PURIFICATION OF COAL FLY ASH LEACH LIQUOR FOR ALUMINA RECOVERY.

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A dissertation submitted to the faculty of Engineering and the Built Environment, University of Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering.

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.

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Mohau Rampou

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ABSTRACT

Over the years, much work has been done on the extraction of alumina from coal fly ash (CFA). Previous works were motivated by the results of the quantitative analysis of CFA that showed a high content of alumina; comparatively ranking second to the primary bauxite ore. Thereafter, research studies have been dedicated to finding efficient routes of recovering alumina from CFA. Amongst recent studies, a 2-step leach process developed by researchers from the University of Witwatersrand gave promising recovery results. The current work is an extension of the 2-step leaching process, where an attempt is made to purify the leach liquor recovered from this leaching process in order to generate a purer aluminum solution by removing iron and titanium, which are considered as the two major impurities. The aim is to obtain an impurity free solution that can be used to generate smelter grade alumina.

In this study, solvent extraction using Primene JMT in kerosene was applied to remove the impurities from the leach solution. Optimum parameters tested during the solvent extraction process included contact time, extractant concentration and the organic to aqueous (O/A) ratios. As expected, most of the titanium was extracted in the organic phase and much of the aluminum remained in the aqueous phase. However, the results showed that most of the iron, which occurred in solution as iron (III) and iron (II), also remained in the aqueous phase. This was an unwanted occurrence, as this residual iron would then co-precipitate with the alumina leading to a contaminated product. Two approaches were then applied for a more effective separation of iron from aluminum. The first approach (Route 1) considered the reduction of the iron (III) species into iron (II) prior to solvent extraction for titanium removal. Alumina crystallization then followed and since iron (II) precipitates at higher pH than aluminum, there was reduced contamination of the alumina product. The second approach (Route 2) firstly considered solvent extraction to remove titanium ions and any iron ions. This was followed by the reduction of residual iron (III) to iron (II). In both approaches, aluminum was crystallized out and iron (II) precipitated using $(NH_4)_2SO_4$. Titanium (IV) was stripped from the organic phase using NH_4OH. The results obtained showed a successful purification of the coal fly ash leach liquor for both processes. Route 1's disadvantage is that it used more metal iron filings for iron (III) reduction to iron (II) than route 2. Route 2's disadvantage is that due to the 2-stage stripping applied, it used more excess reagents, therefore implying higher operational costs than route 1. As a result, Route

1 was considered for further tests. The final alumina product generated with the route 1 purification process had a 99.4% Al purity. This purity level meets the smelter grade alumina product specifications. The grade of the final product therefore, indicates that the applied process route was successful.

Key words: coal fly ash, alumina, leaching, solvent extraction, crystallize, stripping, reduction.

DEDICATION

Dedicated to my mother, Moipone, and my family as a whole, for their continued support throughout the duration of the project.

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PUBLICATIONS AND PRESENTATIONS

This work has produced the following publications:

Journal Publications

1. Sibanda,V., Ndlovu, S., Dombo, G., Shemi, A., Rampou, M. (2016). Towards the Utilization of Fly Ash as a Feedstock for Smelter Grade Alumina Production: A Review of the Developments. *Journal for Sustainable Metallurgy*, Vol. 2, pp. 167-184.
   Contribution: Co-author

2. Rampou, M., Ndlovu, S., Shemi, A. (2016). Purification of Coal Fly Ash Leach Liquor for Alumina Recovery Using an Integrated Precipitation and Solvent Extraction Process. *Journal of Sustainable Metallurgy; DOI 10.1007/s40831-017-0142-4.*
   Contribution: Lead author

Conference Proceedings

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   Contribution: Lead author for a poster presentation

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Coal fly ash (CFA) is one of the by-products of combustion of coal; specifically produced in coal-fired power generating plants. Huge amounts of fly ash are produced in power plants where massive amounts of coal are combusted to generate energy. In South Africa, Eskom and Sasol are the major producers of CFA. According to Eskom's 2010 annual report, Eskom has combusted 122.7 million tons of coal and generated a net of 215940 GWh power with an emission of 0.39 Kg M Wh^{-1} of particulate matter, in 2010 alone. Most of this particulate matter is in the form of CFA. Despite the environmental pollution it causes and its potential harmful effects on life on earth, coal fly ash production is still increasing because many power plants throughout the world heavily rely on coal combustion.

In the past, CFA was considered only as waste and a pollutant that was a potential hazard to the environment and all types of life forms, without any significant beneficial applications (WU, et al, 2012). Most of the fly ash produced from the power plants has traditionally been disposed of in controlled landfills or waste containment facilities. Only a small portion, about 10- 20 % of CFA produced in the country is being used for productive purposes, mainly in cement manufacturing and road construction-related applications (Landman, 2003).

A chemical analysis of CFA shows that it typically contains about 26 – 31% alumina (Al_2O_3), arguably second only to bauxite in alumina content. Bauxite, a naturally occurring ore, considered as the primary source of alumina, contains about 50% alumina (Rahaman, et al, 2013). The relative abundance of Al_2O_3 in the coal fly ash is significant enough to justify an attempt to exploit it commercially (Stuckey, 1983; Martjie et al, 2005). Although South Africa has no known exploitable high-grade bauxite ore deposits, it has some of the world's largest aluminium smelters. The potential presented by developing an alternative source of alumina through CFA would provide a significant source of raw material for these local smelters and at the same time cut down on import costs, unlock large tonnage of previously unavailable raw material as well as be a solution to an apparent environmental hazard. This, therefore, implies

that CFA can be a possible secondary source of alumina if an economic and highly efficient extraction process route can be developed.

Conventionally, the conversion of bauxite ore to smelter-grade alumina is done through the Bayer process. However, the high amount of silica in the CFA (40-60% SiO_2) makes the Bayer process and other direct alumina extraction processes unsuitable for the recovery of alumina from CFA. This difficulty has prompted intense research aimed at developing alternative routes for extracting alumina from CFA (Fass et al, 1994; McDowel and Seeley, 1981a, 1981b, Murtha, 1983, Murtha and Burnett, 1983, Padilla and Sohn 1985, Hill and Raistrick, 1981, Shcherban et al, 1995, Li et al, 2011; Wu et al, 2012). Most notable of these process routes are those that involve pre-treatment of CFA using sinter methods (Martjie et al, 2005; Yao et al., 2014). This is because non-sinter methods have been found to be largely uneconomic due to limitations such as slow kinetics, insufficient metal selectivity, low extractions and high lixiviant costs caused by high evaporative losses.

It is important to note that CFA contains two dissimilar phases, amorphous (38%) and mullite (62%), which play a key role in alumina dissolution kinetics. The amorphous phase is reactive, soluble in inorganic acids and needs no heat application to achieve metal dissolution, whereas the mullite phase is refractory and not amenable to dissolution using inorganic acids. Mullite requires pre-treatment and phase transformation into acid-soluble phases prior to leaching. Sinter methods are thus, popularly applied as they rely on a thermal attack on the refractory glass matrix of the ash particles to break the crystalline mullite phase ($3Al_2O_3 \cdot 2SiO_2$), so as to liberate Al_2O_3 for effective leaching (Matjie et al., 2005, Murtha et al., 1983).

Although there is significant amount of information and research conducted on the development of economical and highly efficient methods for leaching of aluminium from CFA, less work has been done on the downstream processes. Not much attention has been paid on the processes such as the purification process of the leach liquor leading to the final generation of alumina, which meets the specification required for a feed source to the smelter i.e. smelter grade alumina which is comparable to that produced in the Bayer process. This work will therefore focus on the

downstream processes, with particular attention being given to the generation of a pure solution that can be used for the final alumina recovery.

Previous studies by Shemi (2012) resulted in a novel method for the extraction of aluminium from South African CFA. The method involved the application of a 2-step leaching process; first by leaching the CFA in its as-produced state to generate a leached residue-CFA body in which the surface morphology of the CFA has been modified by reaction with sulphuric acid. This was then followed by preparing a sintered body from the first stage leach residue in which the mineralogy of the alumina phase was modified by reaction with suitable additives, followed by a second acid leaching stage. This extraction technique was called a 2-step 'pre-sinter and post-sinter' leach. This 2-stage leaching process resulted in 88% Al extraction. The whole process is shown in **Figure 1.1**. The work in this proposal is therefore an extension of the 2-step acid leach process developed by Shemi (2012). The objective is to extend the work from the leaching stage to the alumina recovery stage by investigating processes for leach liquor purification and alumina recovery.

Thus, in this work, the separation of aluminum-dissolved species from other leach impurities before the final stage of alumina recovery will be considered. Solvent extraction, precipitation and crystallization are the process that will be taken into account. The final process will incorporate the calcination step in order to obtain the solid alumina.
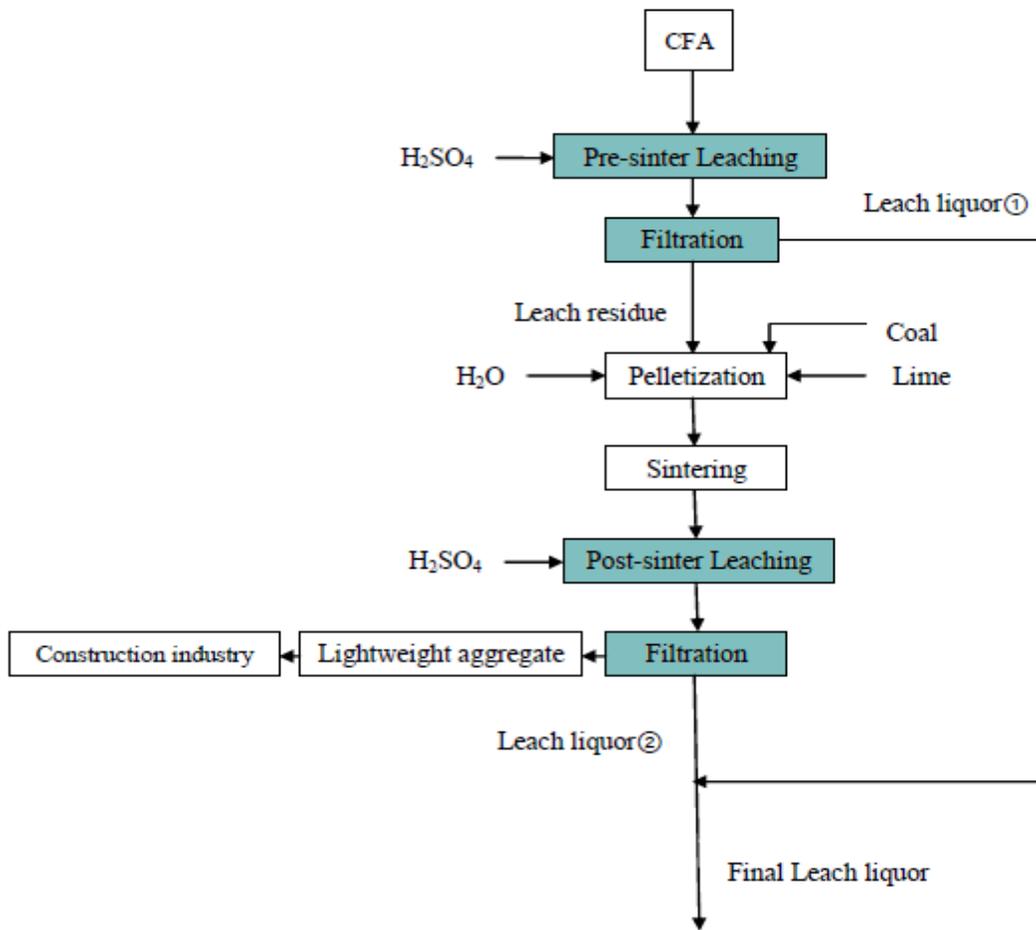
Figure 1.1 The proposed 2-step acid leach process for aluminium extraction from CFA (Shemi , 2012)

1.2 Problem Statement

CFA has been identified as a potential secondary source of alumina. Although there is considerable amount of information on the leaching of aluminium from CFA, not much work that has been done on the downstream processes such as subsequent purification of the leach liquor leading to the final recovery of a solid alumina product. Without such information, the economic, commercial feasibility and the competitiveness of the CFA process as an alternative to the existing Bayer process for alumina production cannot be determined.

1.3 Research Objective(s):

The aim of this work is to add new knowledge on the beneficiation of coal fly ash, by developing a process route for the recovery of smelter grade alumina through leach liquor purification. The work will be an extension of a process previously developed by a researcher in the School of Chemical and Metallurgical Engineering at Wits University. The proposed steps to be investigated include purification and recovery steps such as precipitation, solvent extraction, crystallization and calcination.

The specific objectives are:

- To determine the feasibility of purifying a 2-step CFA leach solution by considering either a combination of or a sole technique from solvent extraction, precipitation and crystallization methods
- To determine the optimum level of process parameters affecting the recovery of alumina from the leach liquor
- To undertake a preliminary cost assessment of the developed process route by paying particular attention to reagent consumption.

1.4 Research Methodology

The research methodology for this study involved the following major tasks: Literature review, experimental design, laboratory testing, and laboratory test data analysis, drawing conclusions from results, recommendations and documentation.

1.5 Dissertation Layout

The complete dissertation has six chapters, where each chapter initially presents a brief introduction that outlines paramount topics discussed in the different sections.

Chapter 1 *Introduction:* This chapter provides the motivation for the research, the problem statement and the overall objectives of the study.

Chapter 2 *Literature Review:* This chapter reviews related literature on the extraction of alumina from CFA. The review also includes general knowledge on CFA, sources mineralogy and the current metallurgical extraction processes.

Chapter 3 *Experimental Design:* This chapter describes the materials and methods used in the study as well as laboratory tests undertaken to meet the objectives of the research.

Chapter 4: This chapter presents and discusses the results and the findings.

Chapter 5 *Conclusion*: This chapter provides conclusions based on the findings in *Chapter 4*.

References: This section lists detailed references of all articles used in the study. The dissertation concludes with an appendix section, which provides relevant laboratory test results and other important data.

1.6 Summary

In this introductory chapter, the background, problem statement and study objectives were discussed. This was followed by a short description of the research methodology and dissertation layout. The next chapter discusses the literature review.

2.1 Introduction

There has been a lot of research focused on finding alternative routes for alumina recovery from CFA. These investigations have been motivated by extensive work that has found the conventional Bayer process inapplicable due to the high silica content of CFA (Fass et al, 1994; McDowel and Seeley, 1981a, 1981b, Murtha, 1983, Murtha and Burnett, 1983, Padilla and Sohn 1985, Hill and Raistrick, 1981, Shcherban et al, 1995, Li et al, 2011; Wu et al, 2012).

This chapter will focus on reviewing past investigations regarding alumina extraction. The review will present and discuss the different previously explored alumina extraction routes from CFA. The investigations include parameters that were tested for optimum alumina extraction, the main impurities in the overall alumina product and attempts at producing smelter grade alumina through separation techniques for alumina leach liquor purification purposes. Some of the purification methods presented in this chapter include crystallization, precipitation and solvent extraction.

2.1.1 Aluminium Occurrence

Aluminium is one of the most abundant elements on earth and comes only third to oxygen and silicon, making up eight percent of the earth's crust. Aluminium holds certain advantages over other metals. Its low density, compared to metals such as copper and iron, allows it to be used in the transport industry in larger volumes, offering extensive rigidity. Compared to conventional copper used for electrical wiring, aluminium has a higher electrical conductivity. The high affinity for oxygen, which usually results in a protective oxide layer, gives aluminium anti-corrosive properties in humid environments (Grjotheim and Welch, 1998).

The main source of aluminium is bauxite ore. Bauxite consists of three major aluminium minerals, which are gibbsite ($Al_2O_3.3H_2O$), boehmite (γ-AlO(OH)) and diaspore (α-AlO(OH)). Boehmite and diaspore have a similar chemical composition although diaspore is denser and harder than boehmite. Alumina (Al_2O_3), silica (SiO_2) and iron oxide (Fe_2O_3) are the major

components of bauxite. More than 85% of mined bauxite is used for the extraction of alumina for the production of the aluminium metal. Australia is the major producer of bauxite. In 2015, it contributed about 29% of the world's full production of bauxite as seen on **Table 2.1** (U.S Geological Survey, 2016). South Africa has no bauxite reserve but serves as a major refinery for alumina imported from countries such as Australia.

Table 2.1 World's alumina and bauxite production for year 2014 and 2015 (U.S Geological Survey, 2016)

Country	Alumina (10^3 tons)		Bauxite (10^3 tons)		Reserves(10^3 tons)
	2014	2015	2014	2015	
United States	4,390	4,000	NA	NA	20,000
Australia	20,500	20,200	78,600	80,000	6,200,000
Brazil	10,600	10,300	34,800	35,000	2,600,000
China	47,800	57,000	55,000	60,000	830,000
Greece	800	800	1,900	1,900	250,000
Guinea	-	-	17,300	17,700	7,400,000
Guyana	-	-	1,600	1,700	850,000
India	5,060	5,470	16,500	19,200	590,000
Indonesia	240	300	2,550	1,000	1,0000,000
Jamaica	1,850	1,950	9,680	10,700	2,000,000
Kazakhstan	1,600	1,600	5,200	5,200	160,000
Malaysia	-	-	3,260	21,200	40,000
Russia	2,570	2,580	5,590	6,600	200,000
Suriname	1,300	970	3,000	2,200	580,000
Venezuela	650	650	1,500	1,500	320,000
Vietnam	485	500	1,090	1,100	2,100,000
Others	10,600	11,400	7,200	8,500	2,400,000
World total (rounded)	108,000	118,000	245,000	274,000	28,000,000

Alumina is conventionally produced from bauxitic ores through the Bayer process whose commercial application has found wide industrial acceptance. The route uses alkaline NaOH to affect the dissolution of aluminium. However, the co-dissolution of SiO_2, which can only be removed at the expense of extracted aluminium (Shcherban et al., 1995), is a major concern in the Bayer process. For this reason, bauxite that contains > 7% silica is generally considered uneconomic. Because of this, the Bayer process is not suitable for treatment of CFA due to its high silica content, which is typically 40-60%. It has been noted that alumina is amphoteric (Grjotheim and Welch, 1998) and that only a negligible amount of silica dissolves in most acids especially sulphuric and hydrochloric acid (Lehner and Merril, 1917). These observations therefore motivate for the use of acids for aluminium dissolution from CFA.

2.1.2 Coal Fly Ash

The Electric Power Research Institute (EPRI) (2009) described fly ash as minute lightweight particles that exit a high temperature furnace with flue gases during coal combustion. The process of coal combustion normally occurs in power stations that are equipped with devices that trap nearly all the fly ash particles in an attempt to prevent them from being emitted into the atmosphere. Devices such as electrostatic precipitators (ESPs), which use electrically charged wires, and baghouses which use fabric filters, are utilized in order to capture the fly ash (EPRI, 2009).

The color of CFA can vary from light grey to dark grey. This is influenced by the type of combustion technique administered or the unburned carbon content (Kimura et al. 1995). Kelmers et al, (1981) explain that fly ash particles are spherical in shape, which is due to the molten droplets formed after cooling of the combustion gases. The average size of the fly ash collected by the electrostatic precipitators usually ranges from 0.074 to 0.005 mm with a median particle diameter that ranges between 20-25 micrometers (EPRI, 1995).

There are mainly two classes of coal fly ash: Class F fly ash and Class C fly ash. These, according to ASTM C618, differ in calcium, alumina, silica and iron content (**Table 2.2**). The content of the two classes (i.e. Class F fly ash and Class C fly ash) is largely determined by the chemical makeup of the combusted coal; that being either anthracite, bituminous, or lignite

(ASTM C618, 2008). Medina et al. (2010) investigated the morphology of the CFA and found that it contained glassy aluminosilicate, mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), calcite ($CaCO_3$) and magnetite (Fe_3O_4) as the several major phases in the make-up of the CFA.

Lyer and Scott (2001) explored the potential applications of CFA. They found that CFA could be used in various ways such as; adsorbents in wastewater processing, fertilizers in the agricultural industry, cement and brick making in the construction industry and for the recovery of alumina in the metals industry. The recovery of alumina from CFA has seen a lot of intensive research in the past few years, with China leading the research. China has placed significant funding on research focusing on the recovery of alumina from CFA. Furthermore, it is the first nation in the world to build a commercial operational plant for utilization of CFA with the focus being on recovery of smelter grade alumina, silica and other by-products (U.S Geological Survey: Minerals Yearbook: Area Reports: International, 2009). America and some European countries have also shown significant interest in the recycling of CFA for metal recovery.

Annually, South Africa produces over 25 million tons of CFA and only about 1.2 million tons are used for various purposes on a commercial scale. These include uses in the construction field for the production of cement as well as to make bricks. Sasol and Eskom, the major coal consumers in South Africa, produce most of the fly ash (Bada and Potgieter-Vermaak, 2008).

Table 2.2 Fly ash class C and class F specifications according to ASTM (ASTM C618, 2008)

Properties	Fly Ash Class	
	Class F	Class C
Silicon dioxide (SiO2) plus aluminum oxide (Al2O3) plus iron oxide (Fe2O3), min, %	70.0	50.0
Sulfur trioxide (SO3), max, %	5.0	5.0
Moisture Content, max, %	3.0	3.0
Ca, %	10<	10>
Loss on ignition, max, % 6.0* 6.0	6.0	6.0

* The use of class F fly ash containing up to 12% loss of ignition may be approved by the user if acceptable performance results are available.

2.2 Extraction of Alumina from Coal Fly Ash

The high amount of aluminium associated with CFA has led to a lot of research interest aimed at its commercial extraction. Researchers have investigated a number of lixiviants that can be applied for the dissolution of the aluminium from the CFA. Unfortunately, CFA also contains other metals that dissolve with the aluminium and make it difficult to produce an alumina solution that can be exploited for the production of smelter grade alumina (Cao et al, 2008; Rayman et al, 1997; Jiang et al, 2008). The next section looks at the different methods that have been developed throughout the years to extract alumina from CFA.

2.2.1 Leaching of Alumina from Coal Fly Ash

Cavin (1974) published one of the first few papers on the recovery of alumina from CFA. This paved the way for research work done throughout the 1970s by Eisele and Bauer (1976) amongst others, where the focal point was on the technology and processes for the recovery of alumina from CFA. These then served as a foundation for the extensive work done by other researchers such as Gabler and Stoll (1980), on the extraction of leachable metals and recovery of alumina from utility coal ash. Researchers have come up with different leaching processes that can be applied in the dissolution of aluminium from CFA. The leaching processes are mainly classified as acidic, alkaline and acidic-alkaline leaching.

The acidic leaching processes involve the use of acids such as sulphuric acid, hydrochloric acid, nitric acid and hydrofluoric acid for the dissolution of alumina (Torma, 1983 and Kumamoto, 1990). However, low acid concentrations for direct acid leaching under ambient temperature conditions results in low recoveries, even under extended leaching time (Kelmers et al, 1982; McDowell and Seely, 1981).The low recoveries are a result of the formation of an unfilterable silica gel, which follows alumina-silica co-dissolution (Verbann et al., 1989). Alternatively, efficiencies of 82.4% can be reached using extensive methods such as pressure leaching (Wu et al., 2012). The acid-leach method that has shown promising results, giving efficiencies as high as 85 and 98%, is the sinter-acid leach process. This method uses high temperature (900-1050ºC) calcinations of the fly ash to break the refractory mullite, freeing the unleached alumina (Bai et al., 2011; Liu et al., 2012; Ji et al., 2007; Martjie et al., 2005). Further research has also shown

the development of a two-step acid-leaching method, which involves the leach-sinter-leach approach, giving extraction efficiencies in the ranges of 85 to 98% (Marjie et al., 2005; Shemi, 2012)

The alkali method involves the use of lime or soda sintering with CFA. Most of the alkali methods involve the use of NaOH for aluminium dissolution from CFA. NaOH has been used as a desilicating reagent in two-step alkaline hydrothermal reaction systems (Bai et al, 2010). Due to high NaOH consumption rates, the process is not feasible for pilot plant upgrades (Su et al., 2011). Further work by Li et al. (2014) reduced the NaOH usage rate by adding $Ca(OH)_2$ to the hydrothermal reaction system with NaOH. The $Ca(OH)_2$ addition was aimed at forming $2CaO.SiO_2$ and $CaO.SiO_2$ minerals which should be aluminium-free. The addition also resulted in the immobilization of SiO_2. However, the minerals still had a notable amount of aluminium and sodium content (Li et al., 2014).

The acidic-alkali methods require the sintering of CFA with lime first, followed by leaching with HCl to recover the aluminium as aluminium chloride (Kirby et al, 1981). At pH ranges of 11.5 - 13.5, Russ et al. (1978) obtained leaching efficiencies of 89%. This was achieved by using alkaline leaching as a CFA pre-treatment step to dissolve gangue material that could potentially hinder the efficient extraction of alumina. The pre-treatment was performed at a temperature of 120ºC. The pre-treated CFA was then filtered, dried and then leached using HCl as the final step for the aluminium extraction process (Russ et al., 1978). The methods discussed above have been found to have shortcomings, which include a large consumption of both the strong acid and the base used as well as difficulties in the purification of the alumina produced (Kirby et al, 1981; Viktor, 1997).

2.2.2 Purification of Coal Fly Ash Leach Liquor

In order to have an idea on the potential processes to be utilized in the purification of CFA leach liquor, the specific requirement for the composition of the smelter grade alumina needs to be considered. The objective is thus, to develop a process, which can produce a solution that when further processed through crystallization or precipitation, can generate a product comparable to the composition of the smelter grade alumina as shown in **Table 2.3**.

Table 2.3 Composition of smelter grade alumina (Authier-Martin et al, 2001)

Constituents	Wt.% (as Metallic Oxide)
Al_2O_3	99.3-99.7
Na_2O	0.30-0.50
SiO_2	0.005-0.025
CaO	<0.005-0.020
Fe_2O_3	0.005-0.020
TiO_2	0.001-0.008
ZnO	<0.001-0.010
P_2O_5	<0.0001-0.0015
Ga_2O_3	0.005-0.015
V_2O_5	<0.001-0.003
SO_3	<0.05-0.20
*Typically alpha-Al_2O_3 content ranges from 2–30%.	

High purity aluminium is obtained from the electrolysis of alumina through the Hall-Heroult process. The purity of alumina acceptable for the electrolysis plant is 98.7wt% Al_2O_3, 0.02wt% CaO, < 0.01wt% SiO_2, < 0.001wt% P_2O_5 and < 0.001wt% TiO_2 (Authier-Martin et al, 2001). Although the use of sulphuric acid to leach CFA has the advantage of not dissolving silica, it has the disadvantage of dissolving other impurity metals in the CFA. The major impurity metals in CFA are calcium, titanium and iron. **Table 2.3** indicates that the amount of calcium, iron and titanium should be significantly low in the final composition of the smelter grade alumina. Since the CFA contains a significant amount of iron, calcium and to a certain extent, relatively high titanium, it is therefore necessary to purify the leach solution before alumina can be recovered by crystallization then subsequently sent to the smelter. Of these three impurity metals, calcium is relatively simple to remove, mainly because calcium sulphate has a very low solubility of 0.2g per 100ml at 30°C. This low solubility can be exploited to aid in the removal of calcium from CFA leach solutions. Iron and titanium on the other hand are more difficult to remove and, as

such, most processes for the purification of coal fly ash leach liquor tend to focus on iron and titanium removal. As a result, the process to be developed must be able to selectively separate the titanium and iron from the aluminium. If possible, it should also be able to recover valuable metals such as titanium if present in solution in reasonable amounts. The processes that have been applied in the downstream processing of CFA leach liquors include mostly crystallization, solvent extraction and precipitation.

Crystallization Processes

Crystallization is a method that has been investigated for the direct recovery of aluminium from CFA leach solutions (Martjie et al, 2005). Crystallization is the formation of solid crystals from a solution when the saturation solubility of a solute in a solvent is exceeded. Mullin and Zacek (1981) investigated the crystallization of aluminium sulphate by potassium sulphate. It was recorded that the solubility of $Al_2(SO_4)_3$ at 20°C is 36.2g anhydrous salt/100g water, that of K_2SO_4 is 10.9g/100g water whilst that of the double salt K_2SO_4. $Al_2(SO_4)_3.24H_2O$ is 5.9g hydrous salt /100g water. Hence, an equimolar reaction under super saturated conditions should precipitate potash alum:

$$Al_2(SO_4)_3 + K_2SO_4 + 24H_2O \rightleftharpoons K_2SO_4. Al_2(SO_4)_3.24H_2O \qquad (2.1)$$
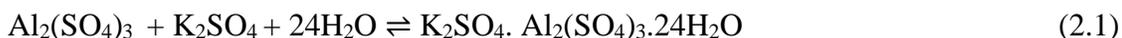
The kinetics of the process was observed to increase with temperature and super saturation of the synthetic solutions employed.

Matjie et al. (2005) employed the crystallization technique for the generation of $Al(NH_4)_2SO_4$ from a CFA leach solution produced from the sulphuric acid leaching of coal fly ash. The addition of ammonium sulphate produced white crystals of $Al_2 (NH)_4SO_4$ at a pH of 1.5 :

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 + 40 H_2O \rightleftharpoons 2Al(NH_4)(SO_4)_2.20H_2O \qquad (2.2)$$

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%. These impurities were crystallized with aluminium ions during the crystallization process. Due to the high levels of impurities in the product, this alumina was found to be unsuitable as feed material for the Al electrolysis plant. On the other hand, studies by

Li et al. (2011) report that crystallization could be applied to the aluminium sulphate, which could then be subsequently calcined. The product powder could then be re-digested and recrystallized to produce metallurgical grade alumina. The work documented by all these researchers suggests that direct crystallization on its own is not adequate as a method of purification. As such, this study will not consider this method solely.

Precipitation Processes

Precipitation is the formation of a solid product from solution as a result of the addition of a reagent to the solution (Jackson, 1986). Charlot (1983) suggests that Ti^{4+}, Fe^{3+} and Al^{3+} ions in aqueous solution can be selectively precipitated as metal hydroxides at pH of 2, 3 and 3.5 respectively. Martjie et al. (2005) obtained an aluminium extraction of 85% following the sulphuric acid leaching of coal fly ash. In the purification process, selective hydroxide precipitation using NaOH was applied to remove metal hydroxides, firstly Ti^{4+} ions at a pH of 2 followed by Fe^{3+} at a pH of 3. The solid precipitates formed were dried, calcined and characterized by XRF and XRD. Following the titanium and iron removal, aluminium was recovered from solution at a pH of 3.5. Martjie et al (2005) also looked at the recovery of aluminium from the coal fly ash leach liquor via a sodium aluminate process. The coal fly ash leach liquor was firstly purified by removing iron and titanium ions using NaOH at a pH of 13. This process resulted in the formation of a sodium aluminate that was then reacted with carbon dioxide gas to produce a metal precipitate that was dried and calcined.

The solid products generated using the selective precipitation process however, contained unacceptable level of impurities such as silica, calcium, phosphorus, titanium and iron. This implies that selective precipitation on its own is not an effective approach for the production of smelter grade alumina. An inspection of the metal hydroxide precipitate diagram (**Figure 2.1**) confirms that co-precipitation is very likely to occur since the equilibrium conditions for the formation of hydroxides of titanium, aluminium and iron lie very close to each other.

The removal of iron from solution has been the center of research in hydrometallurgical processes. In most processes that involve the recovery of valuable metals through leaching, iron has been found to be in appreciable amounts as an impurity. It has been found either as ferrous or ferric depending on the oxidative nature of the leaching reagent used. In cases where it is found

as a ferric species, it is of paramount importance that it is reduced to ferrous so as to use precipitation as a removal method with minimum chances of co-precipitation (Lee and Nam, 2011). After the complete reduction of ferric to ferrous, the pH of the solution must be increased to 6.5-8.5 ranges in order for the precipitation of ferrous hydroxide to occur. This can be seen in **Figure 2.1**.
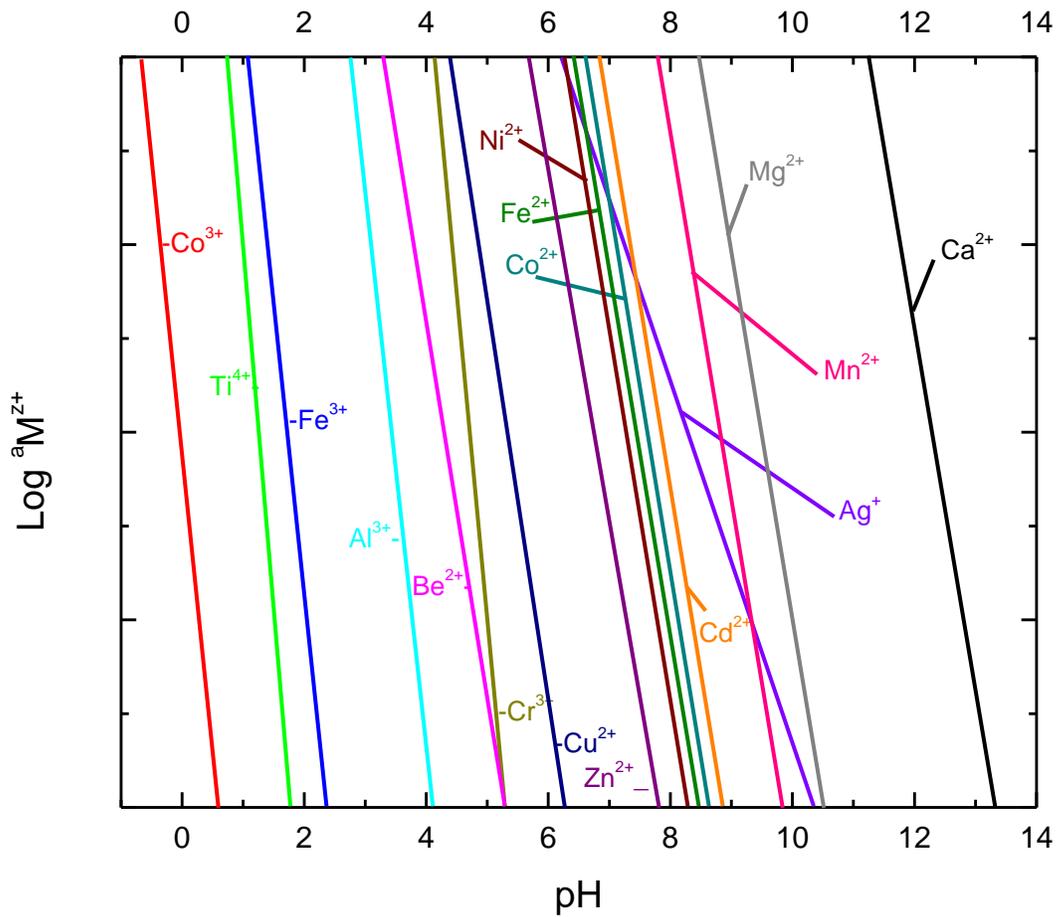
Figure 2.1 Metal hydroxide precipitation diagram (Monhemius, 1971)

Solvent Extraction Processes

Solvent extraction is a method that has been shown to be more successful at purifying CFA leach solutions compared to purification by precipitation and crystallization (Matjie et al., 2005). Solvent extraction 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. While most reports indicate that it is possible to extract aluminium from leach solutions, the desired purity of aluminium can at most be achieved by the prior removal of iron, which is also strongly extracted by most solvent extraction systems (Schrotterová and Nekovář, 1999).

Many researchers have examined the direct extraction of aluminium by solvent extraction (Mohapatra et al., 2007). Preston (1985) investigated the ability of carboxylic acids in a xylene diluent to recover aluminium and other metals from nitrate solutions. Research has also focused on the solvent extraction of impurity metals such as iron and titanium as a means of purifying the leach solutions (Martjie et al, 2005). The work by Tsakaridis and Agatzini-Leornadou (2005) shows that in the extraction of metals from sulphate solutions using Cyanex 272 and phosphoric acid, Fe has the tendency to report to the organic phase under low pH conditions. This therefore, implies that selective solvent extraction by proper pH control can be applied in the overall process by firstly removing iron followed by the recovery of aluminium and titanium.

Organo phosphates such as bis-(2-ethyl-hexl) phosphoric acid (D2EHPA) and tributyl phosphoric acid (TBP) are popular because of their commercial availability and lower price. Da Silva et al. (2007) showed that D2EPHA in n-dodecane was able to extract iron and titanium in 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 possible with D2EHPA due to co-extraction of aluminium (Mohapatra et al., 2007, Matjie et al., 2005). Organo-phosphate extractants are also difficult to strip, requiring expensive stripping agents such as fluorine and hydrogen peroxide to improve the stripping kinetics (Seyfi., 2008; Da Silva., 2008). Hence, their use in the purification of CFA leach solutions is limited.

Factors Affecting Solvent Extraction

Phase separation: The time taken for the complete separation of the organic and aqueous phase after a liquid-liquid extraction is defined as separation time or phase disengagement time (LLE) (Kislik, 2011). The disengagement of the two liquids plays a vital role in the kinetics of LLE, that is, it determines the speed of the solute mass transfer between the two phases (Ridberg, 2004). To improve the disengagement of the two phases, a range of polar and non-polar reagents (diluents and modifiers) are mixed with the extractant (Ajgaonkar and Dhadke, 1997). These enhance the phase separation time by eliminating the formation of an emulsion or third phase. Studies by Saji et al (1998); Ajgaonkar and Dhadke, (1997); Deep et al (2001); Mohapatra et al (2007); Cattrall and Walsh (1974) and Li et al (2011) have displayed a wide range of diluents and modifiers that were tested to enhance the phase separation time in the extraction of titanium, iron and aluminium respectively. According to research, kerosene is the most efficient, relatively safe and preferred diluent in most titanium, iron and aluminium extraction studies (Mellah and Bauer, 1995; Biswas et al, 1998; Martjie et al, 2005; Dessouky, 2008). Kerosene was therefore, chosen as the diluent of choice in the current work.

Extractant concentration: Extractant concentration can affect phase separation time and the loading of a solute onto the organic phase. There is evidence of past work conducted that focused on the effect of extractant concentration on the loading of solutes onto the organic phase. Research has shown the impact of varying the extractant concentration on the uptake of different solutes (Ajgaonkar and Dhadke, 1997). Mohapatra et al (2007) reported a significant increase of solute extraction with an increase in extractant concentration.

O/A ratio: The organic to aqueous (O/A) ratio can be used to test the quantitative extraction efficiencies (Mohapatra et al, 2007). Li et al. (2011) showed the significant impact that the O/A ratio variation has on the extraction of Fe^{3+} by stating that the extraction efficiency of Fe^{3+} increased with the increase of the O/A ratio. However, it is vital to consider economic factors to make the process feasible. Singh et al (2006) reported an increase in the Fe^{3+} stripping efficiency with a decrease in the O/A phase ratio using oxalic acid as a stripping agent. Other studies have also tested the impact of the O/A ratio on the extraction efficiency of certain metal ions (Demopoulos, 1984; Reddy and Sarma, 1996; Zhang et al, 1996). This therefore, motivates for an investigation on the current work.

The solution pH: The pH of the solution also has a significant impact on the loading of certain species onto the organic phase during SX. The effect of the high concentration of H^+ ions has displayed negative effects in the extraction of some species. For example, Fe^{3+} ions have been found to load poorly due to complex formations that only form under highly acidic conditions (Seeley et al., 1981; Li et al., 2011; Chou et al., 1986). On the other hand, Wadood and Alyaa (2009) reported the high extraction efficiency for Fe^{3+} at relatively high pH using MBK, with the extraction of other metal ions showing an inverse extraction trend with the increase in pH.

2.3 Extraction of Fe from Solution

The composition or purity of the extracted alumina should match that of the ideal smelter grade alumina (**Table 2.3)** obtained using the widely accepted Bayer process. However, impurities such as iron can have a significant impact on the product purity if not properly managed. There has been a significant amount of research on the removal of iron from various coal fly ash solutions. In solutions where Fe^{2+} and Fe^{3+} both exist in a solution, the purification process can be rather complex as these two states can respond differently to chemicals and the process environment. The knowledge gained from this review will be employed in this research work in an attempt to purify the CFA leach liquor generated using the 2-step leaching process.

2.3.1   Iron Removal through Solvent Extraction

Although amines are more expensive, they are revealed as more effective at removing iron from sulphate leach solutions than extractants such as carboxylic acids and phosphates in terms of selectivity, extraction yield and ease of stripping (Li et al., 2011). In particular, primary amines have shown the best promise of extracting impurities 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 in the presence of various impurities such as Ca, Mg and Ti. From the 15 diluents tested, benzene and toluene showed best results with Fe^{3+} extraction efficiencies of 73 and 72%, respectively. The results were obtained at H_2SO_4 concentrations of up to 0.1M with an iron distribution ratio of

100. At hydrogen ion concentration greater than 0.1M, the distribution ratio diminished exponentially. Hence, pH adjustment must be exercised for the effective use of the Primene 81R.

Li et al. (2011) examined the removal of iron from industrial grade aluminium sulphate using 25% of the primary amine N-1923 and got an extraction efficiency of 99.99% extraction and selectivity at pH above 1.2 in 50% kerosene as a diluent and 25% octanol as an enhancer. Matjie et al. (2005) used a primary amine, Primene JMT, to remove iron and titanium from CFA leach solution. The pH of the solution was adjusted to 0.05 by using ammonium hydroxide solution. It was found that the amine extractant was very selective for the removal of silica, iron and titanium impurities whilst leaving the aluminium ions in the rafinnate in the form of aluminum ammonium sulphate crystals. An alumina product with a purity > 99.4% was produced on calcination. This product was found to adhere to the specifications for the production of aluminium via the commercial Hall-Heroult process.

Ajgaonkar and Dhadke (1997) used Cyanex 302 in chloroform to separate Fe^{3+} and Al^{3+} from other elements. Fe^{3+} was quantitatively extracted at pH 2.0-2.5 whereas the extraction of Al^{3+} was quantitatively extracted in the pH range 3.0-4.0. Fe^{3+} was stripped from the organic phase with 1.0 M and Al^{3+} with 2.0 M hydrochloric acid. Both metals were separated from multicomponent mixtures. An extraction efficiency of more than 99% for each metal was reported in all the tests undertaken.

2.3.1.1 Extraction of Fe^{3+} from Solutions

Reddy and Sarma (1996) conducted work on the extraction of Fe^{3+} from hydrochloric acid solutions using tri-n-butyl phosphate (TBP) and methyl-iso-butyl ketone (MIBK). The work was based on attaining the TBP: MIBK extractant ratio with the optimum synergistic effect on the Fe^{3+} extraction from solution. The ratios tested involved a 100% TBP and 0% MIBK, 90% TBP and 10% MIBK, 80% TBP and 20% MIBK, 70% TBP and 30% MIBK; 60% TBP and 40% MIBK. There was no significant extraction when an MIBK concentration of <60% was used on its own. The 70% and 30% ratio gave a better and quicker phase separation with no formation of the third phase. It was also discovered that the mixture of the solvent performed better than the results given by the solvents on their individual basis. In addition, the extraction of Fe^{3+} increased with an increase in the acid and solvent concentration. Upon separation of the phases,

Fe^{3+} formed $HFeCl_4$ species in the organic phase. The solvent mixture gave an Fe^{3+} extraction efficiency > 99.4 % and a stripping efficiency of 100% in five stages.

Demopoulos and Gefvert (1984) conducted experiments making use of the method of combined solvents for the extraction of iron ions from solutions. The work involved using a mixture of a conventional base-metal chelating agent Kelex 100 (alkylated derivative of 8-hydroxyquinoline) and D2EHPA (bis (2-ethylhexyl) phosphoric acid) for the sole purpose of extracting Fe^{3+} from strong sulphuric acid solutions. Isodecanol dissolved in kerosene was used as a modifier. The Fe^{3+} loaded in the organic phase was reacted with hydrogen, which reduced it to Fe^{2+} allowing easy stripping from the organic phase. In this case, the stripping was done using a weak acid. The effect of the modifier's concentration was studied and was shown to have a positive effect on the separation time and the loading of the Fe^{3+} onto the organic phase, only if modifier concentration of 0.6M was used, which is considered an intermediate concentration. The solvent mixture also showed a synergistic effect on the extraction of Fe^{3+} over the solvents being used individually.

Alguacil and Amer (1986) conducted a study on the extraction of Fe^{3+} with the aid of Primene 81R in kerosene as an extractant. The extraction was performed at a temperature of 50 ℃ from an aqueous sulphate media. The researchers found that the extractant Primene 81R formed a $3(RNH_3)_2SO_4 \cdot (Fe(OH)SO_4)_2$ complex when isolated from a methanol-acetone mixture at temperatures of 50 ℃ and higher. The R in the stoichiometric formula is associated with the primary amine (R = Alkyl groups). These findings suggested that the reaction was not an ion exchange type but an adduct formation reaction. The results showed that the dissociation of the primary amine and the Fe^{3+} distribution coefficient had an inversely proportional relationship. An increase in the dissociation of the primary amine was associated with a decrease in the Fe^{3+} distribution coefficient. Minute additions of modifiers (n-alcohol) however, enhanced the performance of the Primene 81R sulphate. From the first extraction reaction, Alguacil and Amer (1987) showed a stoichiometry of two Fe^{3+} ions with three amine sulphate groups each; one Fe^{3+} has a coordination number of 5 and the other Fe^{3+} has a coordination number of 6.

Hirato et al. (1992) conducted work on Fe^{3+} extraction from chloride solutions. They used a mixture of extractants to conduct the experiments. The mixture contained D2EHPA and TBP in kerosene. This came after realizing the difficulty of extracting Fe^{3+} using only D2EHPA in the

organic phase, which required a high concentration of HCl. A three-stage extraction procedure was adopted and resulted in an extraction efficiency of over 98%.

Yaman and Kaya (2005) used a 1-(2-pyridylazo)-2-naphthol (PAN)-chlororoform system to separate Fe^{2+} and Fe^{3+} through solvent extraction from tea infusion, fruit juice, cola and pekmez. The results reported showed that PAN extracted maximum Fe^{2+} into chloroform by means of complex formation at pH 0.75-4.0. Fe^{3+} was least favored by the complexing agent showing minimal extraction at pH 0.75-1.25 in water. This method is used in atomic absorption spectroscopy for the speciation of Fe^{3+}. The method is relatively favorable despite the fact that it is very sensitive and uses chloroform, which is a carcinogen. Lee and Nam (2011) used alamine 336 to extract Fe^{2+} from a chloride solution. They established that Fe^{2+} is only active at high HCl concentration as $FeCl^{+}$. However, in ambient conditions with excess oxygen it is readily oxidized to Fe^{3+} that can be easily removed by precipitation. Li et al. (2011) suggested that Fe^{2+} does not load into primary amine extractants and due to limited Fe^{2+} complexometry information, the extraction of Fe^{2+} through solvent extraction was not considered (Hogfelt, 1982).

Parameters affecting iron extraction

Extraction efficiency can be enhanced by altering a few parameters that have a direct influence on the metal's ability to be extracted or the ability of the extractant used to extract the metal from an aqueous solution.

Simpson et al. (1996) performed the extraction of Fe^{3+} from a sulphate solution using salicylaldoxime LIX 860 as an extractant. The concentration of the extractant, concentrations of Fe^{3+} and the pH of the aqueous solution were varied. The effect of the concentration of the extractant, concentrations of Fe^{3+} and the pH of the aqueous solution was also tested. The researchers found the extraction efficiency to improve at pHs greater than 1 while a $\Delta^{o}H$ of 8.6 kJ/mol proved that the extraction reaction was endothermic. The variation of the mentioned parameters had no particular impact on the equilibrium time for the Fe^{3+} extraction, which was established to be 10 minutes. The extraction curves showed an increasing affinity for more acidic conditions at an increased extractant concentration. By varying acid and extractant concentration, Majumdar and De (1970) performed Fe^{3+} extraction tests from a hydrochloric solution with excess cations or metals (specifically $Al^{3+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Ba^{2+}, Cr^{3+}$ and Bi^{3+}). They discovered

that TBP extracted Fe^{3+} in solution with excess cations or metals (specifically Al^{3+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Ba^{2+}, Cr^{3+} and Bi^{3+}). Majumdar and De (1970) conducted the study by varying acid concentrations from 0.25 to 6M and the extractant from 19 to 100%. The extractant was less effective with an increase in dilution. Furthermore, the extraction took place between HCl concentrations of 3-6M. The results led to a conclusion that 6M HCl and 100% TBP are optimal conditions. The optimal conditions resulted in 97-100% extraction efficiencies with a maximum partition coefficient (D) of 70.

An Fe^{3+} extraction efficiency of 98.57% in a chloride leach solution was also found to be achievable using aliquat 338 (a quaternary amine) in kerosene. The third phase formation was eliminated using p-Nonyl phenol as a modifier. The process was optimized through the exploration of various parameters affecting the extraction process (e.g. the effect of extractant concentration on the extraction of Fe^{3+}, the effect of various diluents, the effect of various salts in the feed solution, etc.). An increase in the acid concentration (HCl) and an increase in the extractant concentration led to a significant increase in the extraction efficiency. The extracted species was found to be in a form of $R_3NCH_3 \cdot FeCl_4$ (Mishra et al. 2011).

Saji et al. (1998) used Cyanex 923(Trialkylphosphine Oxide) in xylene to extract Fe^{3+} from a chloride solution. The study indicated that there is an appreciable decrease of Fe^{3+} extraction efficiency with an increase in the acid concentration, in comparison with other metal ions in close contact with Fe^{3+} in an ilmenite leach solution. The inverse relationship is thought to have been a result of the formation of chloro-complexes. The study also included varying the organic to aqueous ratio. At 3:1 O/A ratio and an acid (HCl) concentration of 0.4M, an extraction efficiency of a 100% for Fe^{3+} could be achieved in two counter-current stages.

In some cases, the removal of Fe^{2+} becomes a challenge especially when separating it from the ferric species. Yaman and Kaya (2005) employed the use of PAN and chloroform as an organic solvent. At pH range of $0.75 - 4.0$ the complex Fe^{2+}-PAN was loaded into the chloroform organic phase and at pH range of 0.75-1.25 Fe^{3+} remains in the aqueous phase. The researchers concluded that at pH 1.0, the complex Fe^{2+}-PAN was loaded into the chloroform organic phase while the ferric species remained in the aqueous phase. Sacmaci and Kartal (2005) used AMPC (4-Acetyl-5-methyl-1-phenyl-1H-pyrazole-3-carboxylic acid) as a complexing reagent for Fe^{3+} and MIBK in kerosene as an extractant. The Fe^{3+}-AMPC complex loaded into the MIBK at pH

range of 1.0-2.5 while the ferrous remained in the aqueous phase through all the pH range. They achieved recoveries of over 95% at a shaking time of 2 minutes, pH at 1.5, $1.64 \times 10^{-4} molL^{-1}$ AMPC reagent and a 10ml MIBK.

$FeCl_2$ can be extracted from an HCl solution between the concentrations of 5 to 9M using Alamine336 as an extractant. The Bromley interaction parameter estimated using Alamine 336 can also be used to calculate the activity co-efficient of $FeCl^+$ in a medium of highly concentrated HCl solution (Lee and Nam, 2011). The high concentration of HCl therefore instigates a high concentration of the H^+ giving the solution a higher pH. The results therefore indicate that $FeCl_2$ can be extracted at high pHs.

Lakshmanan et al. (1975) used Versatic 911 and Lix 64N both in kerosene, respectively, to test for the extraction efficiency and synergistic effects of a mixture of the two extractants for the extraction Cu^{2+} and Fe^{3+}. Various parameters were altered in the experiments to test for their effects of the extraction efficiency (i.e. extractant concentration, sulphate ion concentration, pH, metal concentration, time and temperature). It was discovered that the mixture of the extractant had no synergistic effect on the extraction of the Fe^{3+} and Cu^{2+}. It was also established that mixing Versatic 911 with Lix 64N did not compromise the ability of Lix 64N to separate Cu^{2+} and Fe^{3+}. The Lix – Metal complexes that were believed to have formed during the extraction were $Fe(Lix)_3$ and $Cu(Lix)_2$. The test also revealed that an increase in the concentration of the sulphate ion restricted extraction of both metals.

An iron extraction efficiency of 99.99% can be achieved using a primary amine extraction system. Li et al. (2011) used an extraction system which is made up of 25 vol.% N-1923 (Primary amine), 25 vol.% n-octanol (modifier) and 50 vol.% kerosene (diluent) to achieve an optimum Fe^{3+} extraction efficiency of 99.99% from industrial aluminium sulphate. Various parameters were controlled to give optimum results; the phase ratio O/A was 1:2, at pH 1.2 and contact time was 6 minutes. H_2SO_4 and NaCl solution were both used as stripping agents for the iron loaded in the organic phase. H_2SO_4 gave a higher stripping efficiency than NaCl, which was 96.5% at concentrations of 4 M and 2 M, respectively. The stripping or extraction of iron was determined using slope analysis method and IR spectra.

The extraction of Fe^{3+} was studied through the varying of parameters such as pH, equilibrium time, concentrations of the metal ions (ferric and cupric; for comparative reasons), concentration of the extractant and temperature while using commercial aldoxime MOC-55 TD as an extractant. Ocaña and Alguacil (1998) concluded that MOC-55 TD is an effective Fe^{3+} extractant at pH values above 1. It is an endothermic reaction. The cupric extraction appeared to be favored over that of the ferric, with the extraction equilibrium reached at 2 minutes 30 seconds. The extraction reaction proved to be a cationic exchange reaction where the Fe^{3+} appeared to be forming complexes of two species that were in the form of FeR_3 and $FeOHR_2$.

Islam et al (1985) used di-o-tolyl phosphoric acid (HDTP,HA)--benzene--20% hexan-l-ol system to extract Ti^{4+}, Fe^{3+} and Fe^{2+} from an acidic sulphate solution. The researchers found the $Ti^{4+}>Fe^{3+}>Fe^{2+}$ trend of extraction efficiency. They recorded the results under similar conditions for each ion. With a number of variables being adjusted to test for the maximum efficiency, they found that the separation of Ti^{4+} and Fe^{3+} was highly favored at the lowest temperature. Using the equations for the separation factors

$$\beta_1 = \frac{E(Ti(VI))}{E(Fe(III))}$$
(2.3)

and

$$\beta_2 = \frac{E(Ti(VI))}{E(Fe(II))}$$
(2.4)

(where β_1= separation factor and E = extraction ratio), it was found that at HDTP concentrations of 0.10M and H_2SO_4 concentrations of 3.50M β_1=175 and at HDTP concentrations of 0.10M and H_2SO_4 concentrations of 0.50M β_1=7800. The results therefore show great separation efficiency only if iron exists in the solution as a divalent cation.

2.4 Extraction of Ti^{4+} from Solutions Using Solvent Extraction

Titanium is one of the important metals in the world. In this context, it is detected as one of the major impurities that co-leaches or co-extracts with alumina during coal fly ash leaching. In this section, we look at various ways that have been investigated for the removal or extraction of titanium from various solutions.

Mellah and Bauer (1995) did work on the extraction of Ti^{4+} from phosphate solution using p-(l, 1, 3, 3-tetramethyl butyl) phenyl phosphoric acid in kerosene. The phosphate solution contained other metals such as cadmium and chromium. The study found that at a phosphoric acid concentration $\geq 7M$, titanium was preferentially extracted over other metals present in the solution. The extraction preference order followed the trend of $Ti > Cr > Cd$.

Islam and Biswas (1978) studied the kinetics and mechanisms of the extraction of Ti^{4+} from an aqueous sulphuric acid. They used D2EHPA (H_2A_2) in benzene (where A = EHPA). The extracted species was found to be in a form of $[TiOA_2]_3$. The reaction of 3 atoms of Ti^{4+} in a stable chain or ring with 3 molecules of the extractant dimer molecules was found to be the rate determining step of the forward reaction. The reaction of $[TiOA_2]_3$ with a molecule of sulphuric acid was found as the rate determining step of the backward reaction. From the experiments, equilibrium constants for both the equilibrium study and rate study were determined.

Allal et al. (1997) found extraction efficiencies of 95% when studying the extraction of Ti^{4+} using TBP in dodecane and decanol, individually and in a mixed system. The 95% extraction efficiency of Ti^{4+} was a result of the mixed system at an HCl concentration of 10M. The mixed system showed fast extraction kinetics reaching equilibrium in 3 minutes.

D2EHPA in n-dodecane can be used to separate Ti^{4+} from Fe^{3+} in a sulphuric acid solution that contains both ions after ilminite leaching. The separation is achieved by the extraction of Ti^{4+} into the organic phase through a two-stage extraction process. A Ti^{4+} extraction efficiency of 99% can be achieved through this method. However, an iron co-extraction can occur and the iron can be stripped from the organic phase using a sulphuric acid solution. At a pH of 4.5, both metal ions can be extracted using F^- from the organic phase (da Silva et al. 2008).

Singh and Dhadke (2002) conducted a study on the extraction of Ti^{4+} using two different extractants: D2EHPA and 2-ethylhexyl prosphonic acid mono-2-ethylhexyl ester (PC-88A),

respectively. With each extractant used, the experiments were performed at different acidity ranges. At 0.003 M D2EHPA and 0.01 M PC-88A in toluene, the experiments were performed at acidity ranges of 0.01 to 0.1 M (low acidity ranges). At 0.1 M D2EHPA and PC-88A in toluene, the acidity ranges were 9.0 to 10.0M (high acidity ranges). The extracted species were determined through the use of slope analysis. $TiOR_2.2HR$ was the extracted species observed in the lower acidity range and $Ti(OH)_3ClO_4.4HR$ was the extracted species at high acidity ranges. It was found that D2EHPA showed more extraction efficiency for Fe^{3+} than PC-88A.

Using trialkyl phosphine oxides (TRPO) in kerosene as an extractant, Remya and Reddy (2004) detected a titanium species of $TiOCl_2 \cdot 2TRPO$ in the organic phase along with two other extracted species of iron and vanadium, $HFeCl_4 \cdot 2TRPO$ and $VO_2Cl \cdot TRPO$. All of the loaded species can be selectively stripped from the organic phase by adjusting the pH of the stripping agent taking into account the required stripping conditions of each metal ion. The extraction was performed from a chloride solution. Among other metal ions that were left in the raffinate was Al^{3+}, which is one of the metals under consideration. As such, TRPO can serve as a good extractant to be applied for the separation of Ti^{4+} and Fe^{3+} from Al^{3+}.

In making use of bis-(2,4,4-trimethylpentyl)dithiophosphinic acid and bis-(2,4,4 trimethylpentyl) monothiophosphinic acid (Cyanex 301 and Cyanex 302) in kerosene, Deep et al. (2001) detected Ti^{4+} extraction efficiencies of $\geq 98\%$ for both extractants. The 98% extraction efficiency was found to be inversely proportional to the concentration of HCl, that is, an increase in the HCl concentration resulted in a decrease in the extraction efficiency. The increase in acid molarity also led to a decrease in Fe^{3+} and Al^{3+} extraction. HNO_3 and H_2SO_4 also display a similar trend.

In the work by Saji and Reddy (2003) 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene was used as an extractant for Ti^{4+} from an acidic chloride solution. The other metal ions that made up the solution were Mg^{2+}, Al^{3+}, V^{5+}, Cr^{3+}, Mn^{2+}, and Fe^{3+} whose extractions were also investigated as a function of HCl concentration. The extraction and separation of Ti^{4+} from a HCl concentration of 2M using 0.2M concentration of EHEHPA in kerosene, an O/A phase ratio of 1:1 and using 2M H_2SO_4 plus 2% H_2O_2 as a stripping agent showed positive results.

Summary

The studies reviewed in this section display the significant impact of various parameters on the extraction efficiencies of aluminium, iron and titanium. The reviewed literature expresses the importance and efficient use of solvent extraction as a step in a purification method. The use of solvent extraction also includes the choice of a relevant extractant and diluent to use for the separation of specific solutes in aqueous solution. The extractant and diluent that were found relevant for the separation of aluminium, iron and titanium from a 2-step CFA leach liquor were Primene JMT as an extractant and kerosene as a diluent (Martjie, 2005). Factors affecting the extraction efficiency of Primene JMT are also critical. Hence, factors such as phase separation, extractant concentration, O/A ratio and the pH solution will be considered for the test work in this study. These factors play a vital role in the solvent extraction of aluminium, iron and titanium. Furthermore, to attain highly pure solid products, extensive methods such as precipitation and crystallization were reviewed and considered for application in the subsequent test work.

3.1 Introduction

This chapter discusses the preparation of materials as well as the experimental and analytical methods used in the study.

3.2 Experimental

3.2.1 Coal Fly Ash

CFA containing 30.5wt % alumina and 56.1wt% silica was used in this study. The fly ash was characterized by investigating the surface morphology and undertaking chemical analysis. A summary of the full chemical composition of the CFA sample is given in **Table 3.1**. The morphological analysis of CFA was carried out using a Scanning Electron Microscope (SEM) and the precipitate analysis was carried out using a Powder X-Ray Diffractometer. An X-Ray Fluorescence (XRF) spectrometry was used for chemical composition analysis and ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) was used for elemental analysis. The coal fly ash used in the process was obtained from Kendal Power station; a subsidiary of Eskom.

Table 3.1 Chemical composition of CFA

Element	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Cr_2O_3	NiO	*L.O.I
Wt.%	56.1	30.52	0.4	3.25	0.03	1.43	5.03	0.24	0.71	1.67	0.6	0.03	0.01	1.43

*L.O.I – Loss on Ignition

3.2.2 Reagents

Distilled water, analytical grade sulphuric acid (98% w/w), Primene JMT extractant, NH_4OH, NaOH, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, Kerosene diluent and metallic iron filings were used in the

experiments. The reagents were purchased from Merck and Sigma Aldrich whilst the Primene JMT extractant was obtained from Dow Chemicals. All the reagents used in this study were of analytical grade and were used as received without further purification.

3.2.3 Leach Liquor Generation

The leach liquor was obtained using a 2-step leaching process developed by Shemi et al., (2012) from a research undertaken at the University of the Witwatersrand, South Africa. The first step involved the use of H_2SO_4 of 6M concentration to extract alumina from CFA using a 4:1 liquid to solid ratio for 10.2 hours at a temperature of 75℃, with constant agitation. The residue from the first step leach process was made into pellets comprising 50% CFA residue, 40% ($\pm$212µm) coal and 10% $CaCO_3$. The pellets were then sintered at 1150℃ for 180 minutes. The pellets were then finely ground to sizes of $\pm$212µm then leached again using the same parameters applied in the first stage leaching process. The two leach liquors were then combined and analyzed for metal content. **Table 3.2** shows a concentration of 10117.50ppm for Al^{3+}; 2591.44ppm for Fe^{3+}; 411.77ppm for Ti^{4+}; 139.63ppm for Fe^{2+}; 9.20ppm for Na^+; 4.01ppm for Ca^{2+} and 0.56ppm for Si^{4+}. The chemical composition shows Fe and Ti as the two major impurities at high levels of concentration. At these levels, the two impurities are a threat to the chemical quality of the final alumina product, which should ideally match the smelter grade alumina specifications as shown on **Table 2.3**. These impurities need to be removed for the production of alumina of smelter grade specifications. Silicon, calcium and sodium were neglected during calculations due to insignificant concentration values that were expected to have little to no effect on the purity of the major metals investigated. Therefore, Fe, and Ti are the two main impurities investigated in this work.

Table 3.2 Concentration of the CFA leach solution

Element	Fe^{2+}	Fe^{3+}	Al^{3+}	Ti^{4+}	Si^{4+}	Ca^{2+}	Na^+
Concentration (ppm)	139.63	2591.44	10117.50	411.94	0.56	4.01	9.20

The leach liquor obtained from the 2-step leach process was used for the purification experiments. Solvent extraction of Ti from the CFA leach liquor was carried out using a

mixer/settler separating funnel and an Erlenmeyer flask. Primene JMT extractant and kerosene, an organic diluent, were used in the experiment. The aqueous and organic phases were mixed in different ratios, agitated, settled and separated using the afore-mentioned apparatus. The parameters tested included extractant concentration, contact time and organic to aqueous (O/A) ratio. For each test, the mixture was placed in a shaking water bath set at a temperature of 70°C and agitation rate of 120 rpm. The extractant levels tested included 10 % v/v Primene™ JM-T into 90 % v/v kerosene; 15 % v/v Primene™ JM-T) into 85 % v/v kerosene; 30 % v/v Primene™ JM-T into 70 % v/v kerosene; and 50 % v/v Primene™ JM-T into 50 % v/v kerosene. For contact time, the following times were tested: 15, 30 and 60 minutes. For the A: O ratio tests, 1:1, 2:1, 4:1 and 8:1 ratios were used in the experiment. The loaded organic phase was set aside for Ti stripping and the raffinate solution set aside for aluminium crystallization.

After the optimum levels of the purification process at the solvent extraction stage were determined, the second stage of the test work was then undertaken. This stage involved the testing of two process routes for the efficient separation of Fe from Al in the aqueous phase. These process routes were selected based on the preliminary solvent extraction results that indicated that the Fe^{3+} sulphate complex formed in the highly acidic conditions used in the 2-step leach process required much higher pHs to load onto the organic phase. Since the leach solution is highly acidic, addition of alkaline reagents to increase the pH would have a significant impact on the process costs.

Route 1: The first route involved the addition of metallic iron as a reducing agent to the leach solution before solvent extraction in order to try to reduce most of the Fe^{3+} into Fe^{2+}. The process was developed with due consideration to reagent consumption; if all of the Fe^{3+} is reduced to Fe^{2+} then there will be no Fe loading onto the organic phase, thus, reducing the need for a 2-stage stripping process for Ti and Fe. A 2-stage stripping process would involve the use of $(NH_4)_2CO_3$ for the stripping of Fe^{3+} from the Ti^{4+} organic solution, adding more reagent consumption and costs to the process. The development of route 1 was done with the aim of using fewer reagents, therefore decreasing total reagent consumption and costs of the whole purification process. A 2:1 ratio of Fe^{3+} to Fe in the form of metallic fines was applied in both approaches, as shown in the following reaction equation:

$$2Fe^{3+} + Fe \leftrightarrow 3Fe^{2+} \tag{3.1}$$

This was then followed by solvent extraction in order to remove the titanium ions, then crystallization of Al^{3+} and lastly the precipitation of Fe^{2+}. **Figure 3.1** shows the flow sheet for the test works that were undertaken.
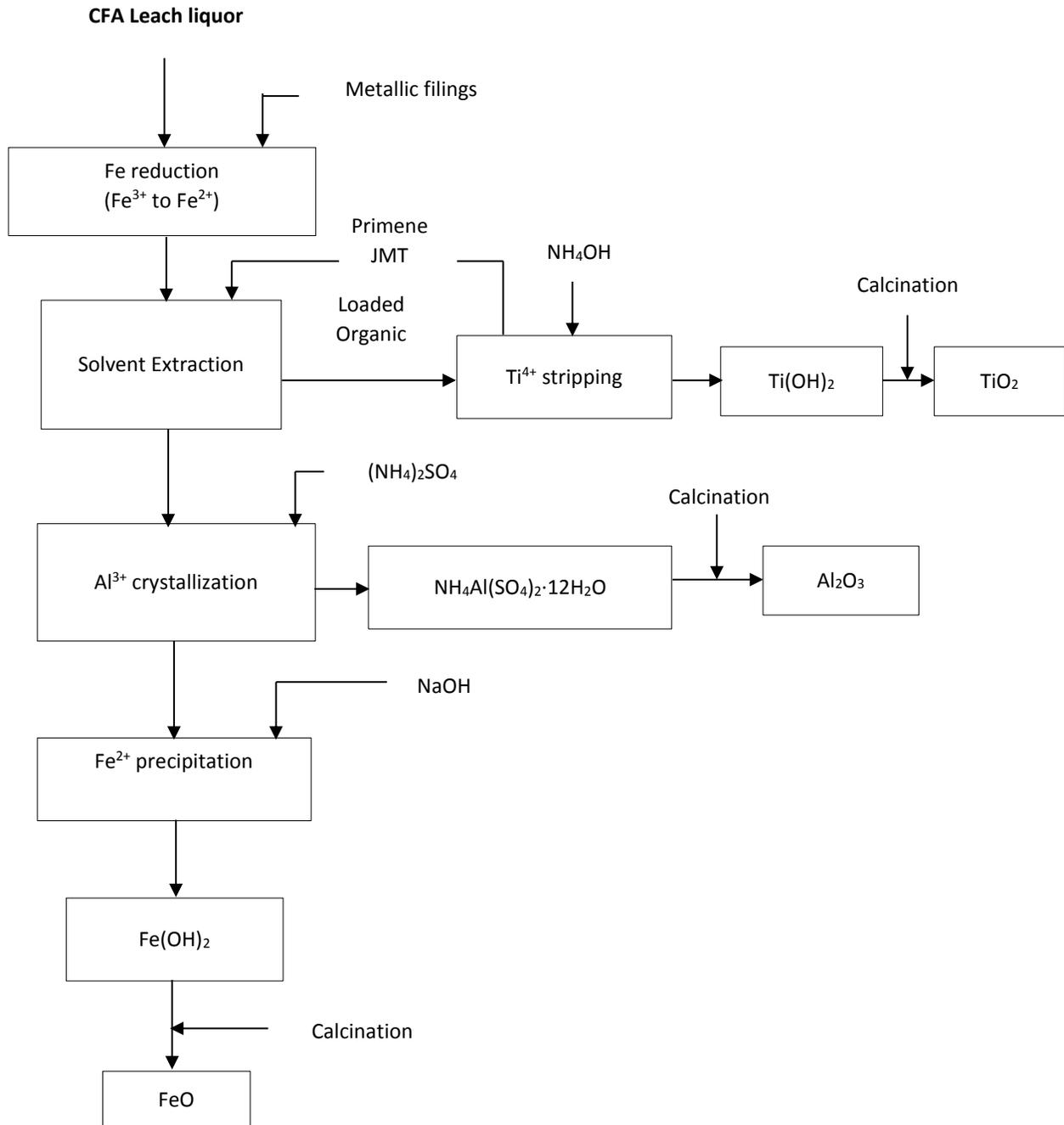
Figure 3.1 A flow diagram of the Fe^{3+} reduction prior to the solvent extraction process.

Route 2: This process route involved performing the solvent extraction process before adding metallic iron filings to the raffinate in order to reduce the Fe^{3+} to Fe^{2+}. The resultant solution then underwent crystallization of Al^{3+}, and the subsequent precipitation of Fe^{2+}. This route was undertaken with due consideration to process costs; if some of the Fe^{3+} ions could be taken out during the solvent extraction process then less metallic iron filings would be needed for the Fe^{3+} to Fe^{2+} reduction process. Although the process would involve double stripping, using less metallic iron filings would offer an advantage of decreasing process costs. However, a comparative cost analysis for the two routes (route 1 and route 2) would have to be conducted since the costs of reagents for stripping could outweigh the precipitation costs. **Figure 3.2** shows the flow sheet for the proposed test works for route 2.
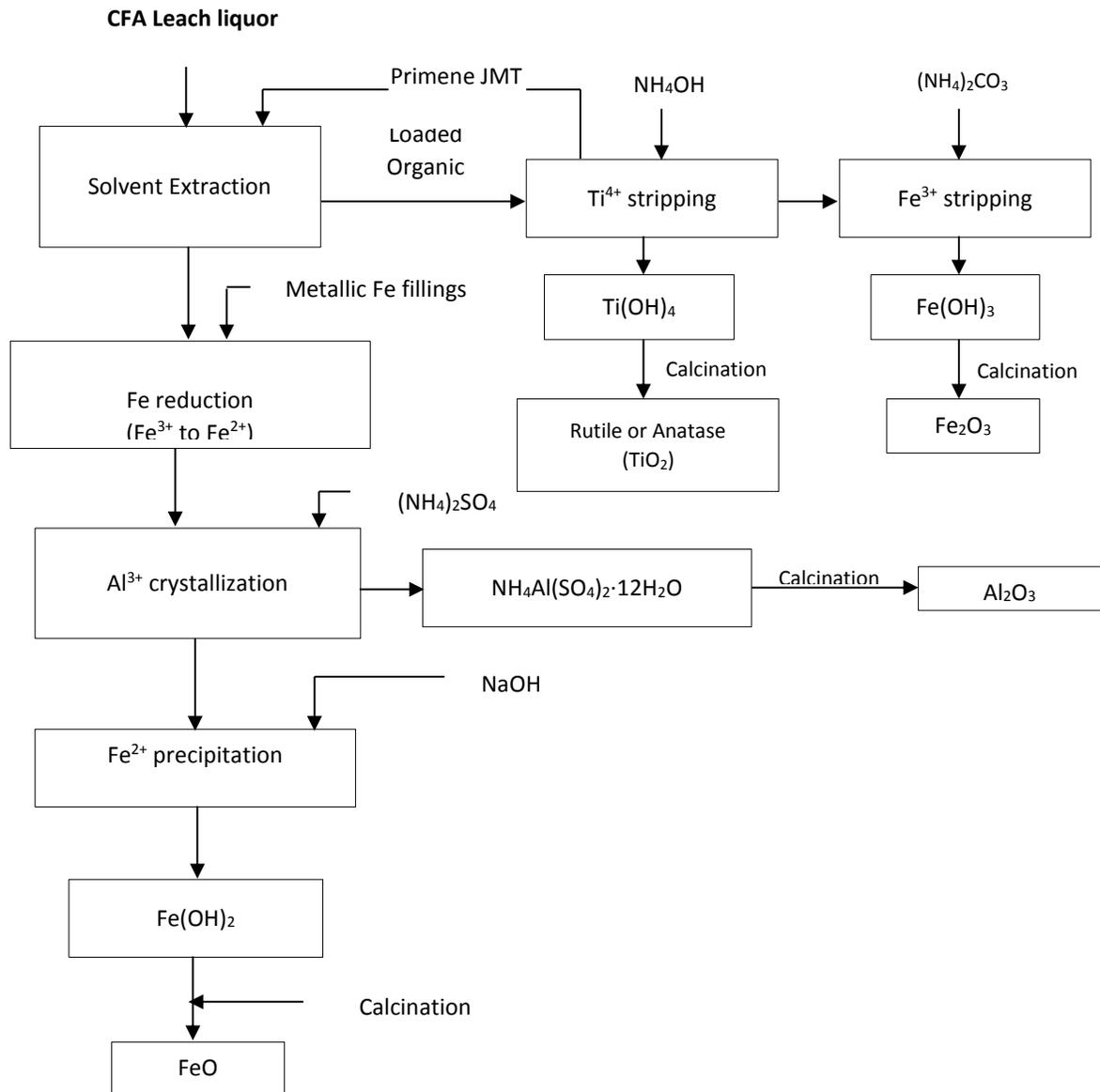
Figure 3.2 A flow diagram of the Fe^{3+} reduction post-solvent extraction process.

It is important to note that for both process routes undertaken, titanium ions were found to load onto the organic phase so their extraction was not of significant concern.

3.2.4 Analysis

The concentrations of Al^{3+}, total Fe and Ti^{4+} in the aqueous phase were determined using ICP-EOS. The concentrations of Fe^{2+} and Fe^{3+} were determined using a redox titration method. In this analysis, standardized potassium dichromate ($K_2Cr_2O_7$) was used to determine the concentration of Fe^{2+} from the 2-step leach liquor solution before and after solvent extraction. The very same

method was applied in determining the concentration of Fe^{2+} after the reduction process. The concentration of Fe^{3+} was obtained by subtracting the concentration of Fe^{2+} from the concentration of total Fe, determined through ICP-EOS. XRD and XRF were used for the analysis of the solid products.

3.2.5 Stripping, Precipitation and Calcination

Ti was stripped by mixing 100 ml of Ti loaded onto the organic phase with 100 ml of 1.14M NH_4OH (Matjie et al., 2005) using a 250ml Erlenmeyer flask. The mixture was transferred into a 400 ml separation funnel, placed in a shaking water bath, agitated at 110 rpm at a temperature of 70°C for 20 minutes. After agitation, phase separation and precipitate formation in the aqueous phase, the precipitate was filtered off and dried at 90 °C for 2.5 hours. The $Ti(OH)_2$ precipitate was calcined at different temperatures of 400°C, 600°C and 750°C for 3 hours and then analyzed using XRD.

Aluminium was crystalized by adding $(NH_4)_2SO_4$ (Matjie et al., 2005), an inorganic salt crystallization precipitant, to the raffinate solution at a pH of 1.7. The solution was first kept at a temperature of 70°C for 20 minutes, and then placed in a cooling bath at 10°C for 1 hour to facilitate the crystallization process according to the reaction:

$$2Al_2(SO_4)_3 + 2(NH_4)_2SO_4 + 12H_2O \longrightarrow 4(NH_4)Al(SO_4)_2 \cdot 12H_2O \qquad (3.2)$$
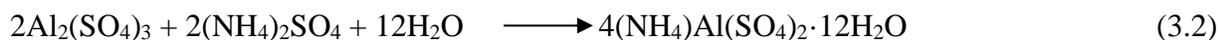
The resulting crystals were filtered off and oven-dried at a temperature of 90°C for 3 hours. The filtrate was kept aside for Fe precipitation. One portion of the dried crystals was analyzed using XRD. The other portion was calcined at 1100°C for 3 hours and analyzed using XRF. The calcination of the alumina product obtained in equation 3.2 proceeded according to reaction (Somiya et al., 2003):

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O \xrightarrow{\text{Pyrolysis}} Al_2O_3 + 2NH_3 + 4SO_3 + 13H_2O \qquad (3.3)$$

Fe^{2+}, in the filtrate obtained from the aluminium crystallization process, was precipitated by adjusting the filtrate pH to 7.5 using 12.5M NaOH. The precipitation of Fe^{2+} after Al^{3+} crystallization was based on the Monhemius (1977) diagram for precipitation of metal salts. Fe^{2+} precipitation proceeded according to the reaction:

$$FeSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Fe(OH)_2 \qquad\qquad (3.4)$$
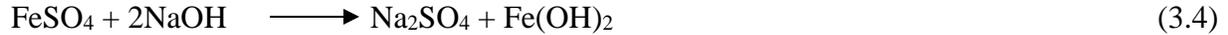
The iron precipitate was filtered off, washed with distilled water and oven-dried at 90°C for 3 hours. Part of the dried precipitate was analyzed using XRD. The other part was calcined at 1100°C for 3 hours and analyzed using XRF.

The concentrations of the reagents used and the level of different process parameters applied were as suggested by literature (Martjie, 2005;Li et al ,2011; Yao et al,2014; Sibanda et al, 2016).

3.3 Cost Analysis

The cost analysis was based on the total reagent consumption of the total leach liquor purification process per tonne of smelter grade alumina produced. The cost analysis was undertaken with due consideration for the quantity of Primene JMT and Kerosene used in the solvent extraction process for the production of 1 tonne of alumina per each process route. The reduction costs were also calculated, taking into account the amount of metal iron filings used to produce a tonne of alumina for each route. Furthermore, there was a cost analysis for the stripping stage. In addition, the crystallization and precipitation costs were analyzed to finalize the comparative cost for both routes. The cost analysis was based only on reagent consumption per route tested.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

Studies have revealed that the application of solvent extraction for the purification of CFA leach liquor is paramount (Chou and Lin, 1986; Martjie et al, 2005). As part of the CFA leach liquor purification process, solvent extraction is used for the removal of titanium and iron impurities from aluminium-rich CFA leach liquor. However, many factors can affect the solvent extraction process. These factors have an effect on the optimum performance of the extractant used in the solvent extraction process. Factors may include the type of diluent used, temperature, pH of the aqueous solution, organic to aqueous ratios and contact time (Schrotterová and Nekovár̆, 1999; Lakshmanan et al., 1975).

The use of primary amines as extractants has proven to be more effective in the production of desirable extraction results. Schrotterová and Nekovár̆ (1999) and Martjie et al. (2005) used Primene™ JM-T for the removal of iron and titanium from aluminium containing sulphate leach solution. The results gave relatively high alumina extraction efficiencies of 99.4%. In this study, Primene™ JM-T was used as an extractant in kerosene for the solvent extraction of metal ions. Kerosene was preferred as the most cost effective and environmentally safe diluent. It has displayed maximum Al^{3+} extraction efficiency during most comparative tests with other diluents (Mohapatra et al, 2007; Biswas and Karmakar, 2013; Alguacil et al, 1987; Mishra et al, 2011). Furthermore, other purification techniques such as precipitation and crystallization were applied to increase the purity of the overall alumina product. This chapter presents and discusses the results of these test works.

4.2 Solvent Extraction

Solvent extraction (Gani et al., 2012) involves the contact of two immiscible liquids such as organic and aqueous liquid phases with the aim of separating two or more solutes from other unwanted solutes in a solution. **Table 3.2** in Chapter 3 shows the concentrations of the main constituents in the CFA leachate. The leach liquor shows a high content of Al, Fe and Ti, thus suggesting the need for the use of solvent extraction to separate Al from Ti and Fe in order to

generate a highly pure alumina product. Primine JMT was found to be the most effective extractant for the separation Ti and Fe from the Al rich leach liquor (Martjie et al, 2005). Kerosene was also found to be the established diluent to use. The solvent extraction testwork was conducted in accordance with the procedure mentioned in chapter three to determine the optimum extraction efficiencies. The tested parameters include the effect of various Primene™ JM-T concentrations, contact times and the O/A phase ratios. The tested concentrations, contact times and O/A ratios were as illustrated in **Chapter Three**.

4.2.1 Effect of Extractant Concentration and Contact Time on Al Extraction

The effect of Primene JMT extractant concentration and contact time on the extraction of Al is presented in **Figure 4.1**. The results shown indicate that an increase in extractant concentration had no significant effect on aluminium loading onto the organic phase, the percent extraction remained largely below 0.5%. The results clearly indicate that Primene JMT has no affinity for Al ions. It is expected therefore, that when processing the CFA leach liquor solution, aluminium will remain in the aqueous phase rather than load onto the organic.

According to Kislik (2012), one of the major contributing factors for the metal ions uptake by the extractant is the concentration gradient. High concentration of the extractant favors faster loading of the metal ions onto the organic. This is shown to be true for 50% Primene JMT concentration in the first 15 minutes. The results also show a slight decrease in the Al loading after 30 minutes for the 50% extractant concentration. However, the small percentage drop in extraction from 30 to 60 minutes (0.5-0.45%) is statistically insignificant. indicating that maximum loading was really attained in the first 15 minutes. The 10% extractant concentration showed slower loading kinetics in the first 15 minutes. However, the overall loading capacity similar to that obtained on the 50% extractant concentration in 15 minutes was obtained in 60 minutes. The 50% extractant maximum loading is attained over a shorter period, whilst that of the 10% extractant concentration is attained over a longer period which therefore, supports the role of the concentration gradient in the reaction kinetics (Kislik , 2012).

These results indicate that the maximum loading that could be attained by both the 50% and 10% extractant concentration is the same; the only difference being the time required to reach

maximum loading. Futhermore, the loaded amount is very low, which is also a true reflection of the lack of affinity of the extractant for the Al ions.
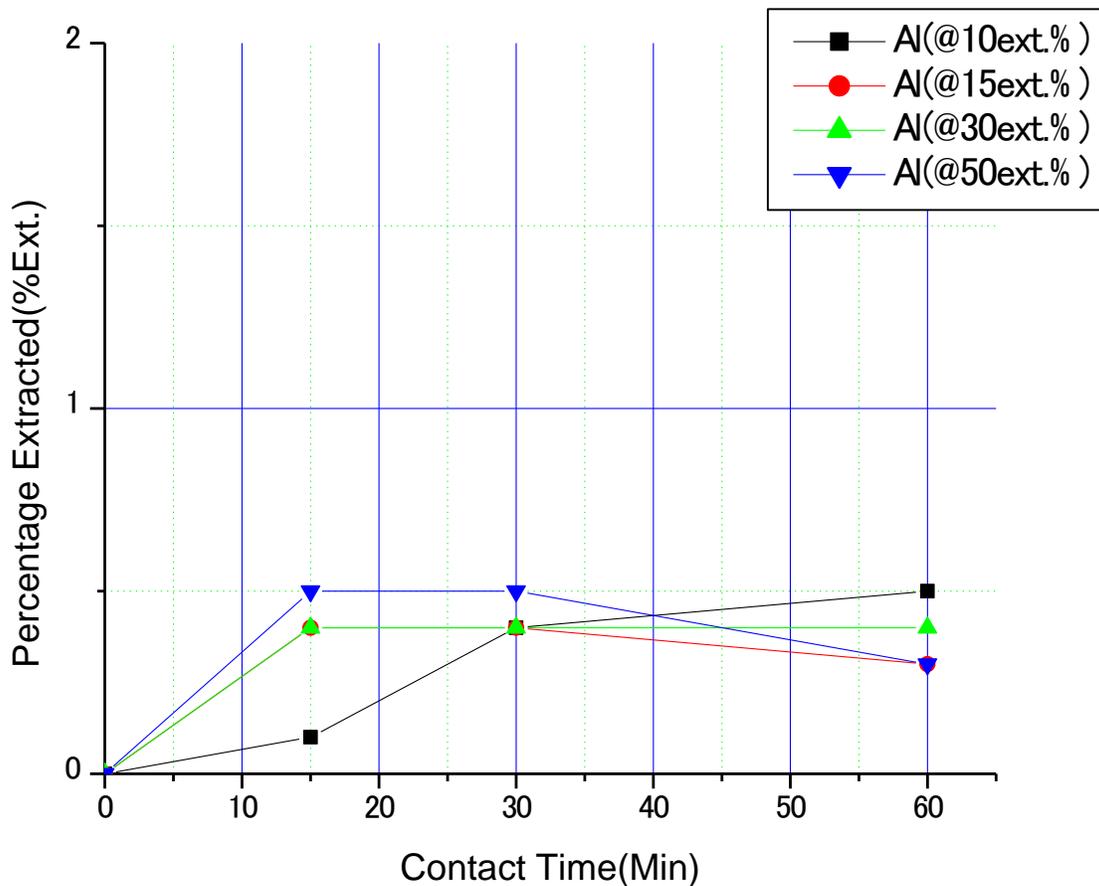
Figure 4.1 The effect of Primene JMT extractant concentration and contact time on Al extraction

4.2.2 Effect of Extractant Concentration and Contact Time on Fe Extraction

The effect of Primene JMT extractant concentration and contact time on the extraction of Fe is presented in **Figure 4.2**. The results show that for all the extractant concentrations tested, the equilibrium point for Fe extraction was attained within the first 15 minutes. Fe loading kinetics were also observed to be rapid in the first 15 minutes for all extractant concentrations. The

change in the metal percentage extraction in the last 30 minutes was noted to vary with the different levels of extractant concentration. The variation however, is not very significant, and it is likely that the most Fe that can be extracted from the solution occurs in the first 15 minutes regardless of the extractant concentration.

The extractant concentration of 10% displayed the highest extraction efficiency of 19.2% within the first 15 minutes. Therefore, optimum Fe extraction efficiencies were achieved at minimum contact time and low extractant concentration. These results are very important for process development as they impact positively on the throughput and operational costs.
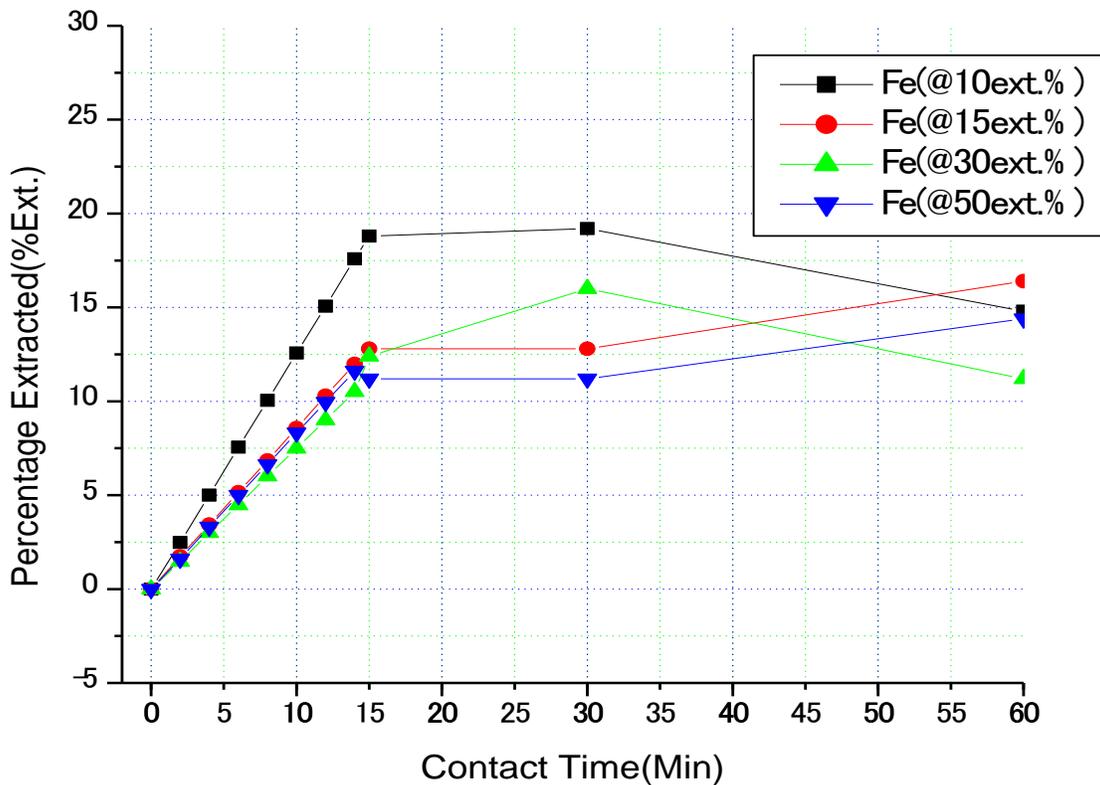
Figure 4.2 The effect of Primene JMT extractant concentration and contact time on Fe extraction

 Seeley et al. (1981) suggests that poor extraction of Fe could be due to the possibility of the formation of some Fe complexes in the aqueous phase that have a lower affinity for the extractant in the organic phase. Chou et al. (1986) further suggest that the poor loading of iron

onto the organic phase is caused by the excess H_2SO_4, which converts the loading Fe-$(RNH_3^+)(SO_4)_2^{2-}$ complex into a poor loading Fe-bisulfate ($FeNH_4(SO_4)_2$) complex. To avoid the Fe-$(RNH_3^+)(SO_4)_2^{2-}$ to Fe-bisulfate complex conversion, the pH of the organic phase must be increased to ranges between 6 and 7. Therefore, Chou et al. (1986) suggest the use of extra reagents to increase the pH of the organic phase. This however, is in contradiction of one of the main objectives of this work, which is to develop an economically feasible process. By conducting the solution purification at the original leach liquor pH of 0.1, neutralization through addition of new reagents that could result in higher operation costs is avoided. This therefore, motivates for identification of the amount of loading and non-loading species of Fe at pH level 0.1 and the subsequent use of other methods for the overall removal of Fe from solution. The identification of the quantity of Fe species has been noted in Chapter 3, section 3.2.3.

According to Li et al. (2011), the Primene JMT primary amine extractant can extract Fe^{3+} onto the organic phase but this is only possible at high pH levels due to the formation of the non-loading bisulfate at very acidic conditions. For this work, the tests were conducted at pH 0.1; highly acidic conditions, which therefore, attests to the minimal amount of Fe^{3+} loading displayed in **Figure 4.2**. This implies that the unloaded Fe^{3+} and the rest of the Fe^{2+} is left in the aqueous phase along with the other metal ions such as Al^{3+} that have little to no affinity for the Primene JMT (Li et al., 2011). The observations made by Li et al. (2011), Chou et al. (1986) and Seeley et al. (1981) suggest that the Fe in the aqueous phase exists as both Fe^{2+} and Fe^{3+} species after solvent extraction. These contaminants will impede the generation of smelter grade alumina and thus, alternative methods for the removal of these Fe species have to be applied.

The two approaches proposed for the removal of Fe from the aqueous solution in this work therefore, include the reduction of Fe^{3+} to Fe^{2+}. The first approach will consider the reduction of the Fe^{3+} species into Fe^{2+} prior to solvent extraction for titanium removal. This helps to avoid any possibility of Fe^{3+} co-loading with Ti^{4+} onto the organic phase during the solvent extraction stage. Although the amount of loaded Fe^{3+} is not expected to be high if reduction to the Fe^{2+} state is not undertaken, it would still reflect an impure organic solution and would thus necessitate a 2-step stripping process in order to obtain pure Ti^{4+}. This would further require the use of more reagents thus, adding to the overall operational costs of the process.

The second approach firstly applies solvent extraction to remove titanium ions and any iron ions followed by the reduction of residual Fe^{3+} to Fe^{2+}. This process would require the use of more reagents resulting in additional process operational costs. In both approaches, aluminium will be crystallised out and Fe^{2+} precipitated using $(NH_4)_2SO_4$. Ti^{4+} will be stripped from the organic phase using NH_4OH.

4.2.3 Effect of Extractant Concentration and Contact Time on Ti Extraction

The effect of Primene JMT extractant concentration and contact time on the extraction of Ti is presented in **Figure 4.3**. The results shows no significant changes in Ti extraction with an increase in extractant concentration. This is due to the titanium bisulfate complex $Ti(OH)_3HSO_4$, which is the dominant titanium species in acidic conditions (Sole, 1999).The $Ti(OH)_3HSO_4$ complex is strongly extracted by Primene JMT into the organic phase (Rushwaya et al., 2017) according to the reaction:

$$(RNH_3)_2SO_4 + Ti(OH)_3HSO_4 \rightarrow (RNH_3)_2SO_4 \cdot Ti(OH)_3HSO_4 \tag{4.1}$$

where $(RNH_3)_2SO_{4(org)}$ represents the protonated Primene JMT. The results demonstrate that Primene JMT has a high affinity for Ti even though literature shows that most of the work on Ti solvent extraction has been conducted largely using phosphonic acids (Zhu et al., 2011). **Figure 4.3** displays that Ti extraction reached maximum extraction by the 15th minute for all extractant concentrations tested with extraction efficiencies ranging between 90-98%. Thereafter, the loading efficiency largely remained constant to the 60th minute. The results further show that the change in the concentration level of Primene JMT in the range of 10 to 50% did not have much effect on the amount of Ti loaded onto the organic phase. In addition, maximum extraction was achieved using the 10% Primene JMT within the first 15 minutes. It is possible that the low content of titanium ions present in the feed solution led to the efficient and effective removal of these ions from the solution, even with the application of lower extractant concentration levels. This also validates the insignificant effect of the extractant concentration level on the Ti ions extraction.

The results show that Primene JMT, as used in kerosene diluent in this study, is an effective extractant for the separation of Ti^{4+} from Fe and Al metal ion species in CFA leach liquor (Mohapatra et al, 2007; Biswas and Karmakar, 2013; Alguacil et al, 1987; Mishra et al, 2011).
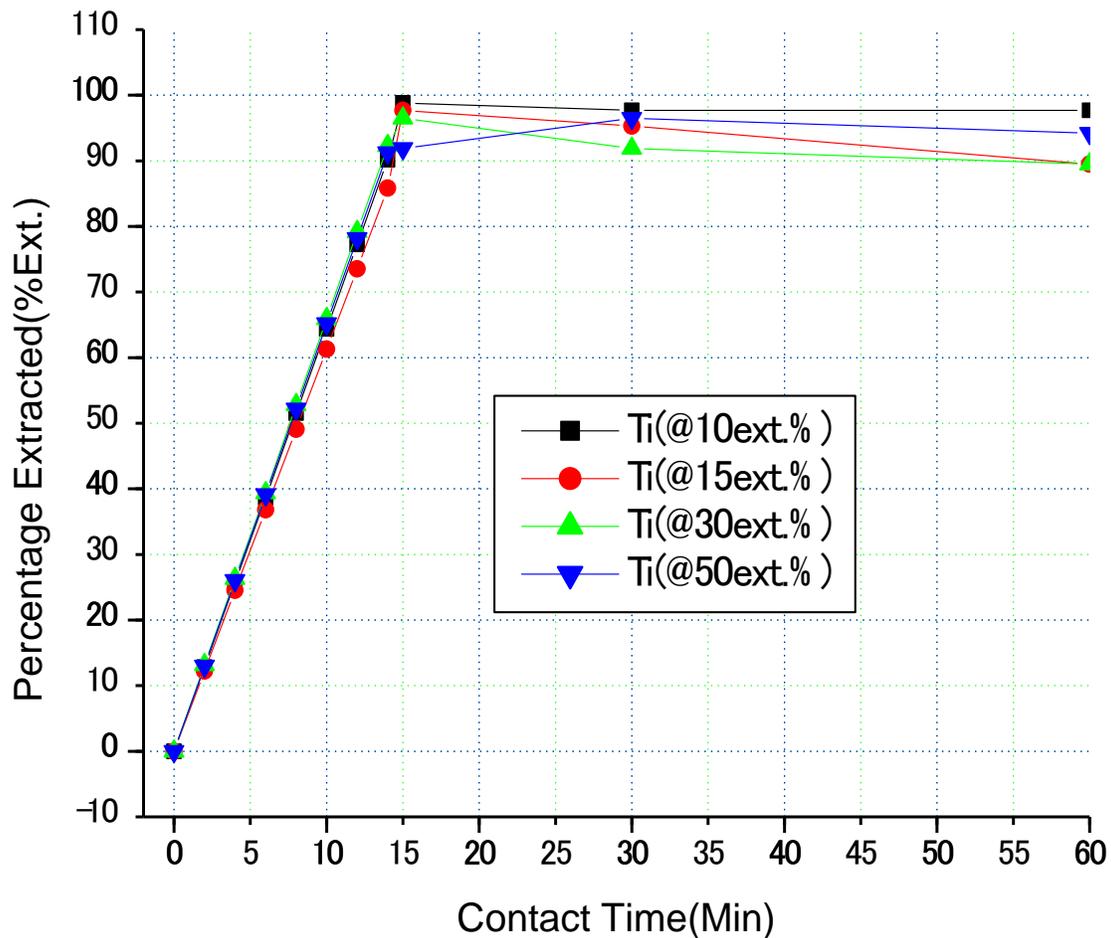
Figure 4.3 The effect of Primene JMT extractant concentration and contact time on Ti extraction

Figure 4.1, **Figure 4.2** and **Figure 4.3** have evidently displayed the difference in Primene JMT affinity for aluminium, iron and titanium, with titanium loading more efficiently than aluminium and iron. Therefore, the results lead to solvent extraction employed solely for the removal of titanium and a different route employed for the removal of iron to ultimately acquire smelter grade aluminium products. The extractant concentration of 10% Primene JMT and contact time of 15 minutes were therefore, adopted as the pertinent solvent extraction parameter levels as they

were observed to be the parameters that best suited the effective loading of Ti ions onto the organic phase.

Table 4.1 shows the loading of Al^{3+}, $Ti^{4+,}$ Fe^{2+} and Fe^{3+} ionic species onto the organic phase. The results were obtained after using 10% Primene JMT concentration and a contact time of 15 minutes as these had been identified as pertinent solvent extraction parameter levels. The results validate the results shown in Figures 4.1, 4.2 and 4.3. They show a maximum loading efficiency for Ti^{4+} and a very poor loading efficiency for Al^{3+}, Fe^{2+} and Fe^{3+} at 10% Primene JMT concentration and contact time of 15 minutes. These results support Li et al. (2011)'s suggestion that Fe^{2+} does not load onto the primary amine; the Fe^{2+} readily forms the non-extractable $FeSO_4$, which cannot be extracted by the amine. The partial loading of Fe^{3+} is due to the high concentration of hydrogen ion, which results in the formation of the none extractable Fe^{3+} - sulphate complex ($FeHSO_4^{2+}$) instead of the extractable $Fe(OH)SO_4$ (Li et al., 2011). It can, therefore, be confirmed that iron in the aqueous phase exists as both the partially loading Fe^{3+} and the non-loading Fe^{2+} species.

Table 4.1 Solvent extraction using 10% extractant at a 15 minutes contact time

Element	CFA Leach Liquor (ppm)	After solvent extraction (ppm)
Fe^{2+}	139.63	139.63
Fe^{3+}	2591.44	2104.25
Al^{3+}	10117.50	10087.78
Ti^{4+}	411.77	13.54

4.2.4 Effect of Extractant Concentration on Phase Separation Time

Phase separation time is the time taken for the complete separation of an aqueous and organic phase after equilibrium is reached during solvent extraction (Gani et al, 2006). The phase separation time is an important factor that determines the time it takes for the solutes to be evenly distributed between the aqueous and organic phase. Therefore, it determines the kinetics of the process (i.e. the shorter the phase separation time, the faster the kinetics of the process) (Kislik, 2012). Various factors can affect the phase separation time. These include: the temperature of the solvent extraction mixture, the type of extractant used and the concentration of the extractant used. In this study, the effect of extractant concentration on the phase separation time was investigated. The extractant concentration was chosen as an immediate factor to study since the loading efficiency of the different concentrations also formed part of the scope of the current work. Factors affecting extraction were not studied as the study was focused on process development rather than process optimization.

The effect of extractant concentration on phase separation time during the solvent extraction of metal species from CFA leach liquor is shown in **Figure 4.4**. The figure shows a separation time of 60 seconds at 10% extractant concentration and shows a 40% increase in separation time duration at 15%. The separation times further show a significant increase in duration of 500% and a 1003% at 30% and 50%, respectively, from the 10% extractant concentration.

The rate of separation between the two phases is directly proportional to the rate of coalescence and the increase of interfacial surface tension. Kerosene, as a diluent, increases the interfacial surface tension, which when increased in proportionality to the Primene JMT will positively affect the coalescence rate of the extractant, giving a shorter separation time between the organic phase and aqueous phase (Kilslik, 2012). That is, the increase in extractant concentration (that is the decrease of kerosene in the extractant) will increase the duration of the separation time, negatively affecting the process economically due to longer production times. According to Li et al (2011), primary amines have low solubility in kerosene, resulting in a frequent appearance of a third phase. To eliminate the formation of the third phase, modifiers such as alcohols have to be employed as they increase the solubility of primary amines in kerosene (Martjie, 2005). The high efficiency of Primene JMT extractant at a concentration of 10%, within a minimum separation time, displays promising process results. Therefore, the phase separation time of 60 seconds at an

extractant concentration of 10% was adopted as the pertinent parameter level for operating the solvent extraction process.
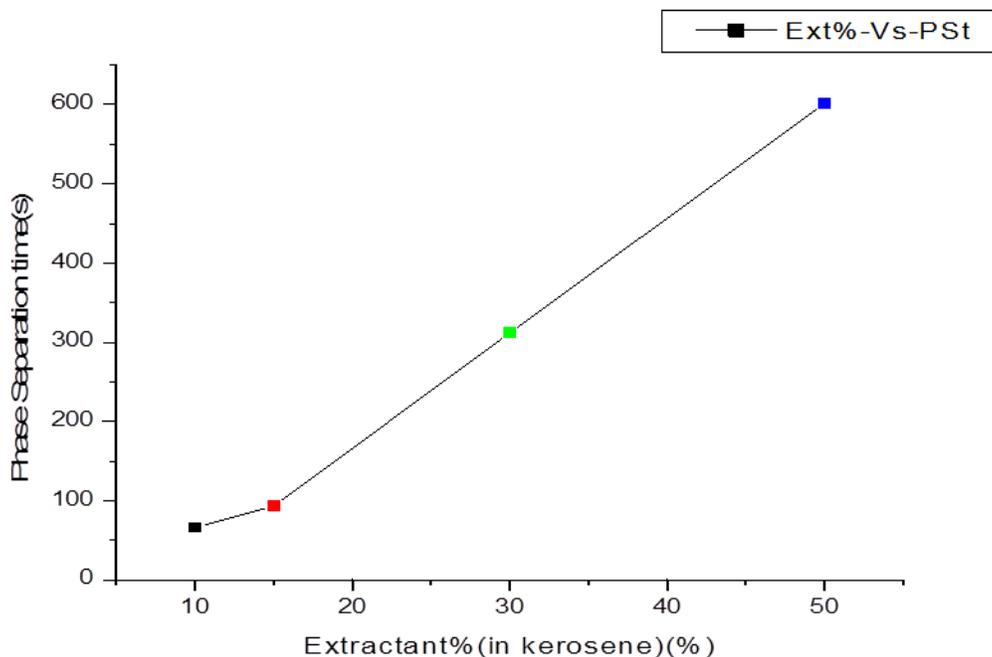
Figure 4.4 Effect of extractant concentration on phase separation time

4.2.5 Effect of organic to aqueous (O/A) ratio

High organic to aqueous (O/A) ratio results in high overall extraction and high extraction rates. However, the high O/A ratio increases the amount of extractant used. This negatively affects the overall process costs. Table 4.2 shows the results of the organic to aqueous ratios for Ti^{4+} and Fe^{3+} extraction. The O/A ratios of 1:8, 1:4, 1:2 and 1:1 were tested using contact time of 15 minutes and 10% extractant concentration. The results show that the extraction efficiency increased with an increase in the O/A ratio. This therefore demonstrates that an increase in extractant concentration results in higher extraction efficiencies. Both the extraction of Ti^{4+} and Fe^{3+} displayed similar results: extraction efficiency increasing with an increase in the O/A ratio. Ti^{4+} showed the lowest extraction efficiency of 13.32% at an O/A ratio of 1:8 and a maximum extraction efficiency of 96.51% at an O/A ratio of 1:1; displaying an exceptional extraction

efficiency improvement of 83.19%, with an increasing O/A ratio. Fe^{3+} also showed a 17.20% extraction efficiency improvement, with the lowest extraction efficiency at an O/A ratio of 1:8 and the highest at an O/A ratio of 1:1. The increase in the extractant ratio also affects the loading kinetics; the higher the O/A ratio, the faster the loading kinetics, until equilibrium is reached in a number of certain counter-current loading stages. The highest extraction efficiency was achieved at an O/A ratio of 1:1 for both metal ions. To determine the economic feasibility of the process as the extractant concentration was increased, the cost of the extractant was considered in relation to the extractant concentration increase and the extraction efficiency. Therefore, the 1:1 ratio was used in the construction of McCabe-Thiele diagrams for Ti and Fe solvent extraction as shown in **Figure 4.5** and **Figure 4.6**, respectively.

Table 4.2 Extraction efficiencies for Ti and Fe extraction at different organic to aqueous ratios

O/A Ratio	Ti^{4+} Extraction (%)	Fe^{3+} Extraction (%)
1:8	13.32	1.61
1:4	72.14	5.61
1:2	81.32	6.03
1:1	96.51	18.81

The McCabe-Thiele diagram can be used to determine the number of theoretical counter-current stages to effect the required level of extraction using the equilibrium curve (McCabe and Smith, 1976). Therefore, in this work the McCabe-Thiele diagrams were applied to determine the number of theoretical counter-current stages that were required to achieve the reported Ti and Fe levels of extraction in **Figure 4.2** and **Figure 4.3**. The efficiency of each theoretical counter-current stage was determined for both Ti and Fe, respectively.

The McCabe-Thiele diagram in **Figure 4.5** shows that Primene JMT has a strong affinity for Ti and that maximum Ti loading can be achieved in four counter-current stages at an O/A ratio of 1:1. The calculated extraction efficiencies based on the diagram suggests a cumulative Ti^{4+} extraction efficiency of 15.71% in the 4th stage, 28.15% in the 3rd stage, 72.34% in the 2nd stage and 96.51% in the 1st stage (calculations shown in Appendix A).
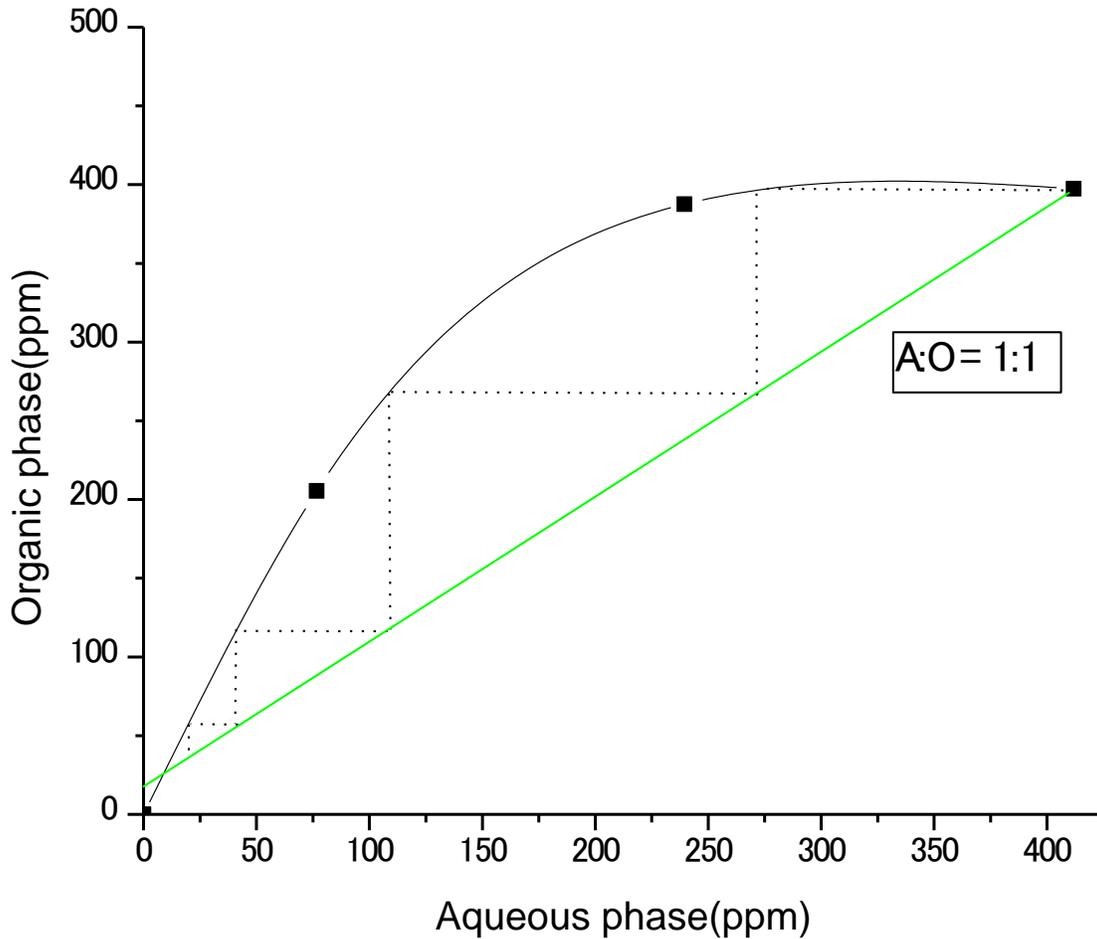
Figure 4.5 The McCabe-Thiele diagram displaying the theoretical counter-current stages for the solvent extraction of titanium

A validation of **Figure 4.5, Table 4.3** shows the reproducibility of the results for the Ti^{4+} loading tests under experimental conditions. The results presented in **Table 4.3** and the McCabe-Thiele diagram (**Figure 4.5**) (theoretical counter-current stages for the extraction of Ti^{4+}) show

negligible differences with the maximum extraction efficiency for both tests standing at 96%. This therefore, validates the reproducibility of results under experimental conditions.

Table 4.3 Results validating the counter-current stage-wise solvent extraction of titanium

Stage	concentration (ppm)	Extraction Efficiencies (%)
4	64.06	15.55
3	114.77	27.86
2	309.08	75.03
1	398.26	96.68

The McCabe-Thiele diagram in **Figure 4.6** shows that from a total Fe^{3+} concentration of 2591.44 ppm, only 487.45ppm of Fe^{3+} loaded onto the organic phase in three counter-current loading stages. A cumulative iron extraction efficiency of 2.67% for the 3rd stage, 9.11% for the 2nd, stage and 18.81% for the 1st stage was observed (calculations shown in Appendix A). The low extraction efficiency is due to the incomplete loading of Fe onto the organic phase, resulting from the unfavorable loading conditions for Fe^{3+} as explained by Seely (1981).
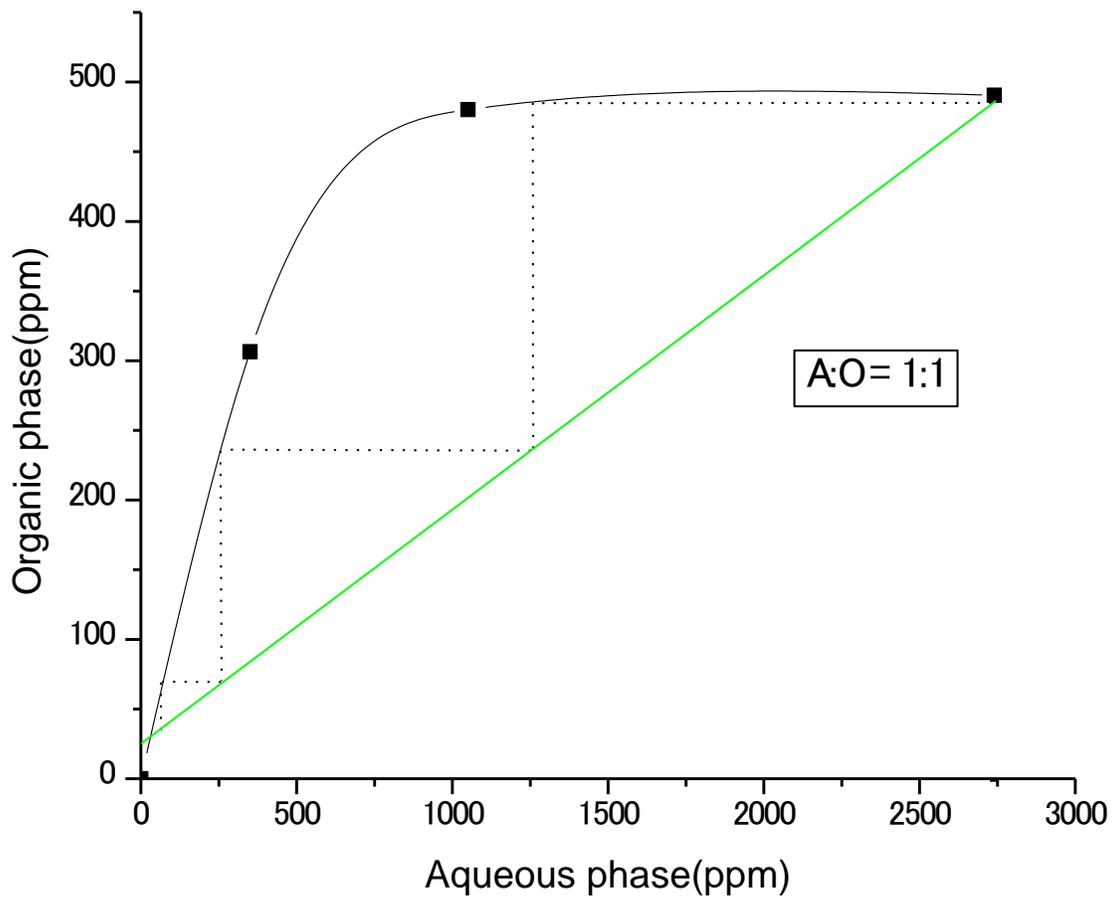
Figure 4.6 The McCabe-Thiele diagram displaying the theoretical counter-current stages for the solvent extraction of iron

Table 4.4 validates the results displayed in **Figure 4.6**. This is to show the reproducibility of the results for the Fe^{3+} loading tests under experimental conditions. As with Ti, the McCabe-Thiele diagram (**Figure 4.6**) and **Table 4.4** both display similar extraction efficiencies with negligible differences between theoretical calculations and the practical tests done. The results show a maximum extraction of 18.79%. This further proves the reproducibility of the solvent extraction method as applied to the extraction of both Fe^{3+} and Ti^{4+}.

Table 4.4 Results validating the counter-current stage-wise solvent extraction of iron

Stage	concentration (ppm)	Extraction Efficiencies (%)
3	78.00	3.01
2	264.33	10.2
1	486.93	18.79

The results from the solvent extraction experiments discussed in the preceding sections showed no loading of Fe^{2+} onto the organic phase, a partial loading of Fe^{3+} and a high loading of Ti^{4+} indicating that a 2-stage stripping of the Fe^{3+} and Ti^{4+} ions from the organic phase would be required in order to separate the two metal ions. The ineffective removal of iron from the leach liquor would further result in a subsequent low purity of the final alumina product. Thus, an alternative method is required to remove the iron from the leach liquor.

4.3 Iron Reduction in CFA Leach Liquor

The low uptake of Fe^{3+} onto the organic phase occurred at a low CFA leach liquor pH of 0.1. Li et al (2011) revealed that the effective loading of Fe^{3+} would require higher pH levels. This would require the addition of alkaline reagents in order to raise the pH. The addition of alkaline reagents, however, would significantly have an impact on process costs. As a result, this approach was deemed uneconomical.

Li et al. (2011) concluded that Fe^{2+} does not load onto primary amines and this test work has supported their conclusions. Therefore, these findings motivated for the development of a route that will ultimately result in the removal of iron from solution. The route considered should include conversion of Fe^{3+} to Fe^{2+} due to the ferrous ion's inability to load onto Primene JMT. The ferrous ion is also known to form a hydroxide precipitate at pH ranges of 7.5 to 8. These metal hydroxide precipitating pH ranges are higher than that for the precipitation of Al^{3+} hydroxide ions (Monhemius, 1977) thus, decreasing the chances of co-precipitating the trace Al^{3+} that did not crystallize out of solution, which would lead to the contamination of the final

ferrous hydroxide product. This increases the chances of obtaining three high-grade products i.e. TiO_2 (rutile and anatase), FeO/Fe_2O_3 and Al_2O_3. However, due to economic considerations, two routes were proposed, tested and economically evaluated to determine the optimum route. The two routes that were developed are as follows:

Route 1: The first route involved the addition of metallic iron as a reducing agent to the leach solution prior solvent extraction in order to try to reduce most of the Fe^{3+} into Fe^{2+}. The process was developed with due consideration to reagent consumption; if all of the Fe^{3+} is reduced to Fe^{2+} there will be no Fe loading onto the organic phase thus, minimizing the need for a 2-stage stripping for Ti and Fe. A 2-stage stripping would involve the use of extra reagent leading to extra project costs. The addition of metallic irons was followed by solvent extraction in order to remove the titanium ions, then crystallization of Al^{3+} and lastly the precipitation of Fe^{2+}.

Route 2: This route involved performing the solvent extraction process first. Secondly, metallic iron fines were added to the raffinate to reduce the Fe^{3+} to Fe^{2+}. The resultant solution then underwent crystallization of Al^{3+}, and lastly, the precipitation of Fe^{2+}.

A 2:1 ratio of Fe^{3+} to Fe in the form of metallic fines for the reduction procedure was applied in both approaches (Kasey, 1971). The 2:1 ratio was based on **equation 3.1.** The parameters and levels used for solvent extraction in both approaches are as identified in the solvent extraction test works.

4.3.1 Route 1: Fe^{3+} Reduction before Solvent Extraction

Table 4.5 shows the concentration of Fe^{2+}, Fe^{3+}, Ti^{4+} and Al^{3+} at each processing stage for each of the proposed process routes for iron removal when Fe^{3+} was reduced before solvent extraction. The aim of undertaking the Fe^{3+} reduction process first is to avoid partial Fe^{3+} loading onto the organic phase. The partial loading of Fe^{3+} is an undesired result as there will be a need for a 2-stage stripping of the organic phase in order to separate Ti^{4+} and Fe^{3+} and subsequently regenerate and reuse the extractant. This will have a negative impact on the economics of the process in terms of reagents used, time and energy consumption.

Table 4.5 reveals that most of the Fe^{3+} was reduced to Fe^{2+} and the reduction had little to no effect on the loading and non-loading of Ti^{4+} and Al^{3+}, respectively. The disadvantage of the reduction process is that there is 50% extra Fe introduced to the CFA leach liquor since the

reduction process involves use of metallic Fe as described by Kasey (1971). **Table 4.5** reflects the 50% increase in the total Fe concentration. The total Fe concentration (i.e. the combination of Fe^{2+} and Fe^{3+} concentration in the CFA leach liquor) increases from 2731.07 to 4026.79 ppm reflecting an increase of 1295.72ppm, which is a 50% increase of the total Fe concentration in the aqueous phase. It can also be seen that after solvent extraction, 99.98% of the Fe (i.e. Fe^{2+}) remained in the aqueous phase, therefore showing that only a very small percentage of Fe loaded onto the organic phase, which is highly advantageous for the process.

Table 4.5 Changes in the concentration of the Fe, Ti and Al for route 1 (Fe $^{3+}$ reduction before solvent extraction)

	CFA Leach Liquor	After Fe^{3+} to Fe^{2+} reduction	After solvent extraction	After precipitation of Al^{3+}
Fe^{2+}	139.63	4026.40	4026.40	4026.40
Fe^{3+}	2591.44	0.39	0.32	0.14
Al^{3+}	10117.50	10117.50	10087.82	7.61
Ti^{4+}	411.77	411.77	14.36	0.45

4.3.2 Route 2: Fe^{3+} Reduction after Solvent Extraction

Table 4.6 displays the results for the metal ions at each stage of the processing route when Fe^{3+} was reduced after the solvent extraction procedure. As there was no Fe^{3+} reduction before the solvent extraction process, the conditions resemble those of the preliminary tests, which ultimately resulted in the partial loading of Fe^{3+} onto the organic phase. Therefore, this means that a 2-stage stripping of the organic phase would need to be undertaken in order to separate Ti and Fe ions. The results from the method presented in **Table 4.6** show use of 18.80% less iron fillings with 18% less total Fe concentration than route 1 **(Table 4.5),** and further use of $(NH_4)_2CO_3$ for the stripping of Fe^{3+} from the organic phase.

Table 4.6 Changes in the concentration of the Fe, Ti and Al for route 2 (Fe^{3+} reduction after solvent extraction)

	CFA Leach Liquor	After solvent extraction	After Fe^{3+} to Fe^{2+} reduction	After precipitation of Al^{3+}
Fe^{2+}	139.63	139.63	3295.73	3295.73
Fe^{3+}	2591.44	2104.25	0.28	0.19
Al^{3+}	10117.50	10087.78	10087.78	8.53
Ti^{4+}	411.77	13.54	13.54	0.49

Route 1 displays promising results because it has a lower reagent consumption compared to route 2. This process begins with iron reduction where 99.98% of Fe^{3+} is reduced to Fe^{2+} using metallic Fe fillings. The reduction process is subsequently followed by solvent extraction in order to remove Ti^{4+} from the leach liquor leaving the Fe^{2+} in the aqueous phase. The solvent extraction process is then followed by crystallization of Al^{3+}, and finally, precipitation of Fe^{2+}. This is the route that will be applied for the successive test works that subsequently incorporated crystallization and precipitation processes.

4.4 Alumina Crystallization

Aluminium was crystallized out from the aqueous solution in a cooling water bath at 10°C at a recorded pH of 3.2. This was done after the solvent extraction and the reduction of Fe^{3+} to Fe^{2+} was performed.

The XRD pattern of Al^{3+} crystals is exhibited in **Figure 4.7**. The XRD analysis was used to confirm the authenticity of the white crystals obtained during CFA leach liquor crystallization. The XRD pattern confirmed that the crystals indeed contained Al^{3+} in the form of $NH_4Al(SO_4)_2 \cdot 12H_2O$. The patterns show high intensity and well-defined Bragg peaks; characteristic of crystal presence, displaying an isometric and diploidal feature with space group PA3 when using the Hermann-Mauguin notation (Vainshtein, 1994). The red peaks along with the properties that were determined confirm that the crystals are tschermigite

($NH_4Al(SO_4)_2 \cdot 12H_2O$). Hence, the result demonstrates that Al^{3+} was successfully extracted from the aqueous phase using crystallization. The XRD patterns confirm that the purification of alumina through crystallization was successful. This is due to no traces of Ti and Fe being found in the aluminium crystal that was formed. In addition, the alumina crystals were found to conform to the aluminium crystalline specifications according to the South African Bureau of Standards (SABS) (Du Toit, 1996).
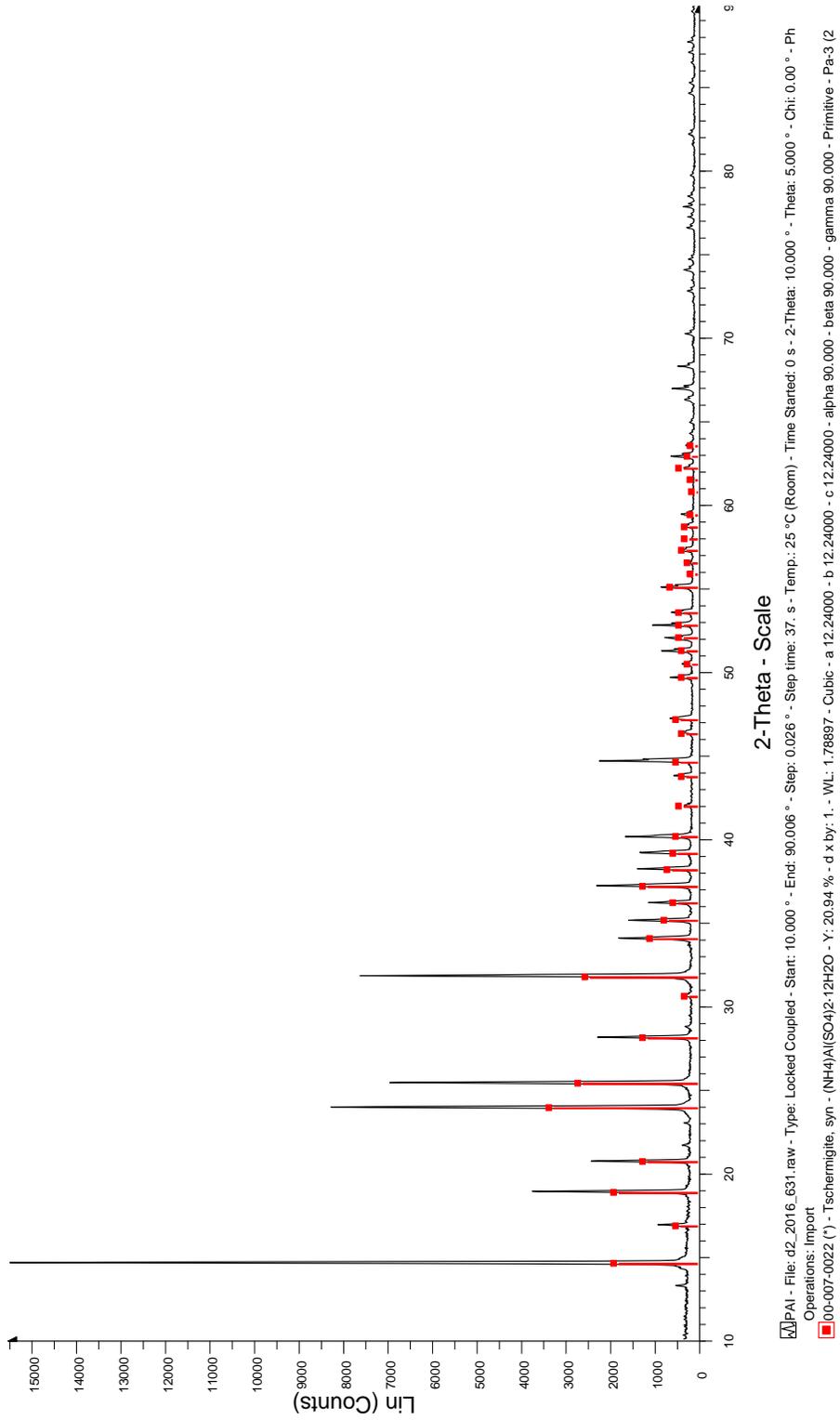
Figure 4.7 The XRD pattern of Al crystals

PAl - File: d2_2016_631.raw - Type: Locked Coupled - Start: 10.000 ° - End: 90.006 ° - Step: 0.026 ° - Step time: 37. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 10.000 ° - Theta: 5.000 ° - Chi: 0.00 ° - Ph

Operations: Import

00-007-0022 (*) - Tschermigite, syn - (NH4)Al(SO4)2·12H2O - Y: 20.94 % - d x by: 1. - WL: 1.78897 - Cubic - a 12.24000 - b 12.24000 - c 12.24000 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - Pa-3 (2

4.5 Iron Precipitation

The crystallization of aluminium was followed by the subsequent precipitation of Fe^{2+} from the aqueous phase. The precipitation of Fe^{2+} was achieved by increasing the pH of the aluminium free aqueous phase to 7.5. The XRD patterns were used to confirm the species of iron and other metals that were present in the resultant precipitate.

The XRD pattern of the $Fe(OH)_2$ precipitate is shown in **Figure 4.8**. The XRD analysis was used to confirm that $Fe(OH)_2$ was successfully precipitated out of the aqueous solution after Al^{3+} crystallization. The broad shaped peaks are characteristic of the amorphous nature of the $Fe(OH)_2$ precipitate. **Figure 4.8** further shows hematite presence in the precipitate. This could have been the result of the solution being exposed to oxygen, which oxidizes Fe^{2+} to Fe^{3+}. The XRD analysis also shows some traces of non-stoichiometric wustite (FeO). Therefore, the precipitation method is a sufficient and relevant method to apply as part of the purification process.
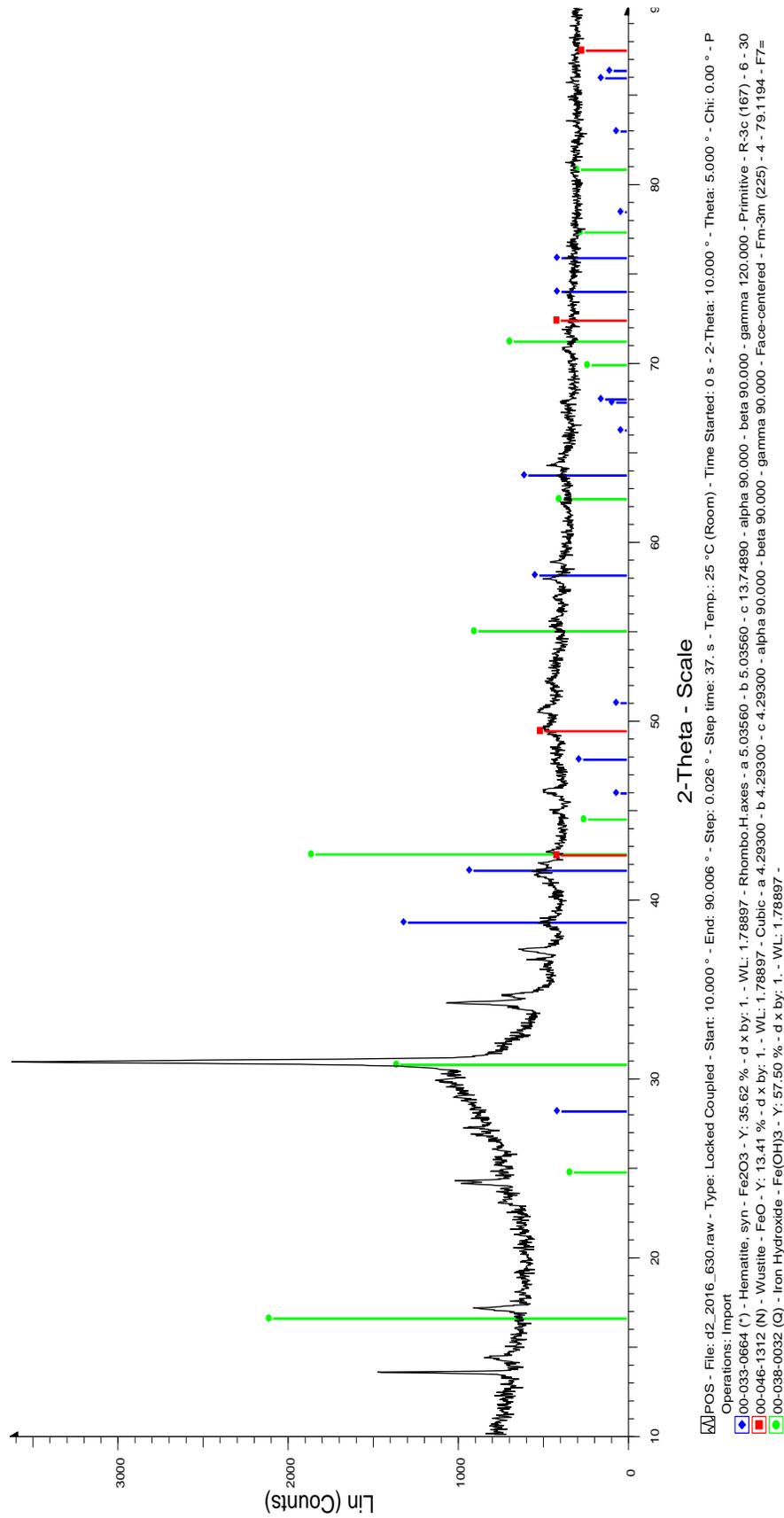
Figure 4.8 The XRD pattern of Fe(OH)₂ precipitate

4.6 Calcination

The XRD patterns for TiO$_2$ calcined at 400°C, 600°C and 750°C are presented in **Figure 4.9**. The patterns show certain characteristics about the different samples calcined at different temperatures. Calcining at 400 °C led to a more crystalline phase, characterized by broad peaks that could be ascribed to anatase. The peak broadening is suggestive of small anatase particles. At 600 °C, only anatase peaks are observed. However, peaks are sharper indicating particle growth by Ostwald ripening. It is interesting to note that at 750 °C, both anatase and rutile peaks are observed. The presence of rutile was confirmed by peaks at 27°, 36° and 55° which is an indication of the rutile species in the sample. The confirmation of anatase in the sample was indicated by peaks at 25° and 48°. The XRD characterization shows that the material is composed of 55% rutile and 45 % anatase.
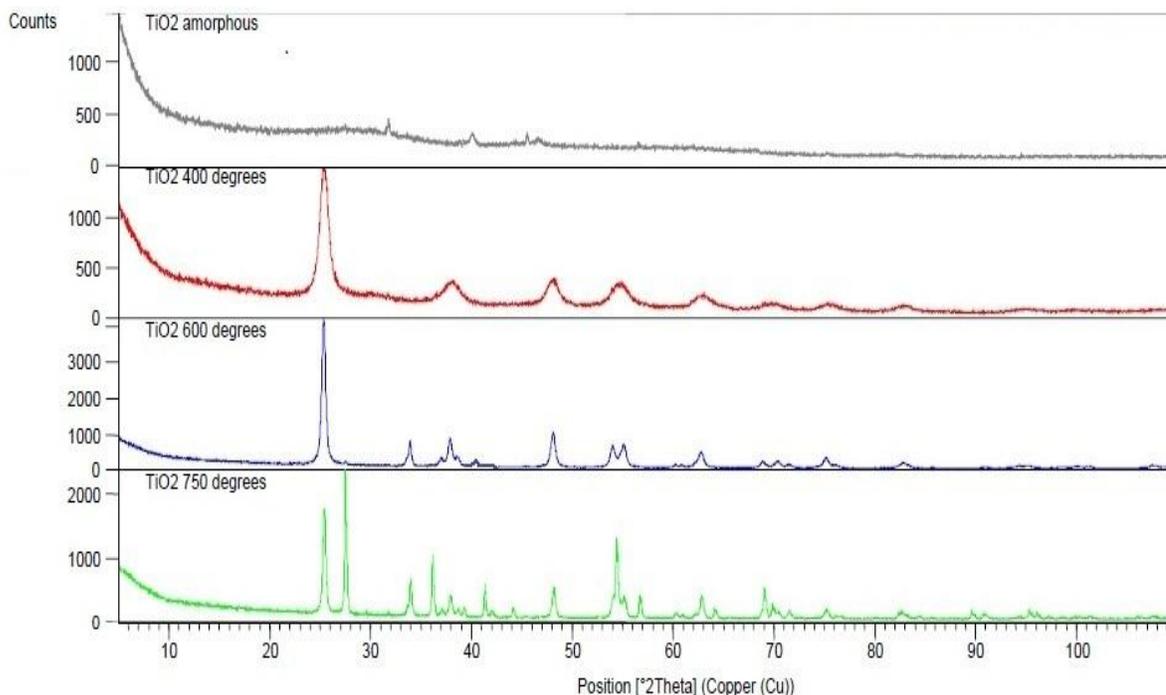
Figure 4.9 XRD patterns for TiO$_2$ calcined at 400°C, 600°C, and 750°C

The XRD analysis for aluminium and iron was deemed unnecessary as an XRF analysis was done for both metal ions to confirm their purity as part of the main objectives. The XRF results

were compared to the smelter grade requirements on **Table 2.3** to determine the efficiency of the method used.

XRF results for the calcined alumina are shown in **Table 4.7**. The calcination was performed at 1150ºC. The table also shows the standard chemical specification of smelter grade alumina. The results show that the calcined alumina product has an alumina content of 99.4%, TiO_2 at 0.006% and Fe_2O_3 at 0.015%. The minimum acceptable alumina grade is 98.3% with TiO_2 and Fe_2O_3 at 0.002 and 0.0014%, respectively. Comparatively, the purity of the calcined experimental alumina product is within the standard smelter grade specifications for alumina. This, therefore, shows that the applied purification process was highly efficient in producing smelter grade alumina.

Table 4.7 XRF analysis of calcined alumina

Constituents	Al_2O_3	Na_2O	SiO_2	CaO	Fe_2O_3	TiO_2	ZnO	P_2O_5	Ga_2O_3	V_2O_5	SO_3	LOI
Calcined Alumina Wt.%	99.361	0.260	0.022	0.017	0.015	0.006	0.009	0.001	0.012	0.001	0.101	0.195
Smelter Grade Alumina Wt.%	98.3	0.310	0.013	0.016	0.014	0.002	0.010	0.0004	0.015	0.005	0.200	1.00

Results for the calcined iron precipitate are shown in **Table 4.8**. The calcination was performed at a temperature of 1000ºC. The table shows that the calcined iron product is predominantly hematite (Fe_2O_3), the primary source of iron metal. The table shows Fe_2O_3 content of 79.29 wt.%, which is equivalent to 55.46 wt.% Fe. Most iron ores mined today comprise the mineral hematite. In terms of grading, the iron precipitate would qualify as a low-grade ore (Muwanguzi et al., 2012). Until recently, iron ore needed to have an average grade of more than 60 wt.% Fe for mining to be commercially viable. However, some deposits can now have iron grades between 56 - 59 wt.% Fe and be commercially viable (Australian Mines Atlas, 2016).

Table 4.8 XRF analysis of iron (II) precipitate after calcination

Constituents	Al_2O_3	Na_2O	SiO_2	CaO	Fe_2O_3	FeO	ZnO	P_2O_5	Ga_2O_3	V_2O_5	SO_3	LOI
Calcined Iron Precipitate Wt.%	0.592	0.233	0.380	3.270	79.292	13.410	0.008	0.495	0.001	0.201	0.312	1.806
Species					Fe	Fe		P			S	
Wt.%					55.5	10.42		0.216			0.125	

Table 4.9 shows the chemical composition of titanium (IV) oxide after calcination at a temperature of 600℃. The results show that the titanium oxide product is predominantly rutile (TiO_2), a precursor for paint pigment. According to the American Standard for Testing and Materials (ASTM,1988), *Type II* titanium pigment should have at least 92% pure rutile content.

Table 4.9 XRF analysis of titanium (IV) oxide after calcination

Constituents	Al_2O_3	Na_2O	SiO_2	CaO	Fe_2O_3	TiO_2	ZnO	P_2O_5	Ga_2O_3	V_2O_5	SO_3	LOI
Calcined Titanium Oxide Wt.%	0.461	0.268	0.399	0.614	3.211	93.346	0.011	0.021	0.009	0.031	0.237	1.113
Type II Titanium Pigment (ASTM) Wt.%						≥92.00						

4.7 Preliminary Cost Assessment

Preliminary process cost analysis was deemed necessary for comparative reasons between the two process routes that were developed and to also determine the costs to be incurred in the production of smelter grade alumina from CFA leaching. In this section, the reagent consumption costs were done for both route 1 and 2 to determine which route is more economically feasible.

The cost analysis was based on the total reagent consumption of the total leach liquor purification process per tonne of smelter grade alumina produced. The cost analysis was undertaken with due consideration for the amount of Primene JMT and Kerosene used for the solvent extraction process for the production of 1 tonne of alumina per each process route. The reduction costs were also calculated, with due consideration for the amount of metal iron filings used to produce a tonne of alumina for each route. Furthermore, a stripping cost analysis was undertaken; and the eventual crystallization and precipitation costs, to finalize the comparative cost analysis for both routes per tonne of smelter grade alumina produced.

According to Alumina Limited (2016), the cash cost of alumina production through the Bayer process per tonne in 2016 was USD 191.71 which amounts to R2, 486.82. The actual calculated cost per tonne of alumina generated from route 1 and route 2 is R 4, 380,000.00 (USD 330, 086.00) and R 4, 880,000.00 (USD 367, 767.00), respectively (See **Appendix A** for the full cost calculation) .Comparatively, the cost of route 1 is not as economically efficient as the Bayer process. However, it costs R 500,000 (USD37, 681) less to produce alumina through route 1 than through route 2. The high process costs indicate that the two process routes are not economically feasible on an industrial scale.

Summary

The overall purpose of employing the integrated method of CFA leach liquor purification is to develop a process route for the production of smelter grade alumina from CFA. In the integrated precipitation and solvent extraction technique, an incombustible fly ash residue was optimally leached using the 2-step leaching method. The Fe^{3+} in the leach liquor was firstly reduced to Fe^{2+} using metallic Fe fillings. The reduction process was then followed by solvent extraction to optimally remove Ti^{4+} from the leach liquor. The loaded Ti^{4+} was ultimately stripped from the organic phase. The Al^{3+} in the aqueous phase was crystallized out followed by the eventual precipitation of Fe^{2+}.

- Experimental results show that Fe and Ti are the two major impurities in the CFA leach liquor and that their removal is key to the purification of the leach liquor and recovery of metallurgical grade alumina.

- Primene JMT can be used in small amounts of ~ 10% in kerosene for short contact times of ~15 minutes using an O/A ratio of 1:1 in order to achieve high extraction efficiencies during the solvent extraction step.

Route 1:

- In the first CFA leach liquor treatment, an iron conversion from Fe^{3+} to Fe^{2+}, of 99.98% was achieved when the leach liquor was contacted with metallic iron fines.

- Although iron reduction before solvent extraction has advantages of preventing the co-loading of Fe^{3+} and Ti^{4+} onto the organic phase and the double stripping of Fe^{3+} and Ti^{4+} metal ions, it uses more iron filings.

Route 2:

- In this process route, solvent extraction of the coal fly ash leach liquor was applied first. The CFA leach liquor was contacted with 10% Primene JMT extractant for 15 minutes at an Organic to Aqueous ratio of 1:1. This was then followed by a 99.98% Fe^{3+} to Fe^{2+} reduction in the aqueous phase using metallic iron filings.

- Applying solvent extraction before iron reduction has an advantage of using 18, 80% less iron filings than route 1, but double stripping is required to separate the co-loaded Fe^{3+} and Ti^{4+} to ensure titanium recovery which can prove financially costly for the process.

- A Ti extraction efficiency of 96.51% was achieved by solvent extraction when CFA leach liquor was contacted with 10% Primene JMT extractant for 15 minutes at an Organic to aqueous ratio of 1:1. Route 1 displayed less than 1% of Fe^{3+} loading while route 2 displayed an 18.81% Fe^{3+} loading efficiency.

- In the third CFA leach liquor treatment, (where Fe removal is performed through an Fe^{3+} to Fe^{2+} reduction, followed by solvent extraction and an eventual Fe^{2+} precipitation following aluminium crystallization) an alumina recovery of 99.62% was achieved when the leach liquor was initially maintained at 70°C for 20 minutes then cooled and crystallized at 10°C for 1 hour.

- The integrated precipitation and solvent extraction route has been identified as an effective option for CFA leach liquor purification and recovery of smelter grade alumina.

- From the preliminary costing assessment undertaken, it was established that route 1 costs R 4,380,000.00 to produce a tonne of alumina, which is cheaper to operate than route 2 that costs R 4, 880,000.00. Although route 1 is cheaper to operate, it is still not economically feasible when compared to the cash cost production of alumina per tonne, which according to alumina limited (2016) report is R2, 486.82. Therefore, the two process routes are not economically feasible on an industrial scale.

CHAPTER FIVE

CONCLUSION

5.1 Introduction

The work undertaken in this study is an extension of a 2-step CFA leaching process for the production of alumina. The process was developed by a researcher from University of the Witwatersrand (Shemi, 2012). The leach liquor produced from the 2-step leaching process was found to have two main impurities, Ti and Fe. These two impurities limited the efficiency of the process in the production of an alumina product that matched smelter grade alumina specifications. The work undertaken in this study was therefore aimed at developing a method of purifying the 2-step CFA leach liquor by removing the Fe and Ti from the Al rich leach solution.

5.2 Solvent Extraction

Literature suggested solvent extraction is paramount for the purification process. Various concentrations of Primene JMT in kerosene and contact times were tested for optimum uptake of Fe and Ti. The concentrations that were tested include: 10, 15, 30, and 50%; and the contact times were as follows: 15, 30 and 60 minutes. Test work revealed that the solvent extraction process reached equilibrium within the first 15 minutes for all extractant concentrations. Of all the tests undertaken, Primene JMT showed no affinity for aluminium. However, the titanium extraction efficiency was found to range between 90-98% from all extractant concentrations tested. Therefore, solvent extraction using Primine JMT appeared to be most effective for the removal of titanium from the CFA leach liquor.

Under very acidic conditions, there was a poor affinity for iron, with the uptake of Fe between 11.2 and 19.2%. A concentration of 10% Primene JMT gave the highest extraction efficiency; of 19.2%. Further, test work showed that iron existed as a non-loading Fe^{2+} (Li et al.,2011) and partially loading Fe^{3+} due to formation of bisulfate complexes in excess H_2SO_4 (Seeley et al, 1981; Chou et al.,1986) in the aqueous phase. This motivated for the consideration of other methods for the removal of iron from the solution. The phase separation time was also seen to increase with an increase in the concentration of the extractant.

The McCabe-Thiele showed three and four theoretical counter-current stages for the extraction of Fe and Ti with 18.80 and 96.51% extraction efficiencies, respectively. The most effective O/A ratio was found to be 1:1 for both Fe and Ti extraction.

With due consideration to reagent consumption, an extraction concentration of 10%, contact time of 15 minutes and O/A ratio of 1:1 were taken as the optimum operational parameters for the purification of the 2-step CFA leach liquor.

5.3 Iron reduction

Li et al. (2011) suggest an increase in the pH solution to allow for Fe^{3+} extraction. This however, would impact on the reagent costs. Therefore, a process involving the reduction of all Fe^{3+} in the aqueous to Fe^{2+} was proposed. Fe^{2+} precipitates at higher pH than Al^{3+}, therefore, minimizing co-precipitation and contamination of the overall alumina product.

There were two processes developed with due consideration of the economic feasibility of both processes.

Route 1: This route involved the reduction of Fe^{3+} in the leach liquor to Fe^{2+} using metallic iron filings before solvent extraction. This process requires the addition of 50% iron to the system in order to avoid the partial uptake of Fe^{3+} and the subsequent double stripping of the organic phase. Double stripping would imply the use of extra expensive reagents; increasing the costs of the purification process. This would then defeat one of the main objectives, which is the development of an economically feasible process.

Route 2: This route involved performing solvent extraction before the reduction of Fe^{3+} in the leach liquor to Fe^{2+} using metallic iron filings. Therefore, this would result in a partial uptake of Fe^{3+} onto the organic phase. Although this process would require double stripping, it uses 18% less iron metal filings than route 1.

Route 1 cost R 500,000.00 less than route 2 to produce a tonne of alumina, which points to route 1 as a more economically efficient route.

Route 1 resulted in the production of an alumina product with a grade of 99.4% Al after first crystalizing out aluminium from the leach liquor and calcining the aluminium crystal. The grade matches the standard smelter grade specifications.

Titanium was stripped out of the organic phase and calcined to produce TiO_2. TiO_2 had a purity of 93.35%, which is within the ASTM specifications to be used as a paint precursor (ASTM, 1988).

Fe^{3+} was stripped from the organic solution and the Fe^{2+} was subsequently precipitated from the aqueous solution after the crystallization of aluminium. The iron product was found largely as Fe_2O_3 at 79.29% due to oxygen oxidation. It was also found existing as FeO at 13.41%.

5.4 Final remarks

The integrated route 1 is the best process route to apply in order to achieve an alumina product of 99.4% Al from CFA leach liquor. The purity of the alumina product shows that the purification process developed in this work is highly effective and has promising industrial applications as long as the costs are optimised.

5.5 Recommendations

For further studies, the following recommendations are proposed:

Economic evaluation

An economic evaluation serves as an important and key aspect of the process. The economic evaluation of the present work showed that the two processes developed were not economically feasible on an industrial scale. The reagent cash cost of alumina production per tonne for process route 1 and process route 2 was compared to cash cost of alumina production per tonne of the conventional Bayer process. Route 1 and route 2 were found to be too expensive to be applied to produce a tonne of alumina. Therefore, this work can be extended to explore other less expensive reagents for the two process routes so as to achieve economic feasibility for both processes.

The effect of temperature on solvent extraction

Temperature plays a vital role in the extraction of metal ions (Mohapatra et al, 2007). It is one of the important factors that affect solvent extraction. This work can also be extended to evaluate the effect of temperature on the loading of Fe, Ti and Al.

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Appendices

Appendix A

Sample Calculations

4.2.5. A. Effect of organic to aqueous (O/A) ratio

Ti⁴⁺ extraction efficiency

For fourth stage:

Actual Ti⁴⁺ in CFA leach liquor = 411.94 ppm

Ti⁴⁺ extracted into the organic phase = 64.72 ppm

$$\text{Extraction efficiency for first stage (\%)} = \frac{\text{Ti4+ extracted into the organic phase}}{\text{Actual Ti4+ in CFA leach liquor}} \times 100$$

$$= \frac{64.72 \text{ ppm}}{411.94 \text{ ppm}} \times 100$$

$$= 15.71\%$$

For third stage:

Actual Ti⁴⁺ in CFA leach liquor = 411.94 ppm

Ti⁴⁺ extracted into the organic phase = 115.96 ppm

$$\text{Extraction efficiency for first stage (\%)} = \frac{\text{Ti4+ extracted into the organic phase}}{\text{Actual Ti4+ in CFA leach liquor}} \times 100$$

$$= \frac{115.96 \text{ ppm}}{411.94 \text{ ppm}} \times 100$$

$$= 28.15\%$$

For second stage:

Actual Ti⁴⁺ in CFA leach liquor = 411.94 ppm

Ti⁴⁺ extracted into the organic phase = 298.00 ppm

$$\text{Extraction efficiency for first stage (\%)} = \frac{\text{Ti4+ extracted into the organic phase}}{\text{Actual Ti4+ in CFA leach liquor}} \times 100$$

$$= \frac{298.00 \text{ ppm}}{411.94 \text{ ppm}} \times 100$$

$$= 72.34\ \%$$

For first stage:

Actual Ti^{4+} in CFA leach liquor = 411.94 ppm

Ti^{4+} extracted into the organic phase = 397.56 ppm

Extraction efficiency for first stage (%) $= \dfrac{\text{Ti4+ extracted into the organic phase}}{\text{Actual Ti4+ in CFA leach liquor}} \times 100$

$$= \dfrac{397.56\ \text{ppm}}{411.94\ \text{ppm}} \times 100$$

$$= 96.51\%$$

A. Fe^{3+} extraction efficiency

For third stage:

Actual Fe^{3+} in CFA leach liquor = 2591.44 ppm

Fe^{3+} extracted into the organic phase = 69.19 ppm

Extraction efficiency for first stage (%) $= \dfrac{\text{Fe3+ extracted into the organic phase}}{\text{Actual Fe3+ in CFA leach liquor}} \times 100$

$$= \dfrac{69.19\ \text{ppm}}{2591.44\ \text{ppm}} \times 100$$

$$= 2.67\%$$

For second stage:

Actual Fe^{3+} in CFA leach liquor = 2591.44 ppm

Fe^{3+} extracted into the organic phase = 236.08 ppm

$$\text{Extraction efficiency for first stage (\%)} = \frac{\text{Fe3+ extracted into the organic phase}}{\text{Actual Fe3+ in CFA leach liquor}} \times 100$$

$$= \frac{236.08 \text{ ppm}}{2591.44 \text{ ppm}} \times 100$$

$$= 9.11\%$$

For third stage:

Actual Fe^{3+} in CFA leach liquor = 2591.44 ppm

Fe^{3+} extracted into the organic phase = 487.45 ppm

$$\text{Extraction efficiency for first stage (\%)} = \frac{\text{Fe3+ extracted into the organic phase}}{\text{Actual Fe3+ in CFA leach liquor}} \times 100$$

$$= \frac{487.45 \text{ ppm}}{2591.44 \text{ ppm}} \times 100$$

$$= 18.81\%$$

B. Reagent Consumption Cost analysis for the two route processes

Cost of solvent extraction

1.1. The Cost of Purifying the CFA Leach Liquor Solution

It was determined that aluminium content in 100mls (0.1L) of CFA leach liquor after stripping was 10117.50 ppm

Aluminium content in 500mls (0.1L) of aqueous solution

$$= 10.1175(gpl) \times 0.5L$$

= 5.06g

Reagent Consumption Cost Analysis for Process Route 1

1.1.1   Amount of Fe^{3+} in 100ml aqueous phase

Fe^{3+}(g) in 0.1L = Fe^{3+} concentration in ppm(gpl) x The volume of the leach liquor in liters

$$= 2.591(gpl)* 0.1L$$

= 0.26g

1.1.2   The Fe^{3+} Reduction Process

1.1.2.1 The Cost of Fe fillings used for the process

According to the Fe^{3+} reduction equation (Equation 1) there is a 2:1 Fe^{3+} to metallic Fe ratio.

$$2Fe^{3+} + Fe \longrightarrow 3Fe^{2+}\ldots\ldots\ldots\ldots\ldots \text{①}$$
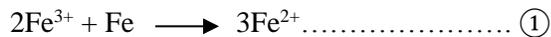
For every 2 moles of Fe^{3+} we need 1 mole of metallic Fe.

0.26g of Fe^{3+} is equivalent to = 0.26g x 1 mole/55.845g = 0.00465moles

0.00465moles of Fe will require 0.00465x1mole/2 = 0.00233moles of metallic Fe

1 mole of Fe = 55.845g of Fe

0.00233moles of Fe = 55.845g x 0.00233moles/1mole = **0.13g**

The cost of metallic Fe = **R127.070/g**

Cost of Fe reduction = R127.070/g x0.13g = <u>R16.52</u>

1.1.3   The Cost of the Extraction Process

❖ Leach liquor to be processed = 100ml

❖ Solvent extractant required based on a 1:1 ratio = 100ml

❖ Solvent extractant composition, 10% Primene JMT and 90% kerosene.

❖ 10% Primene JMT = 10mls; 90% of Kerosene = 90mls.

The solvent extraction was undertaken using an O/A ratio of 1:1. Therefore, the extractant cost will be calculated on the volume of the extractant used per volume of leach liquor processed.

1.1.3.1 The Cost of Primene JMT

Density of Primene JMT = 0.819 g/ml

Primene JMT in 10ml = 0.819g/ml x 10ml

$$= 8.19g$$

The price of 5kg Primene JMT is R809.23 = R809.23/5000g = R0.16/g

The cost of Primene JMT used in the process = R 0.16/g x 8.19g = <u>R1.33</u>

1.1.3.2 The Cost of Kerosene

The price of kerosene = R 9.22/L

Kerosene used in the process = 90ml

The cost of Kerosene used in the process = R9.22/L x 0.09L = **<u>R0.83</u>**

The total cost of the solvent extraction process = R1.33 + R0.83 = **<u>R2.16</u>**

1.1.4   The Cost of the Stripping Process

1.1.4.1 The Cost of Titanium Stripping

100 ml of 1.14M NH_4OH was used to strip Ti^{4+} from a 100ml titanium rich organic phase.

Price of 33% NH_4OH per 2 Litre = R509.96

Price of 33% NH_4OH per Litre = R254.98

Density of 33% NH_4OH = 0.890 g/ml

In 1 Litre of 33% NH_4OH, NH_4OH = 0.890g/ml x 1000ml x 33/100 = **293.7g**

Moles of NH_4OH in **1 Litre** = 293.7g x 1mole/35g = **8.39moles**.

Price of 33% NH_4OH per mole = R254.98/8.39moles = **R30.39/mole**

Moles of NH_4OH consumed = 1.14 moles/L x 0.1L = **0.114moles**.

Cost of NH_4OH consumed = 0.114moles x R30.39/mole = **R3.47**

Total **cost for the 3 stages** of route **1** = Fe reduction + Solvent extraction + Stripping

$$= \textbf{R16.52} + \textbf{R2.16} + \textbf{R3.47}$$

$$= \underline{\textbf{R22.15}}$$

Total amount of aluminium in solution after titanium stripping = **5.06g**

Cost of aluminium extraction per gram

= R22.15/**5.06g** = **R4.38/g**

Cost per kg

= R4.38/g x 1000 = R4, 380/kg

Cost in Rands per tonne

= R4, 380/kg x 1000

= **R4, 380, 000/t**

Cost in USD per tonne

= R4, 380, 000/t /13

= **USD330, 086/t**

A. Reagent Consumption Cost Analysis for Process Route 2

Amount of Fe^{3+} determined in 100ml aqueous phase

Fe^{3+}(g) in 0.1L = Fe^{3+} concentration in ppm(mg/l)*The volume of the leach liquor in liters

$$= 2.104 \text{ (gpl) x } 0.1L$$

$$= \textbf{0.21g}$$

Therefore, there is **0.21g** of Fe^{3+} in every 0.1L of the aqueous phase after solvent extraction.

1.2 The Solvent Extraction Process

The solvent extraction was undertaken using an O/A ratio of 1:1. Therefore, the extractant cost will be calculated on the volume of the extractant used per volume of leach liquor used to generate 1 tonne of Al^{3+};

1.2.1 Cost of Primene JMT

Density of Primene JMT = 0.819 g/ml

Therefore 10ml of Primene JMT = 0.819 g/ml x 10ml

$$= 8.19g$$

And the price of 5kg Primene JMT is R809.23 = R809.23/5000g = R0.16/g

Total cost of Primene JMT used = R 0.16/g x 8.19g = **R 1.33**

1.2.2 The Cost of Kerosene

The price of kerosene = R 9.22/L

And the cost of kerosene used = R 9.22/L x 0.090L = **R0.83**

The final cost for the extractant used = R 1.33 + R 0.83 = **R 2.16**

1.3 The Fe^{3+} reduction process

1.3.1 Price of Fe fillings used for the process

According to the Fe^{3+} reduction equation (Equation 1) there is a 2:1 Fe^{3+} to metallic Fe ratio.

$$2Fe^{3+} + Fe \longrightarrow 3Fe^{2+} \ldots\ldots\ldots\ldots\ldots\ldots ①$$
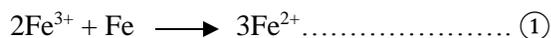
For every 2 moles of Fe^{3+} we need 1 mole of metallic Fe.

0.21g of Fe^{3+} is equivalent to = 0.21g x 1 mole/55.845g = 0.00376moles

0.00376moles of Fe will require 0.00376x1mole/2 = 0.00188moles of metallic Fe

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1 mole of Fe = 55.845g of Fe

0.00188moles of Fe = 55.845g x 0.00188moles/1mole = **0.105g**

The cost of metallic Fe = **R127.070/g**

Cost of Fe reduction = R127.070/g x0.105g = <u>R13.34</u>

1.4   The Titanium Stripping Process

1.4.1   *The cost of titanium stripping*

100 ml of 1.14M NH_4OH was used to strip Ti^{4+} from a 100ml titanium rich organic phase.

Price of 33% NH_4OH per 2 Litre = R509.96

Price of 33% NH_4OH per Litre = R254.98

Density of 33% NH_4OH = 0.890 g/ml

In 1 Litre of 33% NH_4OH, NH_4OH = 0.890g/ml x 1000ml x 33/100 = **293.7g**

Moles of NH_4OH in **1 Litre** = 293.7g x 1mole/35g = **8.39moles**.

Price of 33% NH_4OH per mole = R254.98/8.39moles = **R30.39/mole**

Moles of NH_4OH consumed = 1.14 moles/L x 0.1L = **0.114moles**.

Cost of NH_4OH consumed = 0.114moles x R30.39/mole = **R3.47**

1.5   The Iron Stripping Process

100mls of 2M $(NH_4)_2CO_3$ was used to strip Fe^{3+} from a 100ml iron rich organic phase.

Price of $(NH_4)_2CO_3$ per Kg = R298.31

Density of $(NH_4)_2CO_3$ = 1.5g/ml

1 kg $(NH_4)_2CO_3$, $(NH_4)_2CO_3$ = **1000g**

Moles of $(NH_4)_2CO_3$ in **1 Kg** = 1000g x 1mole/96g = **10.417moles**.

Price of $(NH_4)_2CO_3$ per mole = R298.31/10.417moles = **R28.64/mole**

Moles of $(NH_4)_2CO_3$ consumed = 2moles/L x 0.1L = **0.2moles**.

Cost of $(NH_4)_2CO_3$ consumed = 0.2moles x R28.64/mole = **R5.73**

Final cost for stripping = **R3.47** + **R 5.73**

$$= \underline{\textbf{R9.2}}$$

Total cost for route 2

  i.   <u>**Solvent extraction = R2.16**</u>
  ii.   <u>**Fe reduction = R 13.34**</u>
  iii.   <u>**Stripping = R9.2**</u>

Cost for all the stages = <u>**R24.7**</u>

Total amount of aluminium purified = 5.06g

Total cost of aluminium purification through route 2

= R24.7/5.06g = R4.88 per g

= R4.88/g x 1000 = R4, 880 per Kg

= R4, 880/Kg x 1000 = R4, 880, 000 per tonne

= R4, 880, 000/t/13

= **USD367, 767 per tonne**

Appendix B

Diagrams and Tables

Table 4A. Data used for constructing the McCabe-Thiele diagram displaying the theoretical counter-current stages for the solvent extraction of titanium

Aqueous	Organic
0	0
76.64	205.38
239.5	387.65
411.77	397.41

Table 4B. Data used for constructing the McCabe-Thiele diagram displaying the theoretical counter-current stages for the solvent extraction of iron

Aqueous	Organic
0	0
350.33	306.41
1050.51	480.16
2740.07	490.44