concentration (B) and A/O phase ratio (D) are distant from the best-fit line and are therefore significant factors.

Temperature (A) lies near the best-fit line and is therefore not a significant factor for the extraction of iron by Primene JMT.

A statistical effects model developed by Design Expert® 6 from these chosen significant factors is:

$E_{Fe} = 15.10 + 5.14B - 3.21C - 5.53D - 3.32BD \qquad (4.1)$

Where E_{Fe} is the percentage of iron extracted.

The negative sign on the hydrogen ion concentration factor (C) indicates that to maximise iron extraction, this factor must be at a low level. This finding agrees closely with work done by Alguacil & Amer (1986) and Li et al. (2011). The negative interaction between extractant concentration (B) and the A/O phase ratio (D) means that the effect of (B) is greater at a low level of D.

The ANOVA table for the model equation 4.1 is shown in Table 4.3 below.

Table 4.3 ANOVA for iron extraction

Source	Sum of Squares	DF	Mean Square	F -Value	Prob > F
Model	1253.89	4	313.47	35.61	<0.0001
C	164.48	1	164.48	18.68	0.0007
D	489.74	1	489.74	55.63	< 0.0001
BD	176.76	1	176.76	20.08	0.0005
Curvature	29.28	1	29.28	3.33	0.0896
Residual	123.24	14	8.80		
Lack of Fit	101.38	11	9.22	1.26	0.4759
Pure Error	21.86	3	7.29		
Cor Total	1406.42	19			

The Prob > F for the model and each of the individual model terms is less than 0.05. This indicates that the model and all the individual terms are significant

The Prob > F for curvature and lack of fit are both greater than 0.05, this indicates that curvature and lack of fit are insignificant.

To check the adequacy of this model, Design Expert® 6 plots the normal probability against the studentised residuals as shown in Figure 4.2. For the model to be adequate, the residues should fit closely on the best-fit line. The residues lie close to the best-fit line with a coefficient of determination (R^2) value of 0.977 indicating that the residues are distributed normally and the model is adequate.

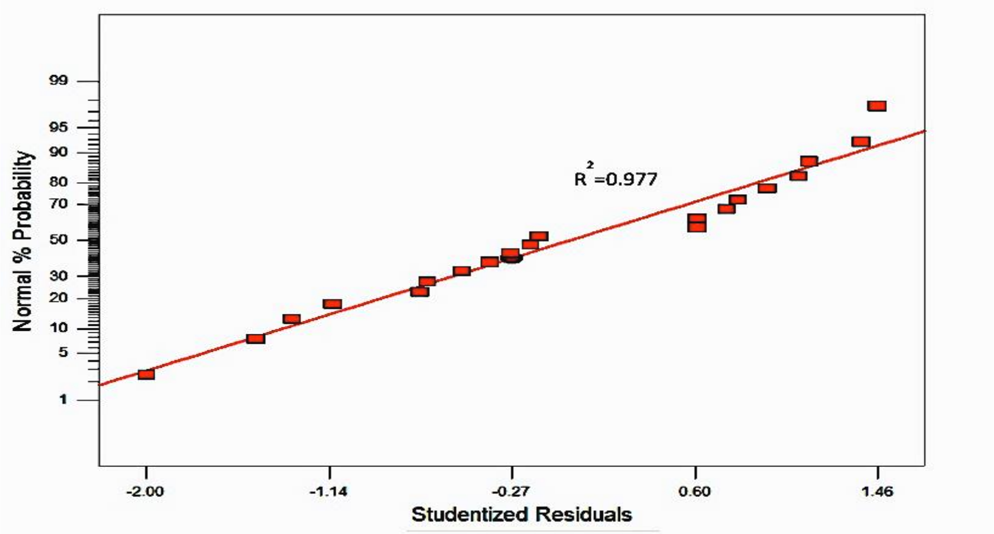


Figure 4.2 Studentised residuals plot for iron extraction

4.2.2 Identification of main factors affecting the extraction of titanium

The full factorial results of the extraction of titanium by Primene JMT are presented in Table 4.2. Design Expert® 6 used the experimental results in Table 4.2 to plot Figure 4.3, a normal probability plot that was used to determine the significant factors for titanium extraction.

The factors temperature (A) and hydrogen ion concentration (C) lie in the vicinity of the best fit line and are therefore, considered to be insignificant factors in the extraction of titanium by Primene JMT between 25°C and 70°C.

The factors: extractant concentration (B), A/O phase ratio (D), and the interaction between extractant concentration and A/O phase ratio (BD) are the significant factors as they are distant from the best-fit straight line as shown in Figure 4.3.

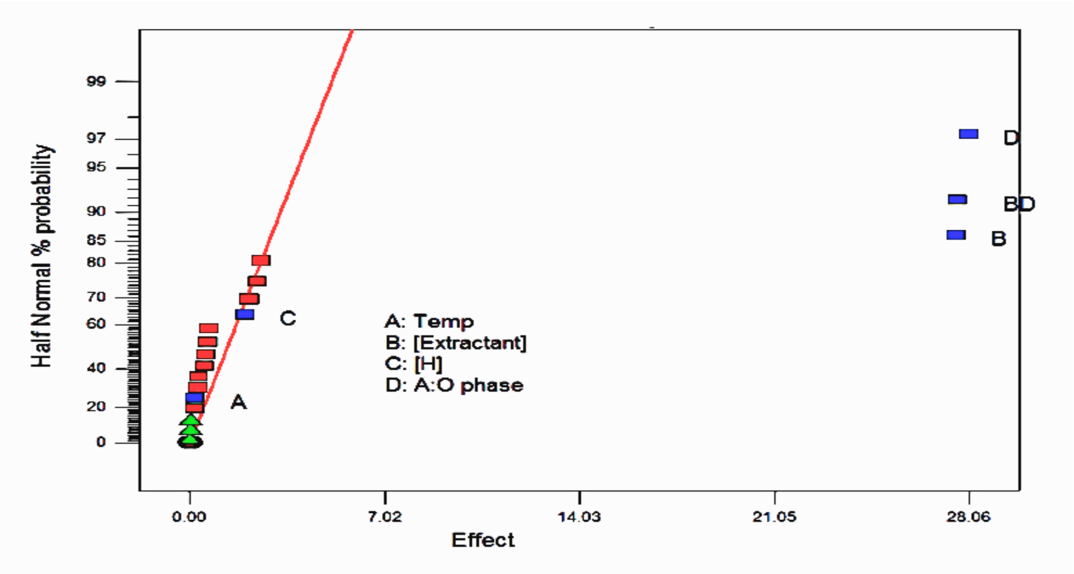


Figure 4.3 Normal probability plot for the effects on titanium extraction

Equation (4.2) is a statistical effects model generated by Design Expert® 6 using the chosen significant factors.

$$E_{Ti} = 85.93 + 13.86B - 13.98D + 13.78BD \qquad (4.2)$$

Where E_{Ti} is the percentage titanium extracted.

The positive interaction between extractant concentration (B) and A/O phase ratio (D) indicates that the effect of B on titanium extraction is greater at a high level of A/O phase ratio. This is in contrast with iron extraction where the interaction is negative. The explanation is that titanium extraction is 99% at a low level of the A/O phase ratio regardless of the extractant concentration, while at a high level of A/O titanium extraction improves from 44% to 99%.

The ANOVA table for the model equation 4.2 is shown in Table 4.4 below. The Prob > F for the model and for each of the terms B, D and BD are less than 0.05 therefore the model and each of the individual terms are significant.

Table 4.4 ANOVA for titanium extraction

Source	Sum of Squares	DF	Mean Square	F-Value	Prob > F
Model	9251.01	3	3083.67	506.63	< 0.0001
B	3045.66	1	3045.66	500.38	< 0.0001
D	3150.30	1	3150.30	517.57	<0.0001
BD	3055.05	1	3055.05	501.92	<0.0001
Curvature	617.22	1	617.22	101.40	< 0.0001
Residual	91.30	15	6.09		
Pure Error	0.072	3	0.024		
Cor Total	9959.52	19			

The Prob > F for curvature is also less than 0.05; this indicates that curvature is significant for this model. This implies that the equation that models the extraction of titanium has quadratic terms and equation 4.2 cannot model this curvature. This is corroborated by Figure 4.4, the normal probability plot of studentised residuals by Design Expert® 6, which was used to examine the adequacy of model equation 4.2.

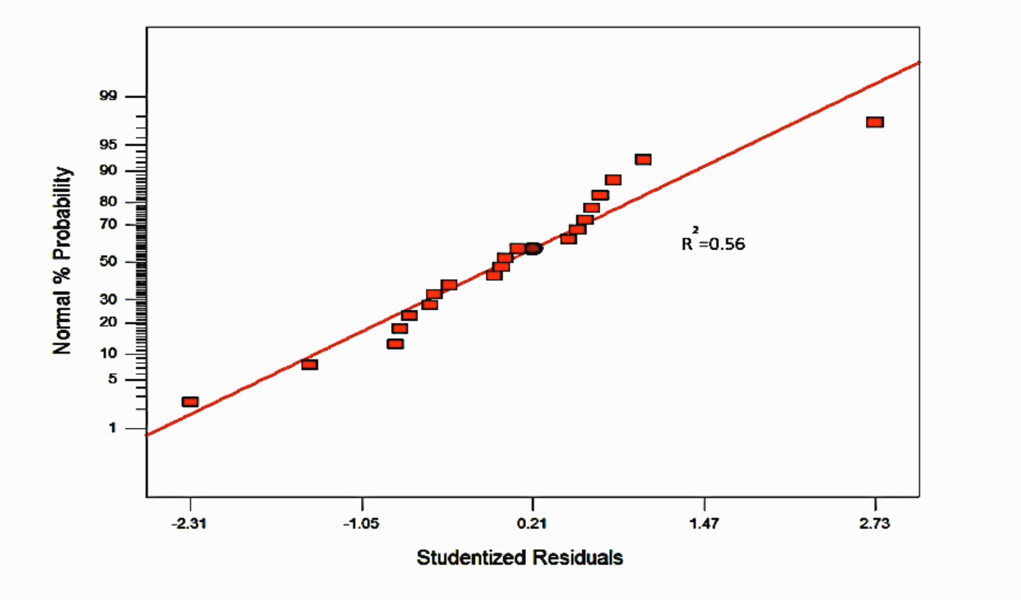


Figure 4.4 Normal probability plot of residuals for titanium extraction

An inspection of the residual plot indicates that the residues are not normally distributed around the best-fit line as reflected by the coefficient of determination R^2

calculated to be 0.56. Therefore, the developed model is not adequate in predicting titanium extraction.

The titanium experimental results in Table 4.2 were used in a central composite design (CCD) to explore the detected curvature. This design is a response surface method (RSM) that fits a second order equation to model the curvature. In the implemented CCD design, ANOVA is used to check the significance of the regression model and each of the model terms. Table 4.5 shows the ANOVA for the fitted model:

Table 4.5 ANOVA for response surface quadratic Model (Aliased)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	8909.52	12	742.46	5.05	0.0201
A	0.20	1	0.20	1.360E-003	0.9716
B	2016.12	1	2016.12	13.72	0.0076
C	13.89	1	13.89	0.095	0.7674
D	3122.30	1	3122.30	21.26	0.0025
A^2	522.99	1	522.99	3.56	0.1011
B^2	515.00	1	515.00	3.51	0.1033
C^2	0.000	0			
D^2	0.000	0			
AB	0.15	1	0.15	1.049E-003	0.9751
AC	1.95	1	1.95	0.013	0.9114
AD	0.12	1	0.12	7.986E-004	0.9782
BC	28.76	1	28.76	0.20	0.6715
BD	3082.75	1	3082.75	20.99	0.0025
CD	20.45	1	20.45	0.14	0.7201
Residual	1028.26	7	146.89		
Cor Total	9937.78	19			

From the ANOVA table it is observed that the regression model has Prob > F of 0.0201 which is less than 0.05 and is therefore significant. The linear, quadratic and interactive terms A,C; A^2,B^2 and AB,AC,AD,BC,CD are insignificant because they have Prob > F greater than 0.05. C^2 and D^2 are flagged by Design Expert® 6 to be aliased, that is, their effect cannot be unambigiously attributed to their influence alone (Mason et al. 2003).

E_{Ti} = 71.75 - 0.091A+9.17B + 0.93C - 13.97D + 7.00A^2 + 6.95B^2 + 0.098AB - 0.35AC - 0.086AD - 1.34BC + 13.88BD + 1.13CD (4.3)

To obtain an improved model, model reduction excludes those terms that have been shown to be insiginifcant including C^2 which was eliminated by the hierachy rule (If C is insignificant then so is C^2). The refitted model after model reduction is shown in equation 4.4:

E_{Ti} = 99.76 + 9.17B - 13.97D - 0.054 B^2 - 14.00 D^2 + 13.88BD (4.4)

Table 4.6 is the ANOVA table used to examine the refitted quadratic model.

Table 4.6 ANOVA for reduced response surface quadratic model

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	8843.99	5	1768.80	22.64	< 0.0001
B	2016.12	1	2016.12	25.81	0.0002
D	3122.30	1	3122.30	39.96	< 0.0001
B^2	0.046	1	0.046	5.917E-004	0.9809
D^2	522.99	1	522.99	6.69	0.0215
BD	3082.75	1	3082.75	39.46	< 0.0001
Residual	1093.79	14	78.13		
Cor Total	9937.78	19			

The terms in the refitted model were examined for significance using the F-test. The term B^2 has Prob > F that is greater than 0.05, B^2 is therefore insgnificant and was removed to improve the model.

After model reduction, refitting by Design Expert® 6 developed the model equation 4.5.

$$E_{Ti} = 99.65 + 9.17B - 13.97D - 13.95D^2 + 13.88BD \qquad (4.5)$$

Table 4.7 is the ANOVA table used to examine the refitted model equation 4.5.

Table 4.7 Anova for refitted model

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	8843.94	4	2210.99	30.32	< 0.0001
B	2016.12	1	2016.12	27.65	< 0.0001
D	3122.30	1	3122.30	42.82	< 0.0001
D^2	622.78	1	622.78	8.54	0.0105
BD	3082.75	1	3082.75	42.27	< 0.0001
Residual	1093.83	15	72.92		
Cor Total	9937.78	19			

An examination of Table 4.7 shows that the regression model and each of the model terms had Prob > F less than 0.05, therefore the regression model and each of the model terms are significant.

The adequacy of this model was checked by Design Expert® 6 by way of a normal probability plot of studentised residuals as shown in Figure 4.5.

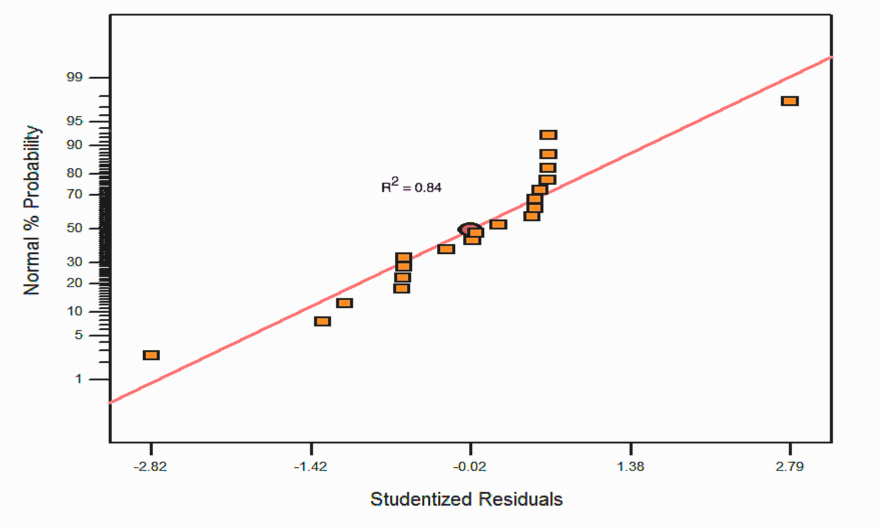


Figure 4.5 Normal probability plot of studentised residuals of refitted model

The goodness of fit of the studentised residuals on the best fit line was measured by the coefficent of determination R^2 which was calculated to be 0.84. The studentised residuals have a reasonable normal distribution on the best-fit line and hence the model was deemed to adequately represent the titanium extraction which is as shown by the response surface in Figure 4.6.

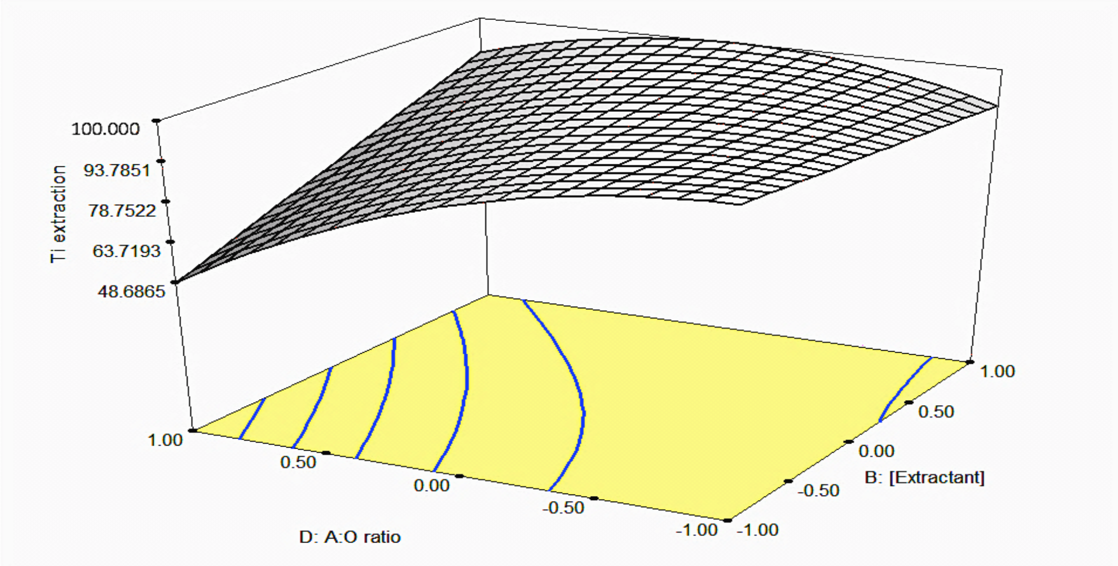


Figure 4.6 Response surface for titanium extraction

4.3 Influence of factors on recovery of Iron

The main influence of a factor can only be interpreted individually if it does not interact with other factors. If there is evidence that it interacts with other factors then the interacting factors should be considered jointly (Box et al., 1978).

4.3.1 Effect of Temperature

Table 4.2 shows that an increase in temperature from 25°C to 70°C did not result in a significant change in iron recovery. However, all those experiments from the factorial design that were done at 70°C exhibited faster phase disengagement time. It took only five minutes for the aqueous phase to become clear compared to a minimum of 30 minutes at 25°C. This is attributed to faster coalescence owing to the reduced viscosity of the organic phase. Rapid phase disengagement allows for higher throughput on an industrial scale SX system but has the disadvantage of solvent loss by volatilisation; this can result in environmental pollution and an increase in reagent makeup costs. The choice of operating temperature is therefore based on an economic assessment.

4.3.2 Effect of hydrogen ion concentration

Table 4.2 shows that a decrease in the hydrogen ion concentration from 10.47M to 4.67M resulted in an increase of 6.4% in the average iron extracted by Primene JMT. Appendix D shows the DOE calculation to obtain the magnitude of this effect. The dissociation of sulphuric acid produces hydrogen ions and bisulphate ions (Reaction 2.28). A decrease in sulphuric acid concentration results in a decrease in both hydrogen ions and bisulphate ions. At high bisulphate concentrations, it is thought that there is competition between extractable iron(III) and bisulphate in the reaction with the extractant (Alguacil et al., 1986):

$$(RNH_3)_2SO_{4\,(org)} + Fe(OH)SO_{4\,(aq)} \rightleftharpoons (RNH_3)_2SO_4^{\cdot}\,Fe\,(OH)SO_{4\,(org)} \quad (4.2)$$

$$(RNH_3)_2SO_{4\,(org)} + 2\,HSO_{4\,(aq)}^{-} \rightleftharpoons 2RNH_3.HSO_{\,(org)} + SO_{4\,(aq)}^{2-} \quad (4.3)$$

This competition from the bisulphate ion results in the reduced available effective amount of extractant leading to lower extraction of iron(III).

Equations 2.28 and 2.29 indicate that in a sulphuric acid environment, the sulphate concentration is small due to the low dissociation of bisulphate as indicated by the small K_3 value in equation 2.29. Figure 2.4 in section 2.6.2 shows that for iron(III)-sulphate-pH system in aqueous solution; as the hydrogen ion concentration increases (corresponding increase in bisulphate: equation 2.28) the iron(III) gets converted to the $FeHSO_4^{2+}$ complex:

$Fe^{3+} + HSO^-_4 \rightleftharpoons FeHSO_4^{2+}$ (4.4)

IR spectroscopy has shown that only the $Fe(OH)SO_4$ complex is extracted by amines (Li et al., 2011). Therefore, high hydrogen concentrations results in less iron(III) existing in the extractable $Fe(OH)SO_4$ form with more of $FeHSO_4^{2+}$ that is not extracted by Primene JMT prevailing in the solution.

4.3.3 Effect of A/O phase ratio and extractant concentration

An interaction between the A/O phase ratio and concentration of Primene JMT exists, as illustrated in Figure 4.7.

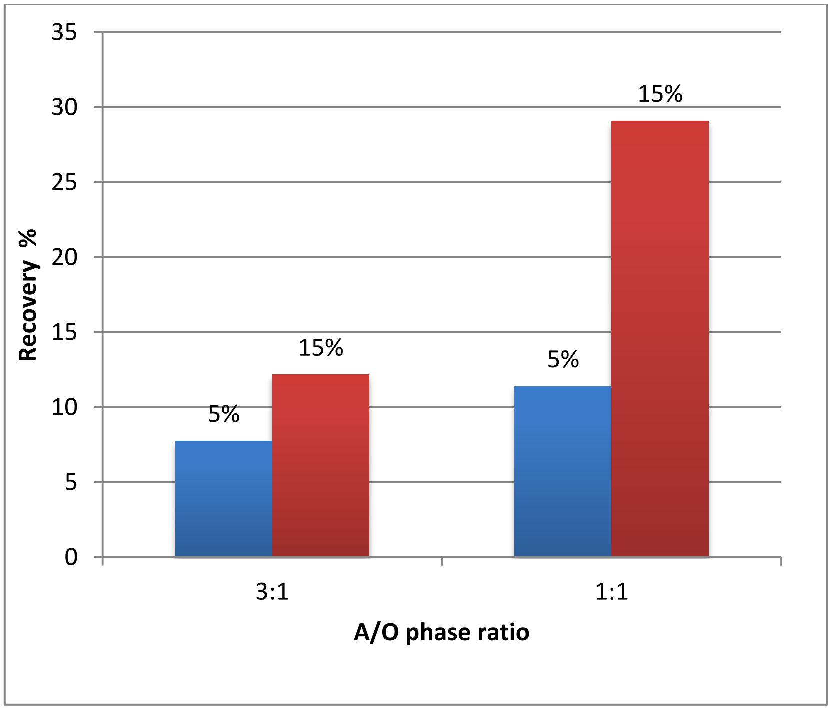


Figure 4.7 Interaction between concentration of Primene and A/O phase ratio for iron

An increase in concentration of Primene JMT from 5% (v/v) to 15%(v/v) at a high level (3:1) of the A/O phase ratio, results in an increase in iron extraction of 4.4%. The increase in extraction at a lower level (1:1) of the A/O phase ratio when the concentration of Primene JMT increases from 5% (v/v) to 15% (v/v) is 17.7%.

Generally, the higher extraction of iron at the increased extractant concentration is attributed to the increased availability of extractant to protonation since the protonated amine is responsible for iron extraction as illustrated by equation 2.18. The equation establishes that the distribution ratio increases with increase in the solvent concentration:

$$\log D = \log K_1 + \log[R_3N] - 2pH \qquad (2.18)$$

The amount of iron extracted is more sensitive to an increase in solvent concentration at a lower A/O phase ratio of 1:1 compared to 3:1. The greater extraction at the lower A/O phase ratio is attributed to the presence of more extractant per unit mass of iron in solution.

4.4 Influence of factors on the recovery of titanium

4.4.1 Effect of Temperature

Table 4.2 shows that an increase in temperature from 25°C to 70°C did not result in a significant change in titanium extraction. There was only a decrease in phase disengagement time at 70°C as reported for iron extraction.

4.4.2 Effect of hydrogen ion concentration

The extraction of titanium by Primene JMT was independent of hydrogen ion concentration. The high extraction of titanium at both levels of hydrogen ion concentration is an indication that the titanium bisulphate complex $Ti(OH)_3HSO_4$ is strongly extracted by Primene JMT. This is illustrated in Figure 2.5 which shows that $Ti(OH)_3HSO_4$ is the dominant species in both alkaline and acidic conditions.

4.4.3 Effect of A/O organic phase ratio and extractant concentration

Figure 4.8 illustrates the interaction between the A/O phase ratio with concentration of Primene JMT. At an A/O phase ratio of 3:1(high level), increasing the extractant concentration from 5% to 15 % has the effect of increasing the titanium extraction by 54.4%. However, at a phase ratio of 1:1 the titanium extraction will be 99% at both 5% (v/v) and 15% (v/v) Primene JMT concentration.

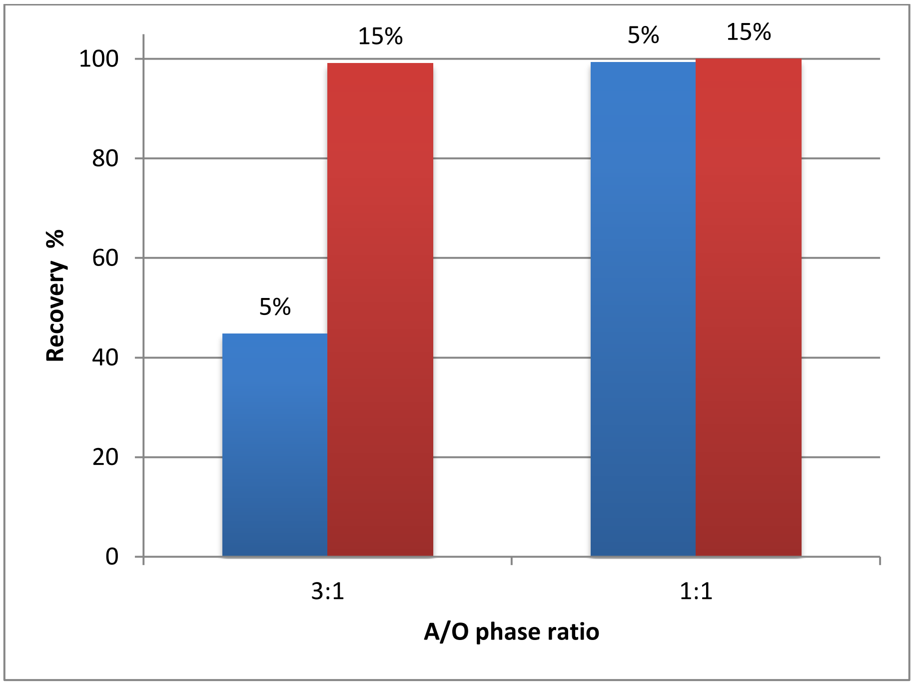


Figure 4.8 Interaction of A/O phase ratio with extractant concentration.

The A/O phase ratio is the more sensitive of the interacting factors because a high titanium extraction could be obtained even at a low extractant concentration.

4.5 Extraction Improvement

One of the aims of this study was to establish whether it was possible to extract iron and titanium at high acid concentrations given that the two step CFA leach liquor is generated at a hydrogen ion concentration of 10.47M. The DOE results show that only 33.8% iron extraction could be achieved at 4.68M hydrogen ion concentration while 99% titanium extraction could be achieved.

In order to improve the extraction of iron it was therefore necessary to adjust the experimental conditions. The effects model for the extraction of iron equation 4.1 predicts that a decrease in hydrogen ion concentration below 4.67M and an increase in extractant concentration could possibly lead to higher iron extraction. The results of the preliminary experiments corroborate this suggestion.

Results of experiments performed at decreased hydrogen ion concentration and increased Primene JMT concentration are shown in Table 4.8.

Table 4.8 Extraction improvement results using Primene JMT

			Extraction %		
Experiment	$[H^+]$	[Primene]	Al	Fe	Ti
1	1M	15%	2.3	82.0	99.3
2	1M	20%	0.6	82.0	99.1
3	0.46M	15%	2.5	86.0	99.4
4	0.28M	15%	0	88.0	98.6

Temperature (70°C) and A/O phase ratio (1:1) were kept constant during all four experiments.

The extraction improvement tests revealed that adjusting the hydrogen ion concentration from 4.67M to 1M resulted in an improvement of the iron extraction from 33% to 82%. An increase in extractant concentration at 1M hydrogen ion concentration from 15%(v/v) to 20% (v/v) did not improve iron extraction. At 15% extractant concentration, decreasing the hydrogen ion concentration further to 0.28M resulted in iron extraction improving to 88%.

The reduction of the hydrogen ion concentration from 10.47M to 0.28M required the use of a large amount of NaOH. This is an additional cost that renders the purification of the CFA leach solution by SX less economically viable. An alternative to reducing the hydrogen ion concentration is the use of Alamine 336 after the addition of chloride ions to the CFA leach solution. This process route is promising in view of Mahi and Bailey (1985) who showed that in chloride media, the SX of iron(III) increased by 71.4% as hydrogen ion concentration increased from 0.58M to 3M.

4.5.1 Confirmatory experimental results

Inorder to verify the accuracy of the results obtained in the extraction improvement experiments, a confirmatory experimental run was carried out with two replicates for the conditions in experiment 1 in Table 4.8. These conditions were selected for verification on the basis that they offer the least operating costs for a potential SX plant. A lower amount of neutralising reagent is required at 1M hydrogen ion concentration and less extractant volume is required for 15% extractant concentration compared to 20%. Appendix B lists the raw results for the confirmatory experiment. Table 4.9 below shows the comparison between the initial extraction improvement experiment and the confirmatory experiment.

Table 4.9 Comparison between extraction improvement and confirmatory tests

			Extraction %		
Experiment	$[H^+]$	[Primene]	Al	Fe	Ti
Improvement	1M	15%	2.3	82.0	99.3
Confirmation	1M	15%	2.6	81.2	99.9

The percentage difference in metal extraction between the improvement and confirmatory experiments for Al, Fe and Ti was found to be 11%, 0.98% and 0.6% respectively. These differences are reasonable and therefore the extraction improvement results at 1M hydrogen ion concentration, a temperature of 70°C , an A/O phase ratio of 1:1 and Primene JMT extractant concentration of 15% are credible.

4.6 Construction of McCabe-Thiele diagrams

Shaking tests with solutions of different A/O phase ratios were used to generate data for plotting extraction isotherms. After mixing and settling for each shaking test, metal assay values from the aqueous phase were obtained for each of the phase ratios, the metal content in the organic phase was then obtained by difference. These assay values were then used to plot metal concentration in the organic phase against metal concentration in the aqueous phase. All the shaking tests were done at 25°C, 1M hydrogen ion concentration and 15% extractant concentration.

Appendix C shows the experimental results and calculations used in constructing the McCabe-Thiele diagrams for iron and titanium extraction by Primene JMT. Figure 4.9 is a McCabe-Thiele diagram showing the extraction of iron.

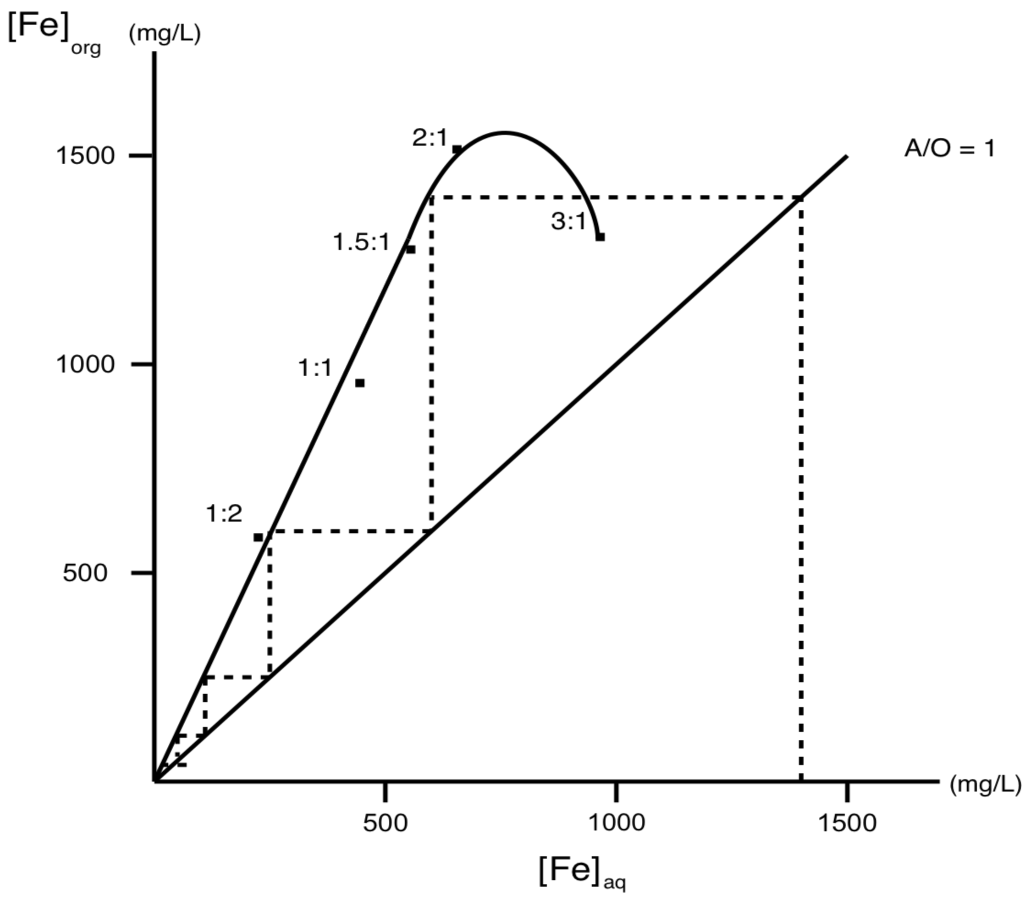


Figure 4.9 McCabe-Thiele diagram for iron extraction

Figure 4.9 shows that the iron(III) assay in the aqueous phase can be reduced from 1400 mg/L to values less than 50mg/L in 4 stages at an A/O ratio of 1.

Figure 4.10 is a McCabe-Thiele diagram for the extraction of titanium from CFA leach solution with hydrogen ion concentration of 1M using an operating A/O phase ratio of 1, the titanium (IV) concentration in CFA leach solution can be reduced to values less than 0.5 mg/L in one stage of solvent extraction.

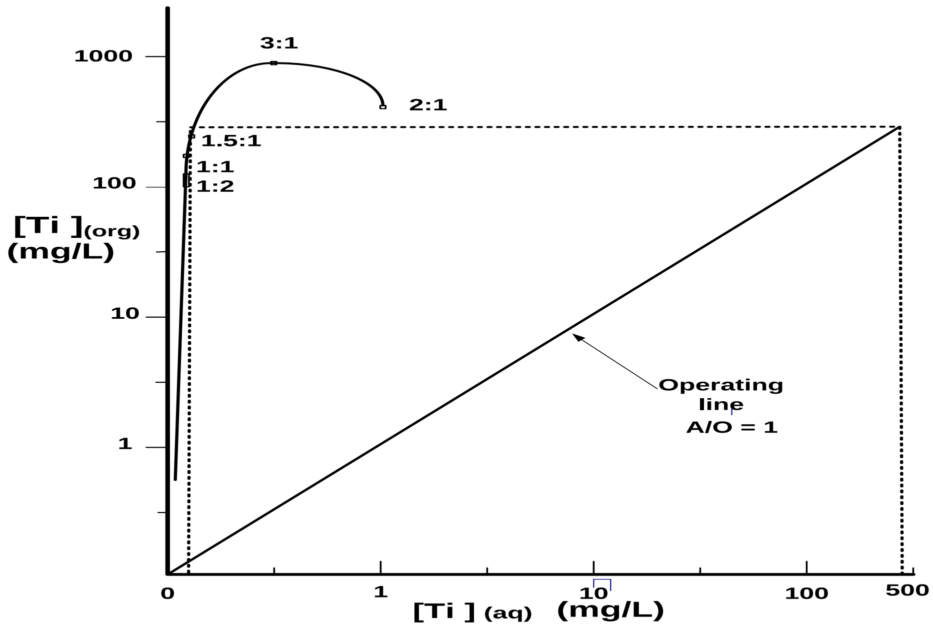


Figure 4.10 McCabe-Thiele diagram for titanium extraction

From these two McCabe-Thiele diagrams, it can therefore, be concluded that the theoretical number of stages that are required to purify the two-step CFA leach solutions is four. The conditions that allow for four theoretical stages are 1M hydrogen ion concentration, 25°C, 15% Primene JMT concentration and an operating A/O volume phase ratio of 1.

4.7 Solvent recycle

The ability of the extractant to repeatedly remove iron and titanium from fresh CFA leach liquor was investigated by the process route shown in Figure 4.11.

The first extraction involved contacting 1M hydrogen ion CFA leach solution with fresh Primene JMT. Thereafter, 1M hydrogen ion CFA leach solution was consecutively contacted with recycled Primene JMT three times.

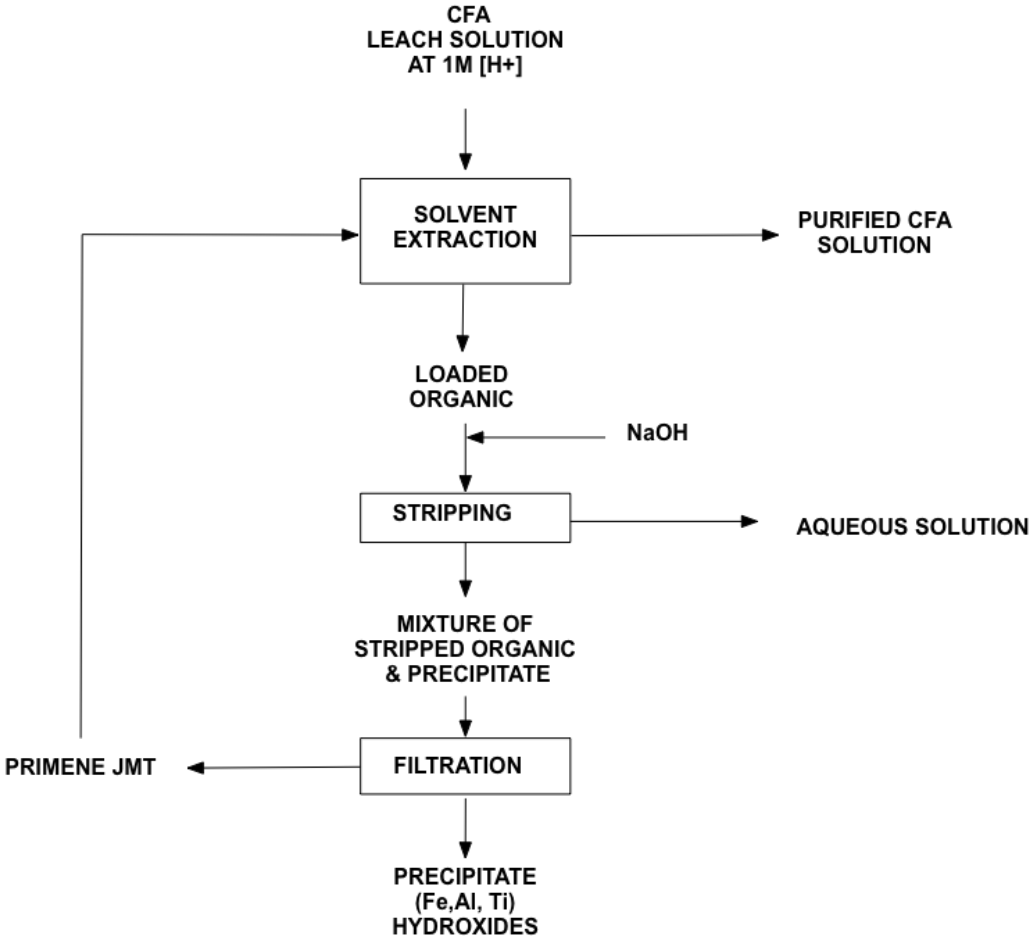


Figure 4.11 Primene JMT recycle

The experimental conditions were: 15%(v/v) Primene JMT concentration, A/O phase ratio of 1:1, hydrogen ion concentration of 1M and a temperature of 70°C. After each extraction, the iron, titanium, and aluminium concentration in the purified solution was analysed to determine the percentage extracted from fresh solution. After each extraction the loaded organic phase was then stripped with 1 M sodium hydroxide.

The precipitate formed was a mixture of iron, titanium, and aluminium hydroxides. The organic phase was then recycled for another successive extraction with fresh solution. The economics of solvent extraction are in part affected by the ability of the extractant to be recycled as it is very expensive to replenish. Table 4.10 presents the results for the extractant recycle experiments with Primene JMT. The experiment recycled Primene JMT three times, after each recycle it was be observed from that the extractive effectiveness of Primene JMT did not deteriorate.

Table 4.10 Successive solvent extraction recoveries of Ti, Fe and Al.

Extraction #	Ti(IV) extraction (%)	Iron (III) extraction (%)	Al co-extraction (%)
1	99.6	82	2.36
2	99.6	81	2.3
3	99.4	83	3.68
4	99.4	82	2.25

The use of 1M sodium hydroxide to strip the pregnant organic phase proved to be an effective method of removing iron and titanium from the CFA leach solution. However, the use of sodium hydroxide presented a drawback during the recycling experiments. The hydroxide precipitate that formed during stripping settled in the organic phase and therefore filtration was required to separate the organic phase from the solid hydroxide. During the filtration process some of the organic phase remained on the precipitate, washing was therefore required to recover this organic phase remaining on the precipitate. This washing process presents additional expense for a potential SX system and is therefore a disadvantage of stripping by hydroxide. The alternative to sodium hydroxide for stripping is the use of sulphuric acid. Alguacil et al. (1987) noted that acid stripping has the disadvantage of the solvent losing extractive strength due to the formation of an amine bisulphate complex. It was reported that the solvent could then be regenerated by the use a base and this process does not result in the generation of precipitate that requires extra equipment to handle.

4.7.1 Physical loss of organic phase

During the solvent recycle experiment not all of the organic phase was recovered. Table 4.11 below indicates the total organic volume remaining after each complete cycle. The initial organic volume used was 60mL.

Table 4.11 Organic loss during solvent recycle

Extraction #	Organic volume remaining(mL)	cumulative % organic lost
1	58	3.3
2	56.5	5.8
3	55.3	7.8
4	54.0	10.0

Figure 4.9 shows that four stages were required to purify the CFA leach solution in the McCabe Thiele diagram. Table 4.11 indicates that after 4 stages the total loss in organic volume is 10%. This is a considerable volume in light of the high cost of extractants.

While the extractive strength of the Primene JMT remained unchanged in each successive recycle, the loss of organic volume suggests entrainment into the aqueous phase and loss of organic to the precipitate after stripping. These losses need to be minimised for any potential SX plant to be economically viable. Effective washing will have to be done and this must be taken into consideration during the design phase of a proposed SX plant.

5 CONCLUSIONS AND RECOMMENDATIONS

The purification of CFA leach solution by the removal of iron and titanium by SX is an important process step in the extraction of alumina from CFA. Existing studies have indicated that the hydrogen ion concentration of the CFA leach solution has an influential role in the removal of these metals (Seeley et al., 1981; Matjie et al., 2005). The principal aim of this work was to determine the significant process factors and their influence on metal extraction from a novel two-step CFA leaching process at high hydrogen ion concentration. The implementation of a DOE methodology allowed for the adjustment of process factor levels, this provides important information on whether adjustment of process conditions can influence metal extraction at high acid concentration.

5.1 Conclusions

DOE methodologies were employed to determine the effect of the following factors on iron and titanium extraction: hydrogen ion concentration, temperature, extractant concentration and A/O phase ratio. A full factorial design and a central composite design were used to determine the main effects and interactions on iron and titanium extraction.

From the factorial experimental results, for the extraction of iron and titanium by Primene JMT in Shellsol D70 as a diluent, the following conclusions were drawn:

1. Between 25°C and 70°C the extraction of iron and titanium is independent of temperature.
2. The maximum iron extraction possible between hydrogen ion concentration of 10.46M and 4.68M was 33.8%. At 0.28M hydrogen ion concentration, the iron extraction was 88%. This finding strongly suggests that the hydrogen ion

concentration is the most important process variable for iron extraction. The extraction of titanium is independent of the hydrogen ion concentration of the CFA leach solution.

3. For iron extraction, there exists an interaction between the A/O phase ratio and the concentration of Primene JMT. At a lower A/O phase ratio (1:1), the magnitude of the increase in iron extraction with an increase in Primene JMT concentration is larger compared to higher phase ratio (3:1).
4. An interactive effect on the extraction of titanium exists between the A/O phase ratio and concentration of Primene JMT. At a high aqueous organic to ratio (3:1) an increase in the Primene JMT concentration will result in a moderate increase in the extraction of titanium. Whereas, at lower organic to aqueous ratios (1:1) the maximum extraction possible (99%) is obtained at both high and low Primene JMT concentrations.

All the work done with the implemented DOE was done at high hydrogen ion concentration between 4.67M and 10.47M. The maximum iron and titanium extracted within this range was 33.8% and 99% respectively. The aluminuim co-extration at maximum iron extraction was 7% which is significant and represents a loss of targeted metal. The iron extraction in this high acid concentration range was poor. The manipulation of the process factors: temperature, extractant concentration and A/O phase ratio did not improve iron extraction. The design of a SX extraction system with this low iron extraction would not be economic. The reason is that the number of SX steps to remove iron from the CFA leach solution would be many. As the number of stages increase, the capital and working costs also increase.

Extraction improvement tests show that there is close agreement with studies by Matjie et al., (2005) and Seely et al., (1981) whose findings showed that the most influential process factor in iron extraction was the hydrogen ion concentration of the leach solution.

McCabe-Thiele diagrams indicate that it is theoretically possible to purify CFA leach solution by a four stage SX process. The conditions that allowed for effective extraction are: CFA leach solution hydrogen ion concentration of 1M, temperature of 25°C and Primene JMT concentration of 15% in Shellsol D50 as a diluent. The diagrams predict that after four stages, more than 95% of the iron and titanium will have been removed from the CFA leach solution.

At the chosen process conditions for a potential SX system, the ability of Primene JMT to be reused a multiple of times was examined. The findings of this test work concluded that the extractive power of Primene JMT is not diminished by reuse up to 3 recycle stages. The co-extraction of aluminium was found to be about 2% and this is an acceptable level from an economics perspective.

The primary finding of this work is that Primene JMT cannot purify the two-step CFA leach solution at high sulphuric acid concentrations by SX. The secondary finding is that a potential commercial SX system can purify the two-step CFA leach solution only after the significant reduction of the sulphuric acid concentration.

5.2 Recommendations

The findings from this work recommend that the following be further investigated:

Recovery of the organic phase for recycle

The stripping of the loaded organic phase by sodium hydroxide has a potential drawback that could be detrimental to the development of a potential SX system. Stripping with sodium hydroxide produces an aqueous phase and an organic phase with a precipitate entrained in it. The efficiency of the separation of this hydroxide precipitate from the organic extractant is not examined in this work. The efficient recovery of the organic phase for recycle is vital for the containment of working costs in the majority of SX extractant systems. The loss of the organic phase in the filtration step to the hydroxide precipitate could significantly increase reagent makeup costs. In this case, sophisticated additional plant and equipment for filtration and washing could be required and this needs to be known beforehand. It is recommended therefore, that work be done to quantify more closely the organic loss to the hydroxide precipitate. In the event that the loss is excessive, investigations into methods of dissolving the hydroxide precipitate or using other reagents to strip the iron and titanium from the loaded organic phase can also be made.

Reductive leaching of CFA

The reductive leaching of CFA by sulphuric acid presents alternatives for the production of alumina that need to be investigated. Reductive leaching allows for the CFA leach solution to contain iron(II) instead of iron(III) in leach solution. The possibility of extracting aluminium directly by solvent extraction or by precipitating the aluminium hydroxide can now be investigated. This is now possible because the iron(III) that contaminated the SX and precipitate products is now in iron(II) form.

Economic Analysis

From an operational point of view, the primary finding of this work indicates that the effective purification of CFA leach solution by SX requires a significant reduction in the hydrogen ion concentration. This was achieved by the addition of a suitable hydroxide. The extraction improvement tests indicated that 82% of iron could be removed at 1M hydrogen ion concentration. A further reduction in the hydrogen ion concentration to 0.28M resulted in 88% iron extraction. The economic feasibility of reducing the acid level needs to be assessed because of the large volume of an expensive hydroxide reagent required. This assessment will determine if the cost of hydrogen ion reduction will not make the purification of the CFA leach solution by SX unviable.

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APPENDICES

APPENDIX A

FULL FACTORIAL EXPERIMENTAL RESULTS

Calculation of metal recovery

The % iron, titanium and aluminium recovered from aqueous solution was calculated by dividing the metal mass before SX by the metal mass after SX.

Example calculation: Iron recovery in Experiment run 1

Mass of iron in aqueous solution before SX = 2.07g/L × 0.09L = 0.1881g.

Mass of iron in aqueous solution after SX = 1.99g/L × 0.09L = 0.1791g

Recovery of Fe^{3+} $= \frac{(0.1881)-(0.1791)}{(0.1881)} \times 100 = 3.86\%$

Experimental results with the calculated metal recovery

Experiment run number 1			
Parameters $[H^+]$ = 10.47M Temperature = 70°C [Primene] = 5%	Organic volume = 30mL Aqueous volume = 90mL Shaking speed =150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.46
After extraction (g/L)	9.59	1.99	0.244
Recovery (%)	3.91	3.86	46.96

Experiment run number 2			
Parameters $[H^+]$ = 10.47M Temperature = 25°C [Primene] = 5% Organic volume = 30mL Aqueous volume = 90mL Shaking speed = 150 rpm			
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.464
After extraction (g/L)	9.68	2.01	0.229
Recovery (%)	3.00	2.90	50.65

Experiment run number 3			
Parameters $[H^+]$ = 4.67M Temperature = 70°C [Primene] = 15% Organic volume = 30mL Aqueous volume = 90mL Shaking speed = 150 rpm			
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.46
After extraction (g/L)	8.75	1.87	0.001
Recovery (%)	12.33	9.66	99.78

Experiment run number 4			
Parameters $[H^+]$ = 4.67M Temperature = 25°C [Primene] = 15% Organic volume = 30mL Aqueous volume = 30mL Shaking speed =150 rpm			
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.46
After extraction (g/L)	9.45	1.37	0.0003
Recovery (%)	5.31	33.80	99.94

<table>
<tr><th colspan="4">Experiment run number 5</th></tr>
<tr><td colspan="4">Parameters
$[H^+]$ = 7.5M Organic volume = 30mL
Temperature = 25°C Aqueous volume = 60mL
[Primene] = 10% Shaking speed = 150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.83</td><td>2.07</td><td>0.39</td></tr>
<tr><td>After extraction (g/L)</td><td>9.28</td><td>1.77</td><td>0.00052</td></tr>
<tr><td>Recovery (%)</td><td>5.60</td><td>14.49</td><td>99.87</td></tr>
</table>

<table>
<tr><th colspan="4">Experiment run number 6</th></tr>
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$[H^+]$ = 7.5M Organic volume = 30mL
Temperature = 47°C Aqueous volume = 60mL
[Primene] = 10% Shaking speed = 150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.83</td><td>2.07</td><td>0.39</td></tr>
<tr><td>After extraction (g/L)</td><td>9.08</td><td>1.78</td><td>0.0013</td></tr>
<tr><td>Recovery (%)</td><td>7.62</td><td>14.00</td><td>99.67</td></tr>
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<table>
<tr><th colspan="4">Experiment run number 7</th></tr>
<tr><td colspan="4">Parameters
$[H^+]$ = 10.47M Organic volume = 30mL
Temperature = 70°C Aqueous volume = 30mL
[Primene] = 15% Shaking speed = 150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.98</td><td>2.07</td><td>0.46</td></tr>
<tr><td>After extraction (g/L)</td><td>9.36</td><td>1.57</td><td>0.0005</td></tr>
<tr><td>Recovery (%)</td><td>6.21</td><td>24.15</td><td>99.89</td></tr>
</table>

Experiment run number 8

Parameters

$[H^+]$ = 10.47M
Organic volume = 30mL
Temperature = 70°C
Aqueous volume = 30mL
[Primene] = 5%
Shaking speed = 150 rpm

	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.46
After extraction (g/L)	9.14	1.81	0.0012
Recovery (%)	8.42	12.56	99.74

Experiment run number 9

Parameters

$[H^+]$ = 7.5M
Organic volume = 30mL
Temperature = 47°C
Aqueous volume = 60mL
[Primene] = 10%
Shaking speed =150 rpm

	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.83	2.07	0.39
After extraction (g/L)	9.39	1.89	0.0015
Recovery (%)	4.48	8.7	99.62

Experiment run number 10

Parameters

$[H^+]$ = 10.47M
Organic volume = 30mL
Temperature = 25°C
Aqueous volume = 30mL
[Primene] = 5%
Shaking speed = 150 rpm

	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.464
After extraction (g/L)	9.98	1.96	0.00056
Recovery (%)	0	5.31	99.87

<table>
<tr><td colspan="4">Experiment run number 11</td></tr>
<tr><td colspan="4">Parameters
[H$^+$] = 4.67M Organic volume = 30mL
Temperature = 25°C Aqueous volume = 90mL
[Primene] = 15% Shaking speed = 150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.7</td><td>1.98</td><td>0.34</td></tr>
<tr><td>After extraction (g/L)</td><td>9.08</td><td>1.7</td><td>0.00069</td></tr>
<tr><td>Recovery (%)</td><td>6.39</td><td>14.14</td><td>99.80</td></tr>
</table>

<table>
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<tr><td colspan="4">Parameters
[H$^+$] =10.47M Organic volume = 30mL
Temperature = 25°C Aqueous volume = 90mL
[Primene] =15% Shaking speed =150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.98</td><td>2.07</td><td>0.46</td></tr>
<tr><td>After extraction (g/L)</td><td>9.31</td><td>1.86</td><td>0.005</td></tr>
<tr><td>Recovery (%)</td><td>6.71</td><td>10.15</td><td>98.91</td></tr>
</table>

<table>
<tr><td colspan="4">Experiment run number 13</td></tr>
<tr><td colspan="4">Parameters
[H$^+$] =4.67M Organic volume = 30mL
Temperature = 25°C Aqueous volume = 30mL
[Primene] = 5% Shaking speed = 150 rpm</td></tr>
<tr><td></td><td>Al^{3+}</td><td>Fe^{3+}</td><td>Ti^{3+}</td></tr>
<tr><td>Before extraction (g/L)</td><td>9.7</td><td>1.98</td><td>0.34</td></tr>
<tr><td>After extraction (g/L)</td><td>8.67</td><td>1.62</td><td>0.0006</td></tr>
<tr><td>Recovery (%)</td><td>10.61</td><td>18.18</td><td>99.82</td></tr>
</table>

Experiment run number 14			
Parameters $[H^+]$ = 4.67M Temperature = 25°C [Primene] = 5%	Organic volume = 30mL Aqueous volume = 90mL Shaking speed =150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.7	1.98	0.34
After extraction (g/L)	8.44	1.71	0.21
Recovery (%)	12.99	13.64	38.82

Experiment run number 15			
Parameters $[H^+]$ = 4.67M Temperature = 70°C [Primene] = 5%	Organic volume = 30mL Aqueous volume = 90mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.7	1.98	0.34
After extraction (g/L)	8.79	1.77	0.20
Recovery (%)	9.38	10.61	40.29

Experiment run number 16			
Parameters $[H^+]$ = 7.57M Temperature = 47°C [Primene] = 10%	Organic volume = 30mL Aqueous volume =60mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.83	2.07	0.39
After extraction (g/L)	9.34	1.84	0.002
Recovery (%)	4.99	11.11	99.49

Experiment run number 17			
Parameters $[H^+]$ =10.47M Temperature = 25°C [Primene] =15%	Organic volume = 30mL Aqueous volume = 30mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.464
After extraction (g/L)	9.77	1.56	0.0003
Recovery (%)	2.11	24.64	99.94

Experiment run number 18			
Parameters $[H^+]$ = 4.67M Temperature = 70°C [Primene] = 5%	Organic volume = 30mL Aqueous volume = 30mL Shaking speed =150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.7	1.98	0.34
After extraction (g/L)	9.34	1.73	0.00051
Recovery (%)	3.71	12.62	99.85

Experiment run number 19			
Parameters $[H^+]$ = 4.7M Temperature = 70°C [Primene] = 15%	Organic volume = 30mL Aqueous volume = 30mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.70	1.98	0.34
After extraction (g/L)	8.97	1.31	0.0003
Recovery (%)	7.52	33.80	99.91

Experiment run number 20

Parameters

$[H^+]$ = 10.47M
Organic volume = 30mL
Temperature = 70°C
Aqueous volume = 90mL
[Primene] =15%
Shaking speed =150 rpm

	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.46
After extraction (g/L)	9.35	1.83	0.005
Recovery (%)	6.31	11.59	98.91

APPENDIX B

Confirmatory Experiment replicate 1			
Parameters $[H^+]$ =1M Temperature = 25°C [Primene] =15%	Organic volume = 30mL Aqueous volume = 30mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.464
After extraction (g/L)	9.70	0.32	0.0003
Recovery (%)	2.81	84.54	99.94

Confirmatory Experiment replicate 2			
Parameters $[H^+]$ =1M Temperature = 25°C [Primene] =15%	Organic volume = 30mL Aqueous volume = 30mL Shaking speed = 150 rpm		
	Al^{3+}	Fe^{3+}	Ti^{3+}
Before extraction (g/L)	9.98	2.07	0.464
After extraction (g/L)	9.74	0.46	0.0009
Recovery (%)	2.40	77.77	99.80

APPENDIX C

EXTRACTION ISOTHERM RESULTS AND CALCULATIONS

Table C1 shows the results of the extraction tests done to construct the extraction isotherm for iron extraction. The temperature was set at 25°C while the hydrogen ion concentration was set at 1M at 15 % Primene concentration for all 5 extraction tests.

Example Calculation 1:2 phase ratio

Mass of Fe^{3+}extracted

$$= \text{Vol. of aqeuos phase} \times \{[\mathrm{Fe}^{3+}] \text{ before extraction} - [\mathrm{Fe}^{3+}] \text{ after extraction}\}$$
$$= 15\{1.41 - 0.222\} = 17.85$$

$$[\mathrm{Fe}^{3+}] \text{ in the organic phase} = \frac{\text{Mass of Fe}^{3+}\text{extracted}}{\text{Volume of organic phase}} = \frac{17.85\text{mg}}{30\text{mL}} = 0.595\text{g/l}$$

Table C1 Extraction isotherm results

A: O ratio	Volume phase Ratio	$[\mathrm{Fe}^{3+}]$ before extraction (mg/L)	$[\mathrm{Fe}^{3+}]$ after extraction (mg/L)	Mass of Fe^{3+} extracted (mg)	$[\mathrm{Fe}^{3+}]_{(Org)}$ [mg/L]
1:2	15:30	1410	222	17.82	595
1:1	30:30	1410	452	28.74	960
1.5:1	45:30	1410	563	38.12	1270
2:1	60:30	1410	657	45.18	1510
3:1	90:30	1410	972	39.42	1310

Table C2 shows the results of the extraction tests done to construct the extraction isotherm for titanium extraction. The temperature was set at 25°C while the hydrogen ion concentration was set at 1M at 15 % Primene concentration for all 5 extraction tests.

Example Calculation 3:1 phase ratio

Mass of Ti^{4+}extracted

$$= \mathrm{Vol.\,of\,aqeuos\ \ phase}\ \times\{[\mathrm{Ti}^{4+}]\ \mathrm{before\ extraction} - \ [\mathrm{Ti}^{4+}]\ \ \mathrm{after\ extraction}\}$$

$$= 0.09\{310 - 0.49\} = 27.85\mathrm{mg}$$

$$[\mathrm{Fe}^{3+}]\ \mathrm{in\ the\ organic\ phase} = \frac{\mathrm{Mass\ of\ Fe^{3+}extracted}}{\mathrm{Volume\ of\ organic\ phase}} = \frac{27.86mg}{0.03L} = 928mg/\mathrm{L}$$

Table C2 Extraction isotherm data

A:O ratio	Ratio [mL:mL]	[Ti^{4+}] before extraction (mg/L)	[Ti^{4+}] after extraction (mg/L)	Ti^{4+} mass extracted (mg)	[Ti^{4+}] (org) [mg/L]
1:2	15:30	310	0.16	4.64	154
1:1	30:30	310	0.09	9.29	310
1.5 :1	45:30	310	0.1	13.94	465
2:1	60:30	310	1.31	18.52	617
3:1	90:30	310	0.49	27.85	928

APPENDIX D

Design of Experiments

Calculation of effect of hydrogen ion concentration on iron extraction.

An effect of the factor hydrogen ion concentration(C) is defined as the difference between the average response when C is high and the average response when C is low.

Effect of C= Average response when C is high - Average response when C is low.

Table 4-2 gives the relevant data giving the response for the desired factor level.

Average response when C is high

= (5.31+12.56+24.64+24.15+2.89+3.86+10.15+11.59)/8

= 11.894

Average response when C is low

=(18.18+12.62+33.8+33.8+13.64+10.61+14.14+9.66)/8

=18.306

Effect of C = 11.894 - 18.306 =6.412