Cape Peninsula
University of Technology

Removal and recovery of aluminium and sulphate ions from an alkaline medium using solvent extraction

by

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Thesis submitted in fulfilment of the requirements for the degree

Master of Technology: Chemical Engineering

in the Faculty of ENGINEERING

at the Cape Peninsula University of Technology

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Cape Town Campus

MAY 2009

DECLARATION

I, **Cleophace Ngoie Mpinga**, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

C. Ngoie Mpinga

ABSTRACT

Throughout the world, many water resources are polluted by industrial and domestic effluents, acid mine drainage, etc. The increasing awareness and concern about the environment has motivated in the recent years extensive research into developing new efficient, cost effective and environmentally sound technologies to treat industrial solutions bearing metals and sludges.

From the literature review, much research has been, and is still being devoted to the performance of solvent extraction (SX) of aluminium or sulphate in acidic solutions and how to improve such performance. There is a general lack of information on liquid-liquid extraction of aluminium or sulphate in an alkaline solution. Thus, the need for a systematic investigation into the solvent extraction of aluminium and sulphate in an alkaline medium was important. This thesis focuses on the study of solvent extraction of aluminium and sulphate from alkaline solutions using Trioctylmethylammonium chloride, (Aliquat 336), in Kerosene as diluent.

In a batch reactor, using a fractional factorial design limiting the number of tests, the influences of the following parameters were investigated: 1) the equilibrium pH, 2) the interfacial area, 3) the temperature, 4) the initial aluminium or sulphate concentration, and 5) the extractant concentration. Extraction experiments were performed to establish the effects and interactions of the abovementioned parameters on the extraction yield of aluminium and sulphate. The slope analysis method was also used for determining the polymerisation degree of extracted species and the extraction thermodynamic parameters.

The results showed that Aliquat 336 diluted in Kerosene is an efficient reagent for aluminium and sulphate extractions from alkaline solutions. It extracted aluminium with an extraction percentage of 65.12%, while sulphate was extracted with a percentage of 85.95% at optimum operating conditions. The optimum operational conditions determined for aluminium extraction were as follows: pH of 11, aluminium feed concentration of 19.84 ppm, extractant Aliquat 336 concentration of 25% (v/v), temperature of 25°C and interfacial area of 19.64 m^2/m^3. For sulphate, the optimum conditions were found to be: pH of 11, initial sulphate concentration of 121 ppm, temperature of 40°C, interfacial area of 19.64 m^2/m^3 and extractant Aliquat 336 concentration of 25% (v/v). Saturation loading capacity of the extractant was evaluated and the results revealed that 25% (v/v) of Aliquat 336 can hold up to 127 g $Al(OH)_4^-$ and up to 144 g $[SO_4^{2-}]_{tot}$ per litre, respectively.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out in the Department of Chemical Engineering at the Cape Peninsula University of Technology between January 2008 and May 2009.

First of all, I thank Jehovah God, the Lord Almighty, for giving me the health, strength and ability to write this thesis.

I wish to express my deepest gratitude to my supervisor, Paul Jean van der Plas, who suggested the research topic and directed the research; stood by me through moments of frustration and encouraged me. I am deeply indebted to him for his valuable support and continuous guidance.

I wish to thank my wife Francine Kabanga Mushiya for her love and positive influence.

I also wish to thank my children, Celine, Herman, Adonai, and Benita. All my friends and colleagues for their encouragement throughout the duration of this project.

In memory of my deceased parents: Gustave Mpoyi Cinemu and Josephine Kabola Makenga.

The financial assistance of the Cape Peninsula University of Technology towards this research is acknowledged. Opinions expressed in this thesis, and the conclusions arrived at, are those of the author, and are not necessarily to be attributed to the Cape Peninsula University of Technology.

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NOMENCLATURE

SYMBOLS	DESCRIPTION	UNITS
a	Interfacial area per unit volume of aqueous phase	[m^2/m^3]
A	Contact area or interfacial area through which mass transfer occurs	[m^2]
A_0	Frequency factor	-
B$_W$	Width of baffles fitted inside the batch reactors to prevent vortex formation at the gas-liquid interface	[mm]
C	Analytical concentration in solution	[M]
C^0	Initial analytical concentration in the aqueous phase before extraction	[M]
C^{st}	Integration constant	-
C_{aq}^t	Analytical concentration in the aqueous phase at time t	[M]
C_{raf}	Analytical concentration in the aqueous phase after extraction	[M]
D	Distribution coefficient	-
D$_i$	Internal diameter of the batch reactor	[mm]
E_a	Activation energy	[J/mol]
$\%E$	Extraction percentage	[%]
$\%E_{eff}$	Extraction efficiency	[%]
ΔG	Gibbs free energy of activation	[kJ/mol]
H	Height of the batch reactor	[mm]
ΔH	Enthalpy of activation	[kJ/mol]
k	Rate constant	[m/min]
K$_a$	Ionisation constant of acid	-
k_{aq}	Mass transfer coefficient in the aqueous phase boundary layer	[m/min]
k_{app}	Apparent overall rate constant	[m/min]
K_{ex}	Extraction equilibrium constant	-
k_{org}	Mass transfer coefficient in the organic phase boundary layer	[m/min]
k_f, k_b	Intrinsic rate constant for forward and back reactions, respectively	[m/min]
$k_f^{'}$, $k_b^{'}$	Apparent rate constant for forward and back reactions, respectively	[m/min]
l, m and n	Reaction orders of the concentrations of aluminium, Aliquat 336 and sodium hydroxide, respectively, for the forward reaction	-

SYMBOLS	DESCRIPTION	UNITS
Me	Divalent heavy metal such as iron, nickel, manganese, etc	-
N	Number of trials required at one level of a variable in a matrix experiment	-
p, q and r	Reaction orders for the back reactions	-
R	Universal gas constant	[J/mol. K]
R^2	Correlation coefficient between experimental and modelled data	-
ΔS	Entropy of activation	[J/mol. K]
$[SO_4^{2-}]_{tot}$	Total sulphur concentration in solution	[ppm or M]
t	Time	[min]
T	Absolute temperature	[K]
V_{aq}	Volume of the aqueous phase	[m^3]
V_{org}	Volume of the extractant in organic phase	[m^3]
W	Weight of the solute in the aqueous solution before extraction	[g/L]
W_{raf}	Weight of the solute left in the aqueous solution after extraction	[g/L]
W_{raf}^{e}	Weight of the solute left in the aqueous solution at equilibrium	[g/L]
Z	Loading ratio: extent to which the organic phase may be loaded with a solute	[%]

SUPERSCRIPTS		**SUBSCRIPTS**	
e	Equilibrium	aq	Aqueous phase
0	Initial state	b	Backward reaction
t	Time	eff	Efficiency
GREEK LETTERS		ex	Extraction
α	Risk of making the first kind error	f	Forward reaction
β	Risk of making the second kind error	g	Gas
η	Separation factor	org	Organic phase
		raf	Raffinate
		s	Solid
		$Std.Meth$	Standard Method
		tot	Total

LIST OF ABBREVIATIONS

ABBREVIATIONS	DESCRIPTION
AMD	Acid Mine Drainage
CESR	Cost-Effective Sulphate Removal
ICP	Inductively Coupled Plasma
INAP	International Network for Acid Prevention
LLE	Liquid-Liquid Extraction
LOC	Limiting Organic Concentration
O/A	Organic/Aqueous volumetric phase ratio
ppm	Parts per million
R_4NCl	Aliquat 336: Tricaprylmethylammonium chloride
SRB	Sulphate Reducing Bacteria
SX	Solvent Extraction
TOMA	Trioctylmethylammonium
% (v/v)	Volume basis: percentage by volume
Wt%	Weight percent

CHAPTER 1 : INTRODUCTION

1.1 HISTORY OF SOLVENT EXTRACTION

Solvent extraction (SX) in hydrometallurgy began in 1942 in the Manhattan Project where ether was used as the extracting solvent for the recovery and purification of uranium from a nitric acid solution. The major breakthrough came with the development of the hydroxyoxime extractants by General Mills Inc. in the 1960s, and their application in the recovery of copper from the sulphuric acid solutions (Douglas, 2005).

In the 1950s, the recovery of uranium as a by-product of gold mining was the first major commercial application of SX technology in the South African hydrometallurgical industry. In more recent years, Southern Africa has seen the execution of this technology for other base, precious and specialty metals (Sole, Feather & Cole, 2005).

1.2 OBJECTIVES OF THE RESEARCH

From the literature review, it was apparent that much research has been, and is still being devoted to the performance of SX of aluminium and/or sulphate in acidic solutions and how to improve such performance. There is a general lack of information on liquid-liquid extraction of aluminium and/or sulphate behaviour in an alkaline solution. Thus, the need of a systematic investigation into the solvent extraction of aluminium and sulphate in alkaline medium was important to ensure a better understanding of the extraction process.

The present study was aimed at liquid-liquid extraction of aluminium and sulphate by Trioctylmethylammonium chloride (R_4NCl), Aliquat 336, from alkaline solutions to determine their potential recovery from process streams or sludges produced by lime/limestone neutralisation or similar agents.

In order to complete the abovementioned aim, the following objectives have been stated for the research, namely:

* To perform extraction tests on synthetic solutions of aluminium and sulphate. Furthermore, the test program should provide the opportunity to elucidate the mechanism of the extraction process.

* To investigate possible factors influencing the extraction process, emphasising the effect of initial aluminium or sulphate and Aliquat 336 concentration, pH, temperature and interfacial area.

* To develop a simple empirical model which can predict aluminium or sulphate extraction.

1.3 IMPORTANCE AND BENEFITS OF THE RESEARCH

This research project will provide the researcher with experimental values, which will be useful for a test on a pilot scale, as well as contribute to the academic discourse and debate within this discipline.

1.4 RESEARCH METHODOLOGY

A fractional factorial design and scrutiny of tests were used to determine the main effects and interactions of the selected factors, and to decide on the optimum conditions for the extraction of aluminium and/or sulphate. The factors considered were: 1) equilibrium pH, 2) temperature, 3) interfacial area, 4) initial aqueous concentration, and 5) extractant concentration.

Finally, a simple empirical mathematical model was developed that adequately simulated the total amount of aluminium and sulphate removed as a function of the most significant parameters and two-factor interactions.

CHAPTER 2 : LITERATURE REVIEW

Acid mine drainage is a natural process in which sulphuric acid is produced when certain sulphide ores, such as chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), arsenopyrite (FeAsS), marcasite (FeS_2) and pyrite (FeS_2) are subjected to the influence of air and water. The predominant acid producers are pyrite and marcasite. This phenomenon occurs from hydrometallurgical and mining processes, both in surface and in underground mines. This introduces an elevated concentration of sulphate, ferric iron and other dissolved metals to groundwater and receiving surface water (Santos, Machado, Correia & Carvalho, 2004).

2.1 CLASSIFICATION OF MINE DRAINAGE

2.1.1 Alkaline mine drainage

Depending on the minerals contained in the destroyed geologic strata, the drainage quality can be acid or alkaline. In general, acidic drainage is produced by a sulphide-rich material but which is carbonate-poor, while alkaline drainage is usually produced by alkaline-rich materials, still with important sulphide concentrations (Carl & Cravotta, 2005a). Thus, certain drainages from some industrial sites are alkaline with a pH = 6.0 or higher, containing alkalinity and dissolved metals that can generate acid by oxidation and hydrolysis according to 2.1 and 2.2 reactions (Rıos, Williams & Roberts, 2008):

$$MeS_{(s)} + 2\,O_{2(aq)} \rightarrow Me^{2+} + SO_4^{2-} \qquad (2.1)$$

$$MeS_{(s)} + 2Fe^{3+} + 3/2\,O_{2(aq)} + H_2O \rightarrow Me^{2+} + 2Fe^{2+} + 2H^{+} + SO_4^{2-} \qquad (2.2)$$

The hydrolysis of dissolved metal ions irreversibly produces additional H^+ ions (mineral acidity) that also necessitate neutralisation, but were not accounted for by the original pH measurement. Net alkalinity and Net acidity concepts consider the pH, alkalinity, acidity and the metals concentration such as Fe, Al and Mn in mine effluents as shown in Equations 2.6, 2.7 and 2.8 below. The Net alkalinity notion is a critical decision parameter employed in the planning of mine drainage treatment (Carl & Cravotta, 2005b).

In general, mine water can be neutralised by the acid consuming species as given by Equations 2.3, 2.4 and 2.5 below:

Hydroxide: $OH^{-}_{(aq)} + H^{+}_{(aq)} \rightarrow H_2O_{(aq)}$ (2.3)

Carbonate: $CO^{2-}_{3(aq)} + H^{+}_{(aq)} \rightarrow HCO^{-}_{3(aq)}$ (2.4)

Bicarbonate: $HCO^{-}_{3(aq)} + H^{+}_{(aq)} \rightarrow H_2CO_{3(aq)}$ (2.5)

$$\text{Alkalinity} = [OH^{-}] + 2[CO_3^{2-}] + [HCO_3^{-}] - [H^{+}] \quad (2.6)$$

$$Net\ alkalinity = (Alkalinity_{Std.\ Meth} - Acidity_{calculated}) \quad (2.7)$$

According to Carl and Cravotta (2005b), the acidity in mg/L as $CaCO_3$ based on pH and analytical concentrations of dissolved Fe(II), Fe(III), Mn(II) and Al(III), can be computed by 2.8 Equation as follows:

$Acidity_{calculated}$ = pH and mineral acidity as $CaCO_3$ =

$$50\left[\frac{2Mn^{2+}}{54.94} + \frac{2Fe^{2+}}{55.85} + \frac{3Fe^{3+}}{55.85} + \frac{3Al^{3+}}{26.98} + 10^{(3-pH)}\right] \quad (2.8)$$

where metal concentrations are in mg/L.

2.1.2 Acid mine drainage

Acid mine drainage formation involves the four simultaneous following reactions 2.9, 2.10, 2.11 and 2.12:

1) Iron sulphide oxidation:

$$2FeS_{2(s)} + 7O_{2(aq)} + 2H_2O \rightarrow 2Fe^{2+}_{(aq)} + 4H^{+}_{(aq)} + 4SO^{2-}_{4(aq)} \quad (2.9)$$

2) Ferrous iron oxidation:

$$4Fe^{2+} + O_2 + 4H^{+} \rightarrow 4Fe^{3+} + 2H_2O \quad (2.10)$$

3) Ferric iron hydrolysis:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (2.11)$$

4) Oxidation of additional pyrite by ferric iron:

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+_{(aq)} \qquad (2.12)$$

The direct or indirect oxidation of bivalent metal sulphides by the action of Fe^{3+} yields the corresponding sulphates, according to 2.1 and 2.2 reactions. It should be noted that the main effect of these reactions is to release H^+ ions, lowering the pH and maintaining the ferric ion solubility, thus resulting in the formation of sulphuric acid and the leaching of heavy metals from the mineralised vein (Peppas, Komnitsas & Halikia, 2000). The sulphuric acid generated is then capable of dissolving metals, for instance aluminium, leading to their discharge into the environment. The oxidising acidophilic bacteria, such as acidithiobacillus ferrooxidans, acidithiobacillus thiooxidans and leptospirillum ferrooxidans play a significant role in speeding up this acid production process (Chockalingam & Subramanian, 2009).

2.2 PRODUCT WATER QUALITY

Pure water is rarely found in nature and its quality criteria depend upon its use. In water, impurities occur in three states: suspended, colloidal and dissolved. However, the water potability is certainly a desirable standard by which to judge other classes (Smethurst, 1988).

The toxicity of aluminium on living beings is dependent on its distribution among various forms or species coexisting in the environment (Matus & Kubova, 2006). The damage caused by sulphate emissions is not direct; however, high sulphate concentrations (accumulation) can perturb the natural sulphur cycle (Benatti, Tavares & Lenzi, 2009). Sulphate content in effluents is deleterious since SO_4^{2-} ions hydrolyze to form H_2SO_4 that is highly corrosive (Murugananthan, Raju & Prabhakar, 2004). Thus, the processing of industrial wastewaters containing substantial quantities of toxic and/or valuable components for their recovery or separation often becomes an absolute necessity.

Governmental bodies establish effluent standards based on the maximum concentration of pollutants discharged into the environment. According to the International Network for Acid Prevention (INAP, 2003), the maximum levels of some contaminants are given in Table 2.1.

Table 2.1: Water quality target

	DISCHARGE	POTABLE	HIGH QUALITY INDUSTRIAL
SO_4^{2-} (mg/l)	500	200	50
Ca^{2+} (mg/l)	300	150	50
Al^{3+} (mg/l)	20	0.5	x

2.3 EXISTING PROCESSES FOR Al(III) and $[SO_4^{2-}]_{tot}$ REMOVAL

Remediation options make use of both active and passive strategies. Active systems promote metal precipitation by chemicals (such as limestone) that neutralise AMD. Passive systems exploit H_2S production by sulphate reducing bacteria (SRB) in order to precipitate metals as sulphides (Kalin, Fyson & Wheeler, 2006).

Several treatment methods have been developed to reduce high sulphate concentration from different wastewaters:

* The limestone/lime process.

* The Barium salts process.

* The Cost-Effective Sulphate Removal (CESR) process.

* The Savmin process.

2.3.1 The limestone ($CaCO_3$) / lime $Ca(OH)_2$ process

Lime neutralisation is the most frequently applied treatment method, consisting fundamentally in raising the pH of the feed water to a level where the metals of interest are not soluble and precipitate (Aubé, Eng, Aubé, Zinck & Eng, 2003). In addition, this method can also be used for sulphate removal (Figure 2.1).

For sulphate removal, the process operates in three stages as described by Equations 2.13 to 2.16 below:

Limestone: neutralisation and CO_2 production

$$CaCO_{3(s)} + H_2SO_{4(aq)} + H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)} + CO_{2(g)} \qquad (2.13)$$

Lime: $Mg(OH)_2$ and $CaSO_4{\cdot}2H_2O$ precipitation

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_{2(s)} + CaSO_4{\cdot}2H_2O_{(s)} \tag{2.14}$$

CO_2: pH adjustment (lowering) and $CaCO_3$ precipitation

$$H_2O_{(aq)} + CO_{2(g)} \rightarrow CO^{2-}_{3(aq)} + 2\,H^{+}_{(aq)} \tag{2.15}$$

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(s)} \tag{2.16}$$

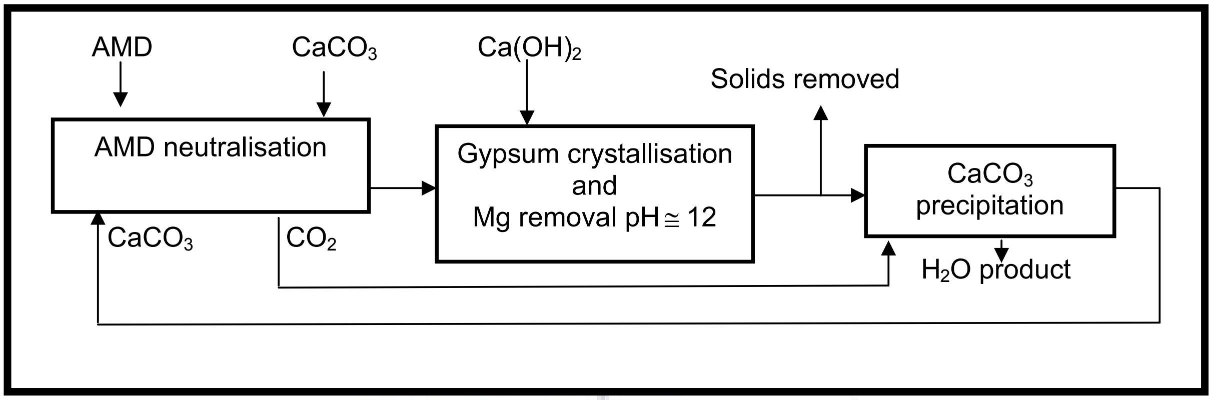


Figure 2.1: Limestone/Lime treatment process (INAP, 2003)

The degree of sulphate elimination depends on the solubility of the gypsum. According to the International Network for Acid Prevention (INAP, 2003), this process can reduce the sulphate concentration to less than 1200 mg/L, a value which is still significantly higher than the target discharge concentration of 500 mg/L. The process presents the advantage of removing trace metal and sulphate ions under gypsum saturation level, but the limited sulphate removal and the production of abundant mixed sludges such as $CaSO_4{\cdot}2H_2O\text{-}Mg(OH)_2$, constitute a disadvantage.

2.3.2 The Barium salts process

The barium salts process is suitable for treatment of sulphate-rich effluents. This process relies on the high insolubility of $BaSO_4$ (Bosman, Clayton, Maree & Adlem, 2006). Like the limestone/lime process, the barium salts process is also a three stage sulphate removal process as described by Equations 2.17 to 2.24 below:

Sulphate removal stage

Sulphate can be precipitated as $BaSO_4$ as shown in Equations 2.17 and 2.18.

$$BaCO_3 + Ca^{2+} + SO_4^{2-} \rightarrow BaSO_4 + CaCO_3 \tag{2.17}$$

$$BaS_{(s)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + H_2S_{(g)} \tag{2.18}$$

BaS and CaO regeneration

Barium sulphide and calcium oxide are regenerated thermally by reducing the $BaSO_4$-$CaCO_3$ with coal at 1000 to 1100°C for approximately 15 minutes as shown in Equations 2.19 and 2.20.

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2 \tag{2.19}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2.20}$$

H_2S-stripping and absorption

H_2S is removed by stripping with CO_2, according to the chemical reactions shown in Equations 2.21 and 2.22.

$$BaS + CO_2 + H_2O \rightarrow H_2S + BaCO_3 \tag{2.21}$$

$$BaS + 2CO_2 + 2H_2O \rightarrow H_2S + Ba(HCO_3)_2 \tag{2.22}$$

The barium carbonate is recycled back to the water treatment step and the hydrogen sulphide is converted into elemental sulphur according to 2.23 and 2.24 reactions:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \tag{2.23}$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S_0 \tag{2.24}$$

Recovery of high grade $CaCO_3$ and elemental sulphur as by-products that can be valorised, reducing the capital and operating costs, constitute the advantage of the process. However, barium salts are expensive and the thermal regeneration process costly.

2.3.3 The Cost-Effective Sulphate Removal (CESR) process

CESR process (also called Walhalla process) operates very similarly to the SAVMIN process, except for:

* Its use of a proprietary reagent known as SX-44 to precipitate dissolved metals and sulphate as the mineral formula ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$) which is easily removed using a conventional clarifier.

* Ettringite is not a recycled compound, and this constitutes its main disadvantage due to the high cost of aluminium salts (Mead, Olthaf & Hirschi, 2005).

The sulphate removal process consists of four stages and can reduce the sulphate concentration to less than 100 mg/L.

2.3.4 The Savmin process

This process consists of consecutive and selective precipitations leading to the formation of insoluble complexes at different stages of the procedure, among them ettringite. This latter constitutes the cornerstone of the process for removing sulphate, calcium as well as aluminium (Ayuso & Nugteren, 2005).

The Savmin process, patented by Mintek and Savannah Mining, seems to be an improvement of the CESR process; because it recycles the relatively large amount of ettringite produced. It includes five principal parts as illustrated by Figure 2.2.

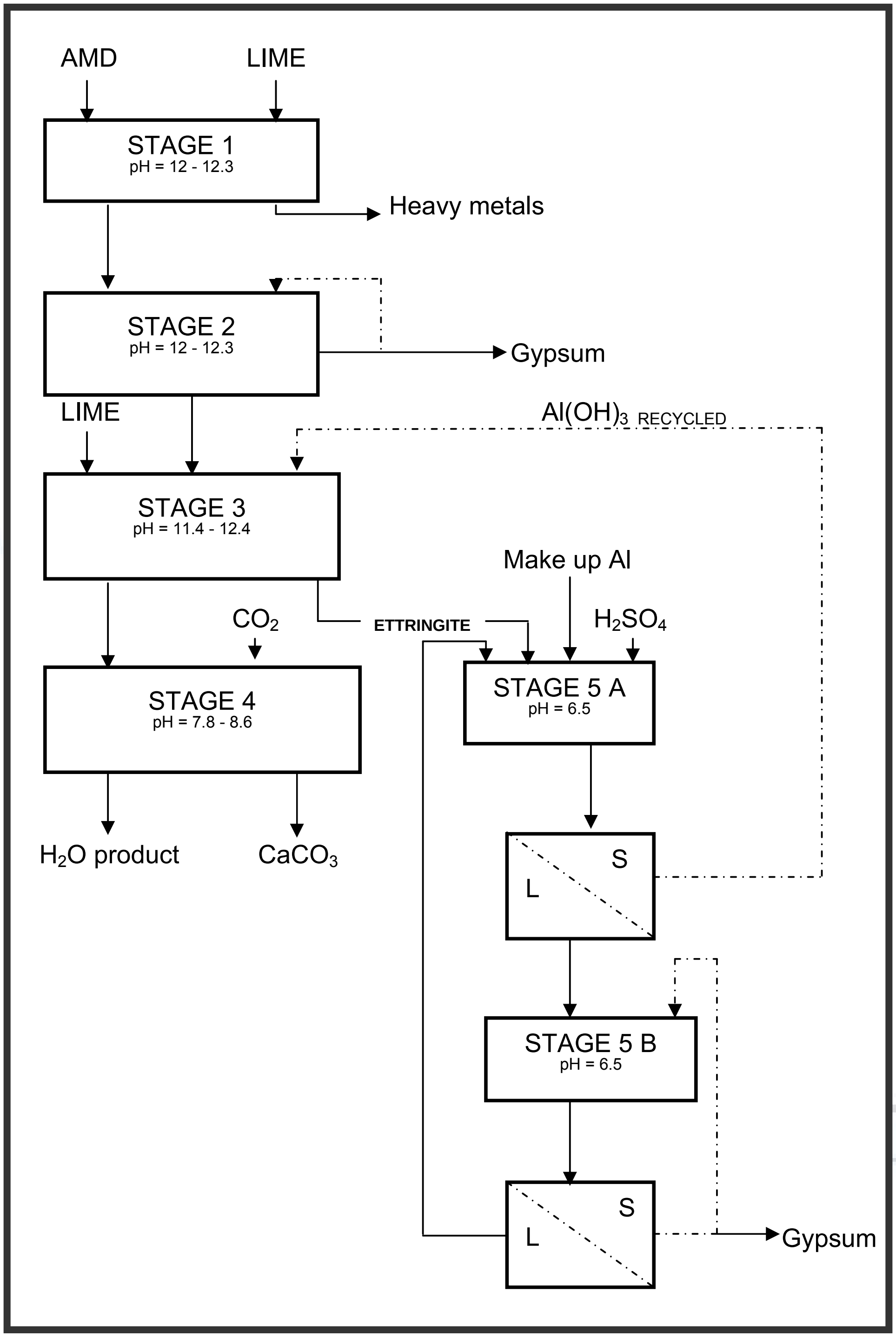


Figure 2.2: Savmin process flow diagram (INAP, 2003)

The sulphate removal process consists of five stages and can reduce the sulphate concentration to less than 100 mg/L (INAP, 2003). The increase of the pH between 11.4 and 12.4 by adding $Al(OH)_3$ and lime (Figure 2.2), leads to an insoluble salt, namely ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$), thereby removing both calcium, sulphate as well as aluminium from the AMD as shown in the reaction 2.25 below (INAP, 2003). Ettringite precipitates in highly alkaline solutions with high activities of Ca^{2+}, SO_4^{2-} and Al^{3+} (Chrysochoou & Dermatas, 2006; Baur, Keller, Mavrocordatos, Wehrli & Johnson, 2004).

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_{3(s)} + 37H_2O \rightarrow 3CaO \cdot 3CaSO_4 \cdot Al_2O_3 \cdot 31H_2O_{(s)} + 6H_3O^+ \tag{2.25}$$

2.4 AQUEOUS CHEMISTRY OF ALUMINIUM

2.4.1 Dissolution of elementary aluminium in aqueous solution

Elementary aluminium is a strongly hydrolysing metal and is generally insoluble in cool or hot water at neutral pH range of 6.0 to 8.0 (Kubová, Matúš, Bujdoš & Medved, 2005). The speciation of aluminium ions in solution is pH dependent; when the pH increases, Al^{3+} gradually undergoes sequential replacement of the water molecules by hydroxyl ions giving successively $[Al(OH)]^{2+}$, $[Al(OH)_2]^+$, $Al(OH)_3$ and $Al(OH)_4^-$ according to the chemical reactions shown in Equations 2.26 to 2.30 (Downs, 1993).

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^+ \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^- \tag{2.26}$$

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \tag{2.27}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \tag{2.28}$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \tag{2.29}$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \tag{2.30}$$

For the pH range above 6.2, $Al(OH)_3$ precipitate formed, starts to redissolve, giving the soluble tetrahedral aluminate $Al(OH)_4^-$. The passage from Al^{3+} to $Al(OH)_4^-$ is carried out in a narrow pH range owing to the proximity of their pK_a values of 5.5, 5.8, 6.0 and 6.2.

However, the dominant species in solution over pH range below 5.5 remain Al^{3+}, while $Al(OH)_4^-$ dominates at pH range above 6.2. Between these two pH values, there is a mixture of species as illustrated in Figure 2.3.

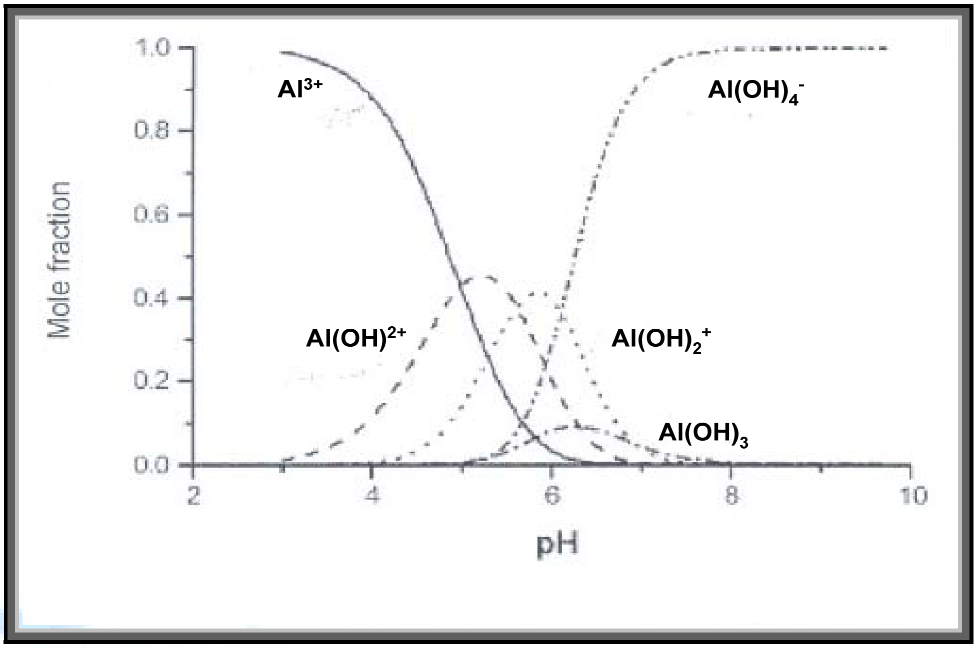


Figure 2.3: Distribution of monomeric Al hydrolysis as a function of pH (Gregory & Duan, 2001)

Figure 2.4 shows that at pH 7, the possible free Al^{3+} concentration is only $10^{-10.3}$M, and that for all soluble species is 2 µM (a minimum solubility), i.e. that aluminium addition at pH 7 implies only the dissolution of a minor amount which is found in soluble form $Al(OH)_4^-$. However, the minimum solubility of aluminium in the region of pH = 7, can be considerably affected by the existence of certain anions (complexing ligands), such as fluoride, phosphate and sulphate (Gauthier, 2002).

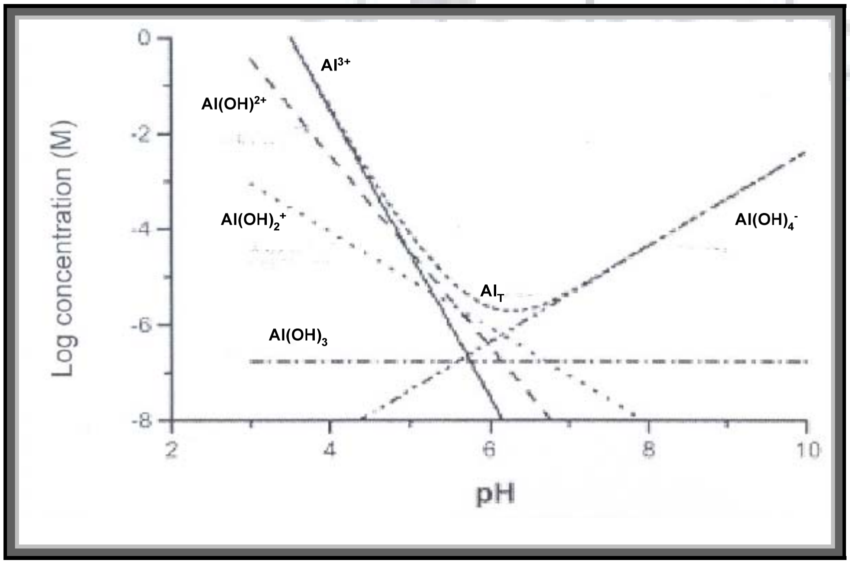


Figure 2.4: Concentration of soluble Al species in equilibrium with amorphous hydroxide (Al_T represents total soluble species) (Gregory & Duan, 2001)

2.4.2 γ-alumina dissolution in aqueous solution

Two forms of aluminium hydroxide $Al(OH)_3$, are well known: the minerals gibbsite (γ) and bayerite (α). The principal structural difference among these two aluminium hydroxide polymorphs arises in the mode of stacking successive layers (Wells, 1984). Nordstrandite is a structurally intermediate between gibbsite and bayerite.

γ-$Al(OH)_3$ gibbsite is therefore a structurally relative of γ-Al_2O_3, it is obtained by low-temperature dehydration (Downs, 1993). The widespread attitude is still that aluminium oxide is basically insoluble in an aqueous medium under ambient circumstances. Nevertheless, hydroxide phases form upon hydration of γ-Al_2O_3 in water as a function of the solution pH and of time. In aqueous suspensions at pH above 4, and for contact times greater than 10 h, γ-alumina not only hydrates on the surface, but also dissolves, leading to supersaturated solutions from which aluminium hydroxide particles precipitate and grow independently from the alumina surface. Xavier *et al*. (2007) plotted, as a function of time, the aluminium concentration in filtrates collected after suspension at pH 11 (Figure 2.5). They found that aluminium concentration goes through a maximum at a contact time of 10 hours and then decreases (the crystallised hydroxide particles start to grow) after approximately 70 hours. Obviously, the bayerite phase formed during the dissolution process is responsible for the equilibrium concentration values at the end of the dissolution process (Frank & Vogelsberger, 2006).

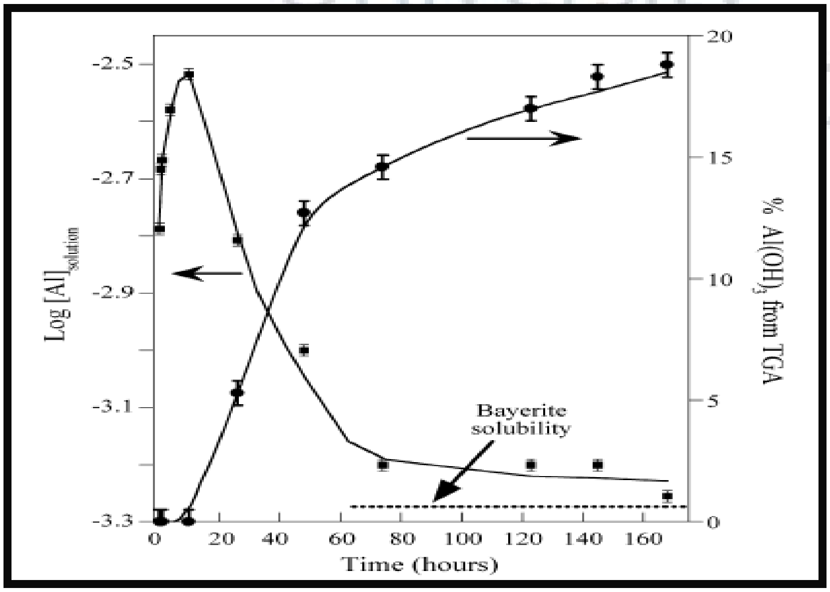


Figure 2.5: Evolution of the amount of bayerite with the aluminium concentration in the filtrates as a function of time after suspension at pH 11 for different times (Xavier *et al*., 2007)

2.5 SULPHATE AQUEOUS PHASE

2.5.1 Sulphuric acid dissociation

The dissociation of sulphuric acid does not happen all at once, due to the two stages of dissociation having different K_a values; each ionisation being treated as a separate step (Equations 2.31 and 2.32). The first dissociation goes to completion (K_{a_1} = 10^3), while the second one will not; it is only partially dissociated (Murry & Fay, 1995). The dissociation constant for the second stage has been estimated by several different methods to be about 0.01, so that even in a relatively dilute solution, ionisation of bisulphate ion is incomplete (Marziano, Tomasin, Tortato & Isandelli, 1998).

$$H_2SO_{4(aq)} + H_2O \rightleftarrows HSO^-_{4(aq)} + H_3O^+_{(aq)} \qquad (2.31)$$

$$HSO^-_{4(aq)} + H_2O \rightleftarrows SO^{2-}_{4(aq)} + H_3O^+_{(aq)} \qquad (2.32)$$

The equilibrium constant for the second dissociation (Equation 2.32) changes with temperature. The reported values of K_{a_2} (Robinson & Stokes, 2002) fit the following 2.33 Equation:

$$\log K_{a_2} = -\frac{475.14}{T} + 5.0435 - 0.018222T \qquad (2.33)$$

The change of $\log K_{a_2}$ for bisulphate ionisation indicates that the protonation of the sulphate ions is much favoured by increasing the temperature (Barnes, 1997). The total sulphur concentration in solution can be expressed as in Equation 2.34. The distribution of species SO_4^{2-}, HSO_4^- and H_2SO_4 in solution is pH dependent.

$$[Total\ sulphur] = H_2SO_4 + HSO_4^- + SO_4^{2-} = HSO_4^-\left(1 + \frac{H_2SO_4}{HSO_4^-} + \frac{SO_4^{2-}}{HSO_4^-}\right) \qquad (2.34)$$

Considering Equation 2.34, the bisulphate ion concentration can be isolated from sulphuric acid and sulphate as shown in Equation 2.35 below:

$$HSO_4^- = \frac{[Total\ sulphur]}{\left(1+\frac{H_2SO_4}{HSO_4^-}+\frac{SO_4^{2-}}{HSO_4^-}\right)} = \frac{[Total\ sulphur]}{\left(1+\frac{H_3O^+\cdot H_2SO_4}{H_3O^+\cdot HSO_4^-}+\frac{H_3O^+\cdot SO_4^{2-}}{H_3O^+\cdot HSO_4^-}\right)} = \frac{[Total\ sulphur]}{\left(1+\frac{H_3O^+}{K_{a_1}}+\frac{K_{a_2}}{H_3O^+}\right)} \qquad (2.35)$$

The same calculations can be made for sulphate and sulphuric acid as expressed by Equations 2.36 and 2.37:

$$SO_4^{2-} = \frac{[Total\ sulphur]}{\left(1+\frac{H_2SO_4}{SO_4^{2-}}+\frac{HSO_4^-}{SO_4^{2-}}\right)} = \frac{[Total\ sulphur]}{\left(1+\frac{H_3O^+}{K_{a_1}}+\frac{H_3O^+}{K_{a_2}}\right)} \qquad (2.36)$$

$$H_2SO_4 = Total\ sulphur - HSO_4^- - SO_4^{2-} = \frac{[Total\ sulphur]}{\left(1+\frac{K_{a_1}}{H_3O^+}+H_3O^+\cdot H_3O^+\cdot K_{a_2}\cdot K_{a_1}\right)} \qquad (2.37)$$

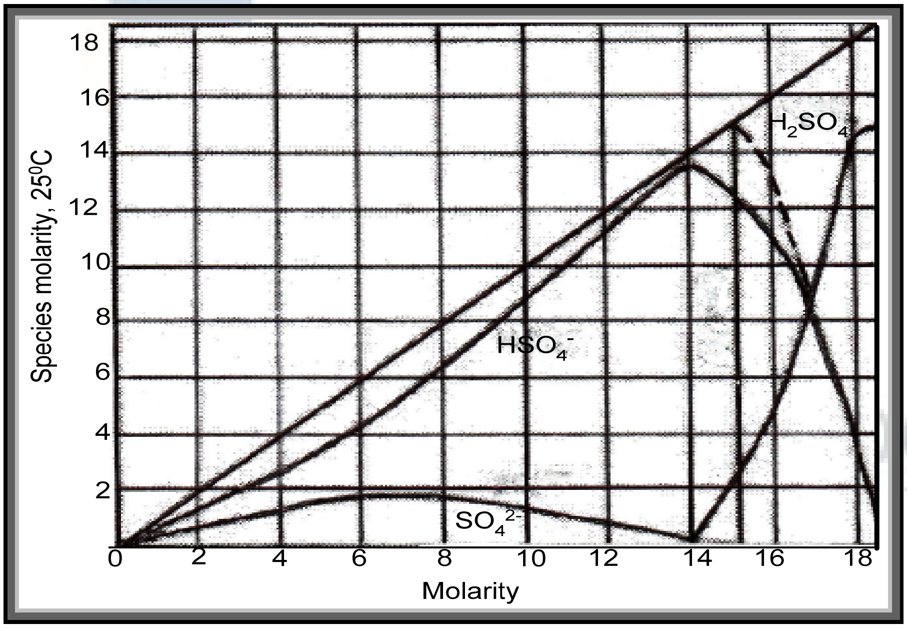


Figure 2.6: Graph illustrating the proportion of H_2SO_4 molecules, HSO_4^- and SO_4^{2-} ions in aqueous sulphuric acid solution (Robinson & Stokes, 2002)

Generally, sulphuric acid contribution in the calculation of total sulphur is very small, and always negligible due to the huge value at the denominator (Equation 2.37). From Figure 2.6, it is clear that the distribution of the main species exists as bisulphate, both in concentrated and dilute acid.

In their studies, Visser, Modise, Krieg and Keizer (2001) revealed that the equilibrium constant pK$_a$ value of the reaction in Equation 2.32 is approximately 1.92; meaning that the HSO_4^- and SO_4^{2-} concentrations are equal at pH of 1.92. At a pH lower than 1.92, HSO_4^- ion prevails over SO_4^{2-}, while the reverse is observed for a pH over 1.92. This crossover is at about a concentration of 800 ppm of H_2SO_4 in water as illustrated in Figure 2.7.

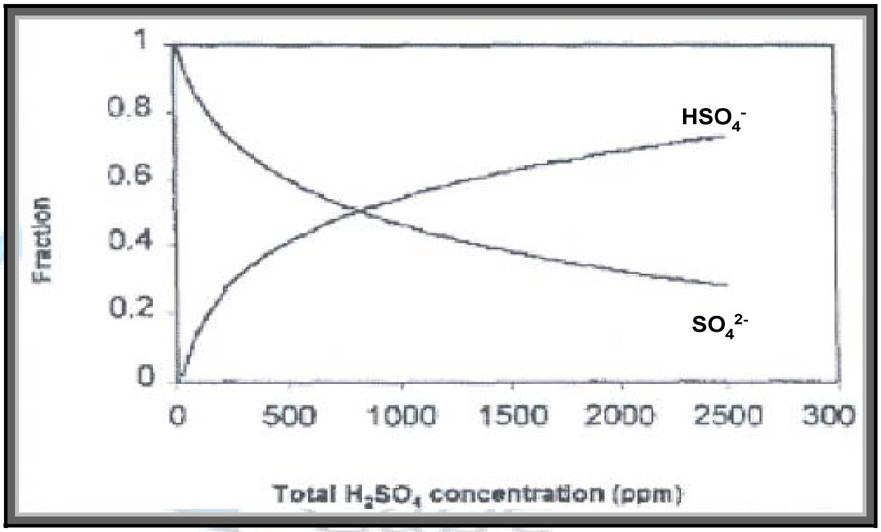


Figure 2.7: Sulphate and bisulphate ions fraction as a function of H_2SO_4 concentration (Visser *et al.,* 2001)

2.5.2 Estimate of SO$_4^{2-}$ extraction constant

From the equilibrium shown in Equation 2.32, sulphate anion will predominate over 'free' bisulphate in strongly alkaline media. On this basis, the reaction between R_4NCl and sulphate ion can be described by the following 2.38 Equation.

$$2R_4NCl_{(org)} + SO_{4(aq)}^{2-} \leftrightarrows (R_4N)_2SO_{4(org)} + 2Cl_{(aq)}^- \qquad (2.38)$$

The equilibrium constant is given by Equation 2.39:

$$K_{ex} = \frac{[(R_4N)_2SO_4]_{org}[Cl^-]_{aq}^2}{[R_4NCl]_{org}^2[SO_4^{2-}]_{aq}} = \frac{V_{aq}D[Cl^-]_{aq}^2}{V_{org}[R_4NCl]_{org}^2} \qquad (2.39)$$

$$\log D = \log K_{ex} - 2.\log\frac{V_{aq}[Cl^-]_{aq}}{V_{org}[R_4NCl]_{org}} \qquad (2.40)$$

The equilibrium concentration of free quaternary ammonium salt $\left[R_4NCl\right]_{org}$ in the organic phase can be calculated from a mass balance as given by Equation 2.41 (Barbara & Apostoluk, 2005):

$$[R_4NCl]_{org} = c^0_{R_4NCl} - [Cl^-]^e_{aq} \tag{2.41}$$

where $c^0_{R_4NCl}$ denotes the initial concentration of Aliquat 336 and $[Cl^-]^e_{aq}$ represents the equilibrium concentration of chlorine ions in the aqueous phase.

A plot of $\log D$ vs. $\log \dfrac{V_{aq}[Cl^-]_{aq}}{V_{org}[R_4NCl]_{org}}$ (Equation 2.40 above) should give a straight line with a slope of two where $\log K_{ex}$ equals intercept.

2.6 SOLVENT EXTRACTION AS AN ALTERNATIVE EXTRACTION TECHNIQUE OF ANIONIC SPECIES

Research has been published on the use of elevated molecular weight amines dissolved in a variety of organic solvents for the extraction of acid, as well as certain anionic metal complexes (Schunk & Maurer, 2002; Gottliebsen, Grinbaum, Chen & Stevens, 2000; Cattral & Slater, 1974). In the same way, a selective and quantitative separation of Al(III) from the alkaline solution can be effected through liquid-liquid extraction. A substantial quantity of work has been published on the removal of Al(III) as an impurity from synthetic Bayer liquors (Kekesi, 2007; Zaki, Ismail, Daoud & Aly, 2005; Borges & Masson, 1994). Not much systematic study has been reported on the SX of Al(III) and SO_4^{2-} from concentrated alkaline solutions.

Solvent extraction (SX), also called liquid-liquid extraction (LLE), is a separation method that allows a selective separation of two or more components owing to their asymmetrical solubilities in two immiscible liquid phases. Usually one phase is aqueous (hydrophilic), while the other is an organic solvent (hydrophobic).

2.6.1 Elementary principles of solvent extraction

As described in Figure 2.8, the basic steps involved in a solvent extraction process include: 1) extraction, 2) scrubbing, 3) stripping, and 4) solvent recovery.

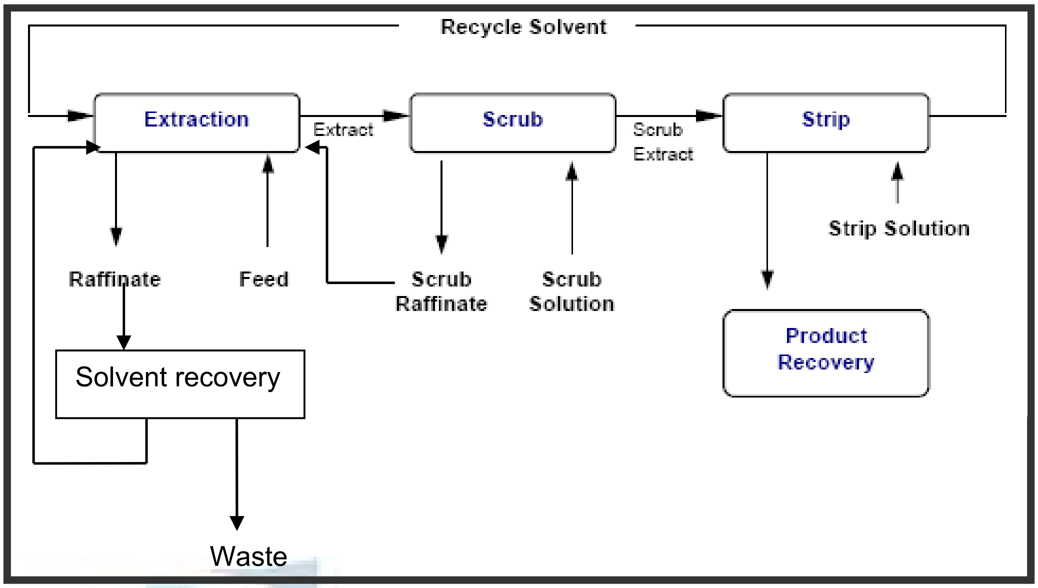


Figure 2.8: Typical flowsheet of SX circuit (Ritcey & Ashbrook, 1984)

2.6.1.1 Extraction

A. Aqueous phase

The aqueous solution containing the valuable metal, often at a low concentration, is mixed thoroughly with an immiscible organic phase containing the active extractant which transfers the desired metal into the organic phase. The extraction path produces a pregnant organic phase containing the metal of interest, and a raffinate, which is the aqueous phase dwindled off the metal. The valuable component is normally as a metal ion or a metal ion complex contained in an aqueous solution. The different extractable species can be categorised into four groups (Ritcey & Ashbrook, 1984):

1) Complex metal anions, for example $Al(OH)_4^-$, $Cr(OH)_4^-$.

2) Metal cations, such as Al^{3+}, Fe^{2+}, and Zn^{2+}.

3) Neutral metal specials, such as $UO_2(NO_3)_2$.

4) Complex metal cations, such as MoO_2^{2+}.

B. Organic phase

The molecular formula of the solute may suggest the type of solvent which may be ion selective, based on the probable affinities between related functional groups (Ritcey & Ashbrook, 1984). The pH of aqueous phase feeds may also be very important (Kabra, Chaudhary & Sawhney, 2007). There are four basic classes of metal extractants as characterised by structure, extraction mechanism and the metal species extracted (Prasad, 1992):

1) Chelating extractants.
2) Amines or ion-pair extractants.
3) Neutral or solvating extractants.
4) Organic acid extractants.

B.1 Al(III) ions uptake by the organic phase

Most of the metal ions precipitate readily as metal hydroxides from alkaline solutions, thus literature on solvent extraction of metals from aqueous alkaline solutions is scarce. However, Sato and Sato (1991) have examined the kinetics of Al(III) extraction from NaOH solutions using Kelex 100 in Kerosene. With regard to aluminium extraction, they concluded that the extraction rate was slow; a prolonged contact time of the aqueous and organic phases was needed to achieve excellent recovery, which was mainly attributable to the formation of activated species such as $[Al(OH)_3]\cdot OH^-$ and $Na^+[Al(OH)_3]\cdot OH^-$.

In a recent study, Kekesi (2007) reported that 14 to 20% of Kelex 100 in pure Kerosene can be applied to gallium separation in the presence of aluminium from Bayer liquors. He achieved a good Ga/Al separation efficiency by taking advantage of the differences in the kinetic behaviour determined by the dehydration of the respective hydroxo-complex species. The dehydration of aluminate species is promoted by increasing ionic strength (adding NaOH) and thus speeding up the extraction of aluminium.

On the basis of the above reports, the conclusion was that the Al(III) extraction was achievable in the alkaline pH region. So, it is indispensable to choose an appropriate extractant and diluent (Ritcey & Ashbrook, 1984).

B.2 Counter-ion, effect of competitive ions: SO_4^{2-} - HSO_4^- extraction

Many studies have been already attempted for the determination of the prevalence between HSO_4^- and SO_4^{2-} in aqueous phase as counter-ion in the extraction using high weight amines dissolved in various organic diluents (Tait, 1993; Cattral & Slater, 1974). The relative affinities of different anions to Aliquat 336 are in the order of $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-}$ which corresponds to the order of complexing ability proposed by Ritcey and Ashbrook (1984). On the other hand, Cl^- will be found in the organic phase if the competitive anion is SO_4^{2-}. Even though HSO_4^- has a greater affinity for the amines than SO_4^{2-} (Braun & Ghersini, 1975), it was observed that sulphate extraction occurred at higher pH values.

Quaternary ammoniums can extract anions and anionic metal complexes as ion-pairs (Sekine & Hasegawa, 1977). Aliquat 336 ($C_{12}H_{54}ClN$), which is Trioctylmethylammonium chloride ($TOMA-Cl$) (also known as: Tricaprylmethylammonium chloride; N-methyl-N,N dioctyl-1-octanaminium chloride, or Methyltrioctylammonium chloride as used in this study), is a water insoluble quaternary ammonium salt made by the methylation of mixed tri-octyl/decyl amine.

C. Chemistry of extraction processes - Third phase formation

According to Vladimir and Eyal (2003), the solvation effects play a huge role in extraction trends. However, the effects of co-extracted water on the degree of extraction remain unclear. In various cases, the complicated behaviour of extraction systems conflicts with classical ion exchange models. In water or other polar and high dielectric constant liquids, metal salts have a propensity to dissociate into ions, since the ions are suitable to be surrounded with a shell of the solvent molecules as solvated ions. They can interact with other oppositely charged and solvated ions (Lo, Baird & Hanson, 1983).

The complex formation phenomenon occurs when, following a stoichiometric relation between the concentrations of chemical species, a metal ion in a solvent associates with one or more other ions or molecules called ‘ligands’. Two types of complex species can be distinguished: 1) the pure complexes and 2) the ion pairs (Stumm & Morgan, 1981).

Pure complexes are formed when the metal ion forms a coordination complex by interacting with a ligand by coordination bonds, and some water molecules are replaced with the ligand. This results in the construction of largely covalent bonds between the metal ion and an electron-donating ligand. Generally, the complex is stable when the charges are larger and/or the distance between their centres at equilibrium is smaller (Stumm & Morgan, 1981).

Ion pairs, on the other hand, are formed when a pair of oppositely charged ions is held mutually by Coulomb attraction with no construction of a covalent bond. There is a distinction between the two types of association. According to Stumm and Morgan (1981), a dehydration step must precede the formation of complexes; whereas the formation of ion pairs may be accompanied by changes in the ultraviolet region.

Amine extractants are best indicated for anionic species extraction. Primary amines (RNH_2) habitually extract anionic sulphate complexes better, while tertiary and quaternary amines extract anionic chloro-complexes best (Ritcey & Ashbrook, 1984). The interaction of quaternary ammonium ions with metal ionic complexes is mainly electrostatic. Thus, the degree of extraction is due to the extent of ion-pair formation. The extraction of metal complexes can proceed by an anion exchange reaction represented by the scheme given in Equation 2.42 (Lo *et al*., 1983):

$$(R_4N^+X^-)_{org} + (MY_{n+1}^-)_{aq} \leftrightarrows (R_4N^+MY_{n+1}^-)_{org} + (X^-)_{aq} \tag{2.42}$$

where X^-, Y^- are anions while M is a metal ion.

According to Xun, Zhengshui, Debao, Huan and Xiaopeng (2000), the organic phase could split into two parts, namely heavy and light organic solutions, when the metal loading concentration in the organic phase is higher than the Limiting Organic Concentration value (LOC). In addition, experimental conditions, such as aqueous acidities, diluents, extractant structure and extracted metals, can affect the third phase formation. The latter (third phase) was observed at the beginning of the tests of this research study.

Lo *et al*. (1983), indicated from their studies that third phase formation is common in the quaternary ammonium salt systems and occurs through solubility problems relating to aggregation. To mitigate this problem, 1-decanol can be used as modifier. The modifier should be very soluble in the organic phase and insoluble in the aqueous phase (Blumberg, 1998).

2.6.1.2 Scrubbing

Scrubbing is a careful elimination of contaminating metals from the pregnant organic phase by treatment with a clean scrub solution or a strip liquor bleed. Next, the scrubbed organic containing the valuable metal is sent to the stripping process (Lo *et al*., 1983).

2.6.1.3 Stripping

Stripping is a process of removing a metal of value from the scrubbed organic phase by reversing the extraction chemical reaction. The strip liquor is the product of the SX circuit (Lo *et al*., 1983).

2.6.1.4 Solvent recovery

In addition to its double objective, namely economic and environmental, solvent recovery operation has an important influence on the extraction scheme adopted (Ritcey & Ashbrook, 1984). Even though extraction may successfully remove the solute from the feed, further separation is required in order to recover the solute from the solvent and to make the solvent suitable for reuse in the extractor (Lo *et al*., 1983). There exist several methods for solvent recovery, such as distillation, evaporation, crystallisation, chemical reaction and liquid extraction (Blumberg, 1998).

2.6.2 Extractant selection

One of the key decisions to make when designing an extraction process is the selection of the solvent to be used. The following factors must be taken into consideration in this selection (Gupta, Gupta, Mukherjee & Pashev, 1990):

1) Distribution coefficient: large values are preferable; they mean that less solvent is required for the separation.

2) High selectivity: the ability to remove and concentrate the solute from the other components likely to be present in the feed. It is necessary to have a separation factor greater than unity, and preferably as high as possible.

3) Ease of recovery: solvent recovery is always preferable for reuse, because the inventory of solvent in the extraction system can represent a significant capital investment. Solvent recovery will need to be as total and as pure as possible to allow a recycle to the extractor, as well as minimising losses, as well as potential pollution problems.

4) Immiscibility: solvent should not be soluble in the carrier liquid (the feed).

5) Density difference: low density difference between the two phases will result in separation problems.

6) Reasonable physical properties:
* A viscous solvent will hinder both mass transfer and overall capacity.
* Low interfacial tension may lead to emulsion problems. The larger the interfacial tension between the two phases, the more easily coalescence occur. However, the higher the interfacial tension, the more difficult the dispersion will be.

7) Toxicity, safety, flammability and vapour pressure: must be taken into account for employee's health considerations, purity of the product, and other environmental issues.

8) Rapid kinetics and chemical reactivity: Kinetics of solvent extraction is naturally much faster. This is attributed to higher mass transfer properties. The solvent should also be inert and stable, to avoid chemical degradation.

2.6.3 Diluents selection

The diluent comprises the bulk of the organic phase and is an inert ingredient whose principal function is to act as a carrier for the relatively small amount of extractant. Diluents are hydrocarbons and can be aliphatic, aromatic, or a mixture of the two (Ritcey & Ashbrook, 1984). By themselves, diluents have no capacity to remove metal ions from the aqueous phase; but they influence quite significantly the extraction, scrubbing, stripping and phase separation processes (Gupta *et al*., 1990). In other words, they significantly affect the physical properties of the organic phase (e.g. density and viscosity) and the interfacial phenomena, as well as the extraction equilibrium, selectivity and kinetics of a solvent extraction process through both chemical and entrainment effects (Mohapatra, Hong-In, Nam & Park, 2007).

According to Mohapatra *et al.* (2007), the reason is that a variety of interactions may take place between the diluent and the extractant, ranging from cavity formation, dipole-dipole interaction, pi-electron interaction and hydrogen bonding. The selection of the diluent can be done on the basis of a flash point, to minimise evaporation loss and risk of fire; viscosity and environmental parameters (Lo *et al*., 1983).

Kerosene is obtained from petroleum distillation. Generally, it contains a mixture of paraffinic, aromatic and naphthenic hydrocarbons. The existence of double bonds in the diluent creates the sites for oxidation reaction and irreversible extraction of metals (Harvinderpal & Gupta, 2000), thus increasing its susceptibility to chemical attacks. Hence, Kerosene treatment to yield aliphatic fractions for use as diluent must be carried out. Generally, aliphatic hydrocarbons have a higher extraction coefficient than aromatic hydrocarbons (Ritcey & Ashbrook, 1984).

2.6.4 Distribution factor and selectivity

Solvent selection is governed by two important parameters: the partition coefficient and selectivity (Lo *et al*., 1983). At equilibrium in dilute solutions, the ratio of solute concentration

(C) in the two phases is called the ‘partition coefficient’ (‘distribution coefficient’, ‘distribution factor’ or ‘distribution constant’) of the solute. It measures how well-extracted a species is. It can be expressed by either Equations 2.43 or 2.44 as shown below:

$$D = \frac{[C]_{org}}{[C]_{aq}} \qquad (2.43) \qquad D = \frac{{}^{V_{aq}}\!/_{V_{org}} \cdot \%E}{(100 - \%E)} = \frac{V_{aq}}{V_{org}}\left(\frac{C^0}{C_{raf}} - 1\right) \qquad (2.44)$$

$$\%E = \frac{W - W_{raf}}{W} \times 100 \qquad (2.45) \qquad \%E = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \times 100 \qquad (2.46)$$

It is desirable for the distribution coefficient to be large, as a large value implies that the majority of the metal is found concentrated in the organic phase and that less solvent will be required for the recovery.

The extraction percentage is expected to be high when using a low value of the aqueous/organic volumetric ratio V_{aq}/V_{org}. However, the O/A ratio of the phases in a mixer has a considerable effect on entrainment. When the O/A ratio is greater than unity, it is preferable to disperse the minority liquid to minimise backmixing (Treybal, 1963).

It is more suitable to measure the performance in terms of the degree of approach to the equilibrium, rather than in terms of the degree of extraction (Equation 2.45 or 2.46). Thus extraction efficiency (% approach to equilibrium) is expressed in Equation 2.47 (Lo *et al*., 1983):

$$\%E_{eff} = \frac{W - W_{raf}}{W - W_{raf}^{e}} \times 100 \qquad (2.47)$$

Finally, if more than one solute is present in the feed solution; the preference or selectivity of the solvent for one (X) over the other (Y) is the separation factor η_{XY} (Sekine & Hasegawa, 1977). It must be greater than unity in order to separate X from Y by solvent extraction. The separation factor can be expressed by Equation 2.48 as follows:

$$\eta_{XY} = \frac{D_X}{D_Y} \qquad (2.48)$$

2.6.5 Loading capacity

The loading capacity of the extractant is important for its commercial applicability. The loading capacity gives the maximum concentration of metal ions which can be extracted from the aqueous phase into the organic phase at a constant pH and temperature (Sekine & Hasegawa, 1977). It is usually preferable to operate under maximum solvent loading conditions. Sometimes, this involves the formation of a third phase. To inhibit third phase formation, a modifier can be added to the solvent to increase the solubility of the extracted species (Kumar, Lee, Lee, Kim & Sohn, 2008).

The loading capacity can be obtained either by contacting a solvent several times with fresh aqueous solution, or by using a concentrated solution of the metal with a high (A/O) ratio, until a maximum loading is achieved (Ritcey & Ashbrook, 1984). From a mass balance of the metal species distributed between the solvent and the aqueous phase, the loading capacity can be evaluated using Equations 2.49 and 2.50 (Gupta *et al*., 1990):

$$C_{aq}^{0}V_{aq} = C_{aq}^{e}V_{aq} + C_{org}^{e}V_{org} \quad (2.49)$$

$$C_{org}^{e} = \frac{V_{aq}}{V_{org}}(C_{aq}^{0} - C_{aq}^{e}) \quad (2.50)$$

The extent to which the organic phase may be loaded with a solute can be expressed as a loading ratio described by Equation 2.51:

$$Z = \frac{[C]_{org}^{t}}{[\text{Extractant}]_{org}^{0}} \times 100 \quad (2.51)$$

The loading ratio (Z) is defined as the total concentration of the metal in the enriched organic phase due to complexation with the extractant divided by the extractant concentration (Rodrigues, da Silva, da Silva, Paggioli, Minim & Coimbra, 2008).

2.6.6 Selection of continuous and dispersed phase

For a rapid mass transfer at the interfacial liquid surface, it is necessary that one of the liquids be spread into thin films or dispersed in the form of small droplets that pass through a continuum of the other (Stevens, 2006). The dispersed phase selection includes the desire of a smaller hold-up (volume dispersed phase / total volume) in the extractor, and also the choice of construction materials, which can influence the relative wetting by the two phases. Thus the type of dispersion has a significant influence on the mass transfer or phase separation properties. The dispersed phase may be either heavy or light. However, it is preferable to disperse the phase with an elevated flow rate, to generate a larger interfacial area (Treybal, 1963).

In baffled vessels, the liquid in which the impeller is immersed when the system is at rest will normally be the continuous phase (Seader & Henley, 1998). According to Blumberg (1998), the mass transfer rate between two fluid phases is generally enhanced when transfer occurs from the organic drops to the aqueous continuous phase and is retarded in the opposite direction. Finally, from the operational point of view, the tendency is to disperse the minor phase into the major phase.

2.6.7 Extraction equipment types

Industrial liquid-liquid extraction equipment can be classified into two main categories: vessels in which mechanical agitation is provided for mixing, and vessels in which the mixing is done by the flow of the fluids themselves (Treybal, 1963).

Mixer settlers: consist of an agitated tank for mass transfer followed by a settling tank to separate both phases, due to a density difference between the two liquids. They are employed when there is only one equilibrium stage in the extraction procedure.

Column extractor: consists of a vertical column which provides continuous counter-current contact between the insoluble phases. The more dense phase enters at the top and flows downwards, while the less dense phase enters at the bottom and flows upwards. There are two different types of column extractors: non-agitated and agitated columns.
For the non-agitated column, such as packed and spray extraction column, the two phases are brought into counter-current contact in a tower: mixing and settling proceed continuously and simultaneously. As for the agitated column, there is a series of disc or turbine agitators mounted on the central rotating shaft.

2.6.8 Factors influencing solvent extraction

There are a number of factors affecting extraction performance such as pH, temperature, concentration of reactants, viscosities of the two phases, the intensity of agitation (surface area) and catalysts (modifiers, surfactants). Some of them are discussed below and in Chapter five of this work.

2.6.8.1 Influence of pH

The extraction and formation of an ion pair are influenced by the pH of the medium (Kabra *et al.,* 2007). The aluminium ions may exist in the aqueous phase in different ionic forms (Downs, 1993). The amount of aluminium and the pH can dictate which particular aluminium ion species will be predominant in the aqueous phase. $Al(OH)_4^-$ anions prevail in alkaline solutions while Al^{3+} cations dominate in acidic aqueous solutions as extractable species (Downs, 1993; Stumm & Morgan, 1981). This reveals that the mechanism of extraction of Al(III) ion is pH dependent and then it (pH) could affect the stability of the complexes (Figures 2.3 and 2.4).

2.6.8.2 Effect of temperature on extraction

The collision theory states that the more collisions in a system, the more likely combinations of molecules will happen (Moore, 1962a). A higher number of collisions in a system imply that more combinations of molecules can occur. The reaction will go faster, and the rate of reaction will be higher. Thus, by increasing the temperature of the fluid, the energy levels of the involved molecules in the reaction increases, resulting in them moving faster; consequently when particles are moving quicker, the time between collisions is less and more collisions will take place per unit time, meaning more reactions will take place increasing the overall rate of the reaction.

The dependence of the rate data on temperature can be treated by the Arrhenius and Activated Complex Theories to find the values of E_a, ΔH and ΔS as described by Biswas, Habib and Mondal (2004). Using the Arrhenius theory, the rate data of temperature dependence can be evaluated from Equation 2.52:

$$k = A_0 e^{-E_a/RT} \tag{2.52}$$

Taking the natural log of both sides of the Arrhenius Equation gives:

$$\ln k = -\frac{E_a}{RT} + \ln A_0 \tag{2.53}$$

At the same concentration, the activation energy values can be obtained from the Arrhenius

Equation by using the k_1 and k_2 values at different temperatures (Levenspiel, 1999).

Thus Equation 2.53 becomes:

$$\ln\frac{k_2}{k_1} = \ln\frac{t_1}{t_2} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.54}$$

In this work, instead of using Equation 2.54, the rate data of temperature dependence have been treated by the Activated Complex Theory for the estimation of E_a as shown in Equation 2.55 (Baruah & Khare, 2007).

$$E_a = \Delta H + RT \tag{2.55}$$

2.6.8.3 Effect of reactant concentration

The collision theory predicts that the frequency of collisions between two reactants increase when the concentration of the reactants increase (Murry & Fay, 1995). If there is less of any of the reactants, there will be fewer collisions, and the reaction will probably happen at a slower rate. The rate of reaction is limited by the concentration of the diluted solution or reactant, and increasing the concentration of the other reactant will make no difference. It is desirable to fix the concentration of one of the reactants to excess, and then one can increase the concentration of the other constituent to produce an increase in the rate of the reaction (Moore, 1962a).

2.6.8.4 Viscosity effect

The viscosity of solvents has significant effect on mass transfer coefficients. It (the viscosity) affects both molecular diffusion and convection inside a drop. Therefore, solvents with higher viscosity have lower mass transfer coefficients (Jie, Weiyang & Li, 2005). Mechanical agitation can promote the mass transfer rate and extractor efficiency because it increases interfacial area between the two immiscible liquids and new surfaces and high turbulence which increase mass transfer coefficients. However, the surfactants - amphiphilic molecules with polar head groups (hydrophilic part) and hydrophobic tails - play an important role with regard to drop size. The surfactants can lower interfacial tension, resulting in smaller drop size formation and increased carry-over (Stevens, 2006).

In many cases, it is necessary to know the mass transfer rate between the phases, which is an important factor in determining the number of stages necessary for a given separation.

One method to determine the rate law for the reaction is to experimentally measure how the concentration of a reactant or product varies over time, and then make characteristic kinetic plots (Levenspiel, 1999).

2.6.8.5 Mixing efficiency criteria

Extraction equilibrium and settling time are controlled by the droplet size (Takahashi & Susumu, 1999). Thus, excessive agitation sometimes causes difficulties in phase separation; while less mixing causes the formation of large droplets which decreases the interfacial area. This reduces mass transfer and decreases stage efficiency; whereas more mixing minimises mass transfer resistance during extraction reactions but contribute to the formation of small droplets or emulsions which are difficult to separate. It is important to supply just the exact amount of mixing required (Pinto, Durão, Fiúza, Guimarães & Madureira, 2004).

2.7 SUMMARY

The technologies discussed in Section 2.3 remove heavy metals and sulphate to different levels. The process streams may contain some levels of sulphate and other dissolved metals such as aluminium. Solvent extraction may provide a complementary method to improve the quality of the process water by removing the sulphate and aluminium from solution.

From the chemistry of aluminium and sulphate, it was determined that both these species are pH dependent. Previous research has indicated the applicability of solvent extraction of these components under acidic conditions. The current research will focus on the applicability of solvent extraction under alkaline conditions.

CHAPTER 3 : MATERIALS AND METHODS

This chapter describes the experimental conditions, procedures and analytical techniques followed in this research study. In order to observe the combined influence of certain factors on solvent extraction rate, equilibrium tests were carried out in a batch reactor using synthetic solutions.

3.1 FACTORIAL DESIGN

Factorial design has been employed to determine the minimum number of experiments required and to obtain a regression model with interactive terms in order to predict the response as a function of independent variables and their interactions. With the one-factor-at-a-time method, the complete factorial design requires 2^5 = 32 trials. This will enable the researcher to estimate all two and three-factor interactions, and also achieve a better estimate of the variance; thus the risk of making the first and second kind errors (α and β respectively) will be much lower than required since N is greater than required.

The design determines which factors have important effects on the response, as well as how the effect of one factor varies with the level of the other factors. The determination of factor interactions could only be done by using statistical designs of experiments, after which an engineering decision could be made (Diamond, 1989).

3.2 SAMPLING

The use of the Plackett-Burman matrix (Resolution III design) depicted in Table 3.1, reduced the number of trials to eight. Thus the experimental condition found in this study is referred to a two-level, five-variable experiment. Each variable is represented by a minus sign (-), the number 1 or absence of a letter at the lower level; while the plus sign (+), or a letter ‘’a’’ in the case of A variable, ‘’b’’ for B etc, are used to represent the upper level of the respective variables.

Samples made according to the Plackett-Burman matrix result in a saving of 87% in direct sample preparation, testing costs and time. The following eight trials cover all combinations of the two levels and five variables as described in Table 3.1.

Table 3.1: Matrix labelling for a 5-variable experiment in eight trials

Trial	A	B	C	D	E	Treatment combinations
1	-	-	-	+	+	de
2	-	-	+	+	-	cd
3	-	+	+	-	-	bc
4	+	+	-	+	-	abd
5	+	-	+	-	+	ace
6	+	-	-	-	-	a
7	+	+	+	+	+	abcde
8	-	+	-	-	+	be

A further advantage is that the information obtained from this matrix-design experiment would be greater than would be obtained by a series of comparative experiments (Diamond, 1989). The five variables that were tested in order to accomplish the set objectives are described in Table 3.2 below.

Table 3.2: High and low levels of the five different parameters

		LOW LEVEL	HIGH LEVEL
A	pH	10	11
B	$Al(OH)_4^-$ or $[SO_4^{2-}]_{tot}$ initial concentration (ppm)	9.92 or 61	19.84 or 121
C	Organic initial concentration (% v/v)	10	25
D	Temperature (°C)	25	40
E	Interfacial area per unit volume of aqueous phase (m^2/m^3)	10.56	19.64

3.3 EXPERIMENTAL COMPONENTS

3.3.1 Chemicals

The synthetic stock solution of metal ions was made up by dissolving 5 g of γ-Al_2O_3, Riedel product, 63 to 67% assay of aluminium, in an open 5 L volumetric flask of sodium hydroxide solution and adjusting the pH between 10 and 11. The solution was stirred on a magnetic stirrer for 70 hours.

At the beginning of the solvent extraction experiments, the suspensions were filtered in air at room temperature through Whatman N°1 filter paper, yielding a final $Al(OH)_4^-$ concentration of 19.84 ppm.

To assess the $[SO_4^{2-}]_{tot}$ extraction, similar aqueous solutions were prepared. In this respect, amounts of Na_2SO_4 (99%), received from Merck, were dissolved in distilled water and the pH was adjusted using NaOH.

The commercial extractant Aliquat 336 in its chloride form (Trioctylmethylammonium chloride from Cognis Corporation), was used without purification and then dissolved in Kerosene (also without further purification) to make an organic phase of 10 and 25% (v/v). Aliquat 336 has an average molecular weight of 442 g/mol, a Brookfield viscosity of 1450 cp at 30°C, density of 0.88 g/ml at 25°C and was assumed to contain about 90.6% of the active substance. The pH level during the experiments was controlled by the addition of either 1 M NaOH or 1 M HCl solutions. All chemicals used were analytical grade.

3.3.2 Materials

Experiments were performed in a batch configuration, using Perspex beakers of 1000 and 3000 mL (as working volume), with a mechanic double stirrer. Four evenly spaced baffles (to prevent vortex formation at the gas-liquid interface) with a width (B_W) of 10 mm each were fitted inside the reactors with an internal diameter (D_i) of 110 and 150 mm, and a height (H) of 150 and 190 mm respectively. Figures 3.1 and 3.3 represent the experimental apparatus used.

The solution kept at a constant temperature in a thermostated water-bath (Figure 3.3), was agitated by a flat-blade turbine (Figure 3.2) double stirrer (made from stainless steel), driven by a Heidolph variable speed overhead stirrer. A photo-contact tachometer was used for speed control.

The Hanna HI 4212 pH meter with a thermostat was used for the pH studies and the effect of temperature. Before measuring, the probe was calibrated using pH 4, 7 and 12 buffer solutions, and the precision of measurements judged by use of pH 11 buffer solution.
A scale (trade mark Mettler HK 60) was used for weight measuring.

3.3.3 Equilibrium tests

Through factorial design using aqueous solutions aged for 70-hours, a set of eight tests were performed where the solution pH, aqueous solution concentration, organic phase concentration, temperature, and interfacial areas were changed. The extraction process was carried out according to the following procedure:

1) Organic/Aqueous volumetric phase ratio (O/A): 1/9 was placed in the plastic beaker, regulated at the required temperature, adjusted at appropriate pH and subjected to mechanical stirring. The position of the flat-blade turbine (Figure 3.2) double stirrer was adjusted to 10 mm below and above the liquid interface. The stirring rate was kept at 70 rpm as this is the minimum speed necessary to keep the interface between the two phases undisturbed (above this stirring speed, waving of interface starts). In this range the liquid-liquid interface was flat and the interfacial area for extraction was equal to the geometric area (circle).

2) Samples (± 10 mL) of the aqueous solution were taken at specific time intervals, and diluted in 20 mL NaOH (2 M) before elemental analysis in order to prevent precipitation of aluminium hydroxide.

3) The effect of alkalinity on the aluminium or sulphate profile was investigated at two different levels, namely pH 10 and pH 11. Sodium hydroxide was used to achieve the desired alkalinity level.

4) The effect of interfacial area on the extraction was examined by using two beakers with different internal diameters (D_i): 110 and 150 mm, respectively (Figures 3.1 and 3.2).

3.4 ANALYTICAL METHODS

The amount of aluminium or sulphate extracted was determined by monitoring the amount of aluminium or sulphate in solution. This was achieved by drawing samples at specific time intervals and analysing them by Inductively Coupled Plasma spectroscopy (ICP) for aluminium and sulphate ions determination, whereas wet chem technique was used for chloride ions determination. The amount of the same element in the organic phase was determined by mass balance.

In the case of sulphate extraction, the concentration was also measured using a Hanna HI 93751 Sulfate ISM device in combination with HI 93751-01 reagents.

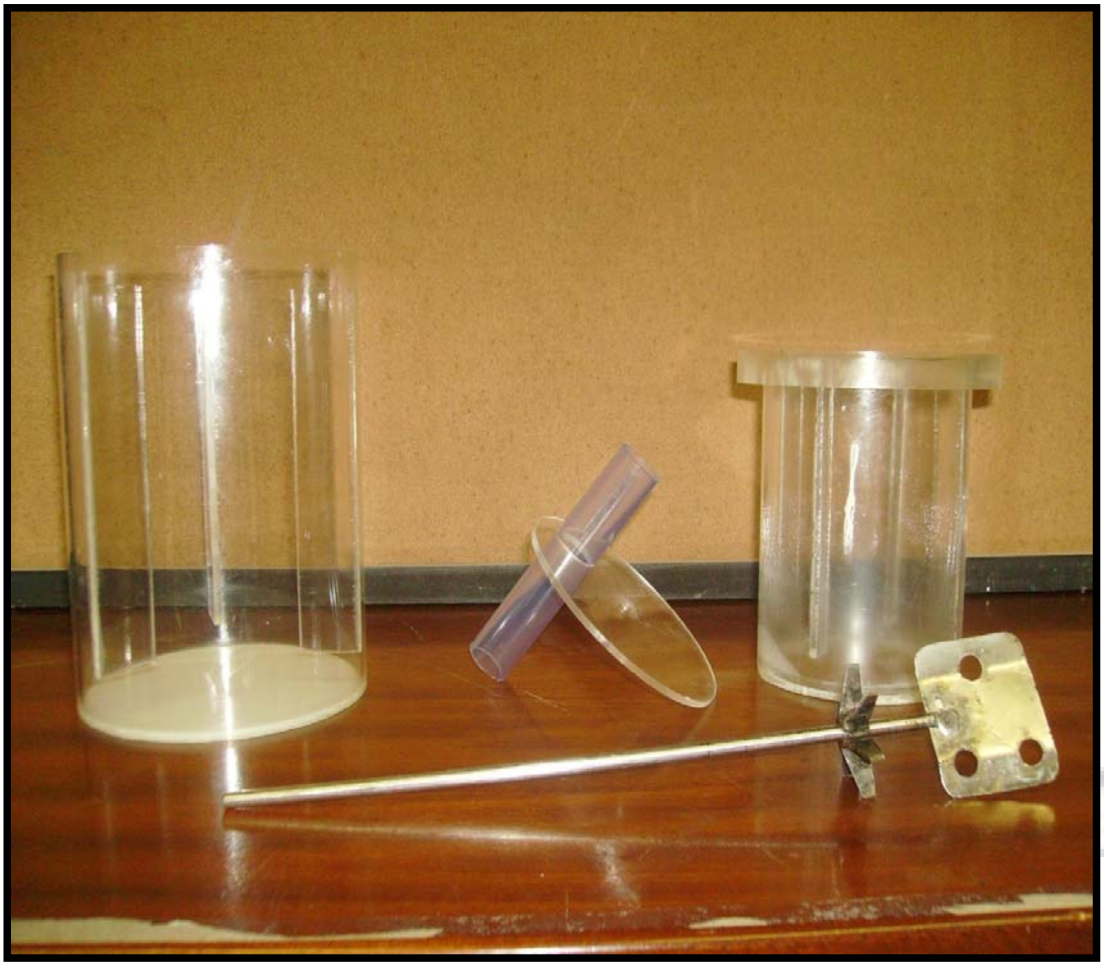


Figure 3.1: Agitated batch reactors (1 and 3) with baffles, flat-blade turbine double stirrer (4) and lid (2)

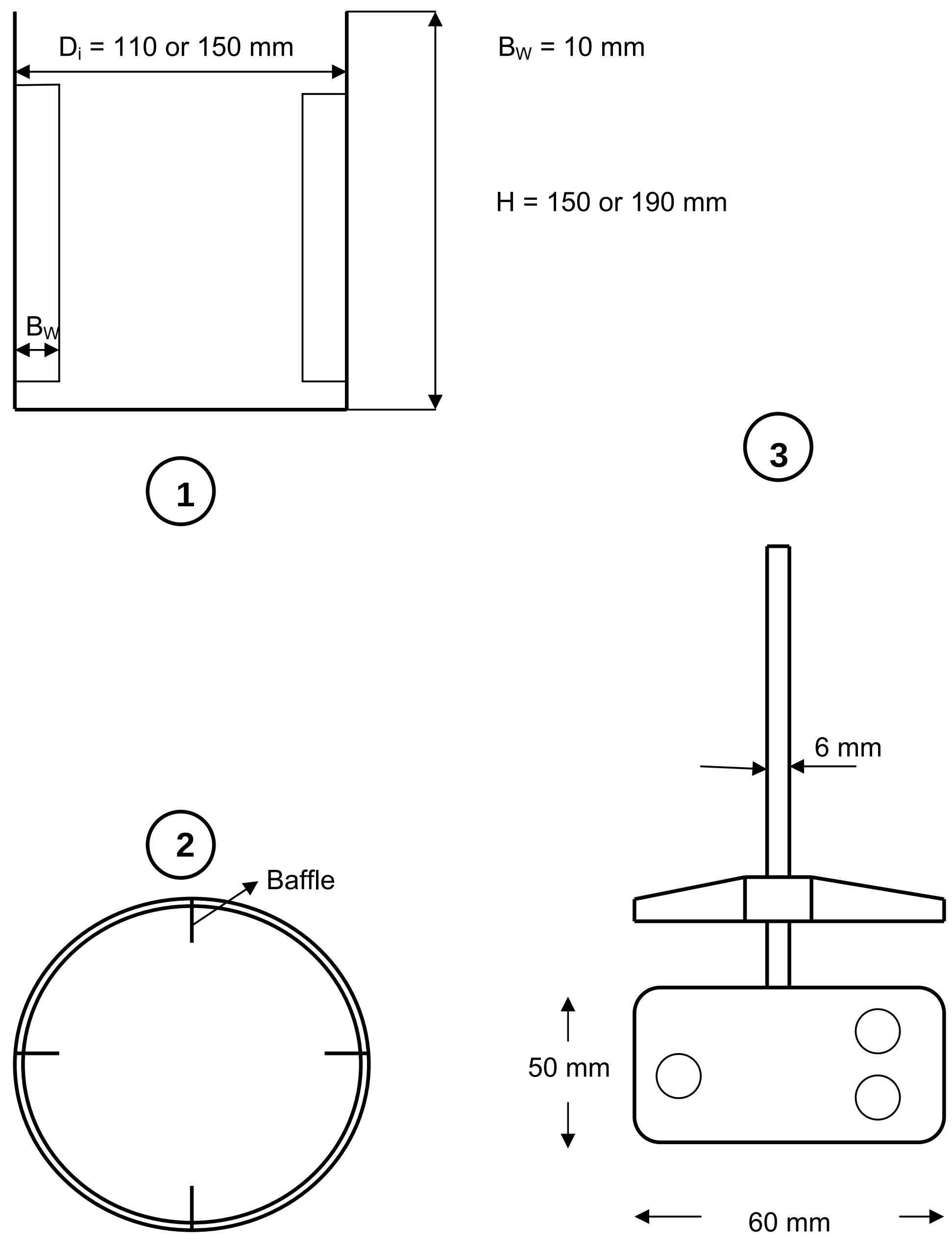


Figure 3.2: Agitated batch reactor (1 and 2) with baffles and flat-blade turbine double stirrer (3)

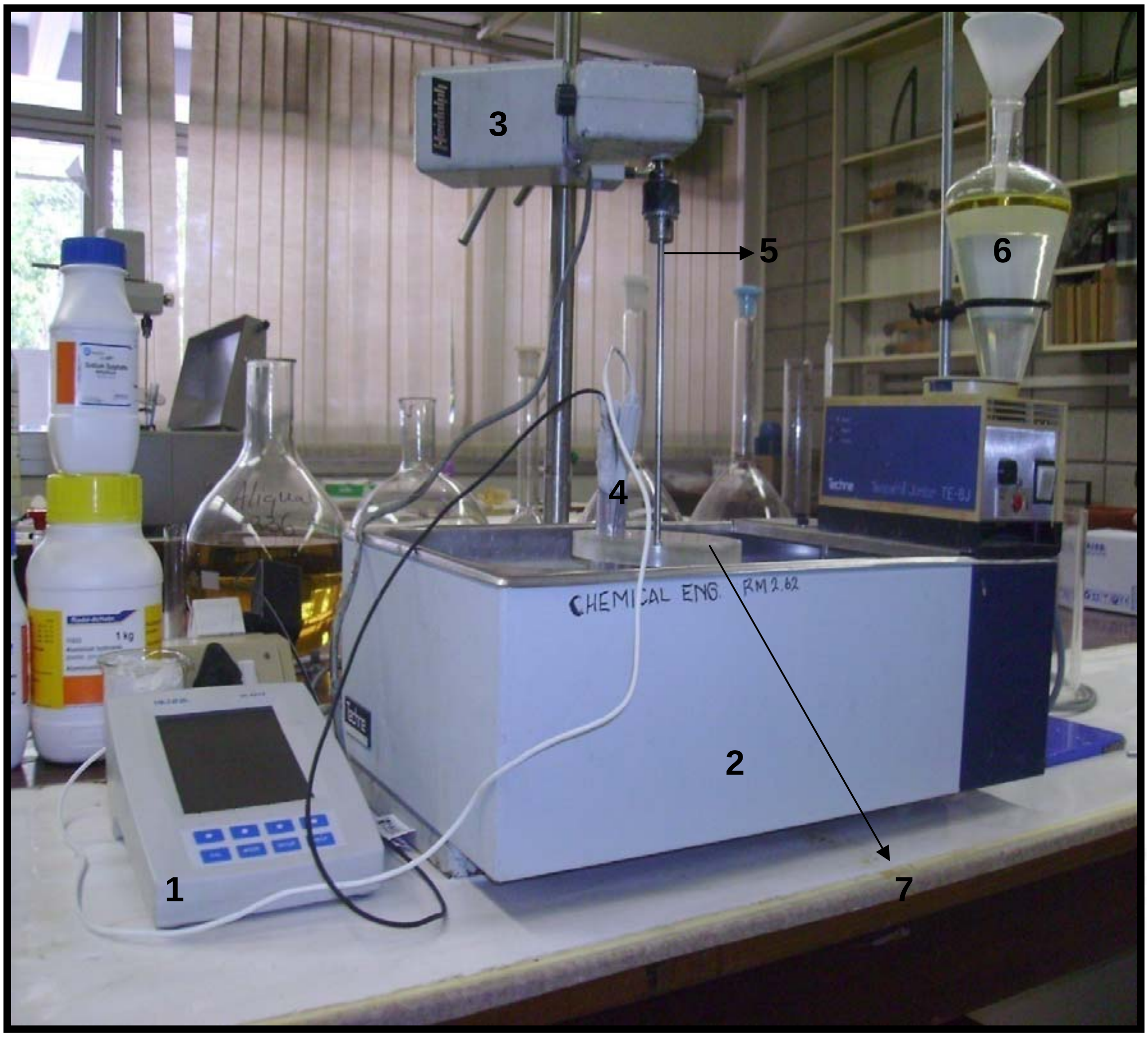


Figure 3.3: Solvent extraction experimental set-up: (1) pH meter Hanna HI 4212 (2) Thermostated water-bath (3) Heidolph variable speed overhead stirrer (4) Probes Hanna HI 1053B-1 and Hanna HI 7662-T for pH and temperature measuring, respectively (5) Flat-blade turbine double stirrer (6) Separating funnel (7) Batch reactor

CHAPTER 4 : A KINETIC MODEL DEVELOPMENT FOR THE ESTIMATION OF MASS-TRANSFER COEFFICIENT

Generally, separation processes that involve contacting two immiscible liquid phases require consideration of mass transfer across the interface separating the liquids. These extraction processes consist of a series of steps, including diffusion of the reactants to the interface, a chemical reaction, and diffusion of the products away from the interface. The rate of extraction is thus controlled by the slowest step (Doungdeethaveeratana & Sohn, 1998).

According to Biswas, Ali, Karmakar, and Kamruzzaman (2007), the same kinetic data in the solvent extraction process of a metal ion by an extractant can be treated, either by a pseudo first-order rate constant method, or the flux method. Both methods give similar reaction orders with respect to the reactant concentrations, but the value of the rate constant k differs due to the fact that the rate constant method ignores the basics of heterogeneous kinetics.

4.1 MODEL ASSUMPTIONS

The model to be presented is subject to the following assumptions:

1) The interphase transport of the quaternary ion-pair species can be considered in terms of the film theory.
2) The total phase (organic and aqueous) volumes remain unchanged during the reaction.
3) The film is treated as a planar layer.
4) Isothermal conditions are assumed during extraction.
5) The two liquid phases are homogeneous, mixed and separated.

4.2 MODEL EQUATIONS

The diminishing rate of aluminium or sulphate concentration in the aqueous phase can be expressed by the general 4.1 Equation:

$$-d(V_{aq}[C]_{aq})/dt = A\left\{k_f [C]_{aq}^{l} [R_4NCl]_{org}^{m} [NaOH]_{aq}^{n} - k_b [C]_{org}^{p} [R_4NCl]_{org}^{q} [NaOH]_{aq}^{r}\right\} \qquad (4.1)$$

Considering that the change of the concentration of Aliquat 336 and sodium hydroxide from before to after the reaction is negligible, and with reference to the assumptions listed above, the rate of extraction expressed in terms of pseudo first-order rate constants with respect to aluminium or sulphate concentration, $l = p = 1$, is expressed in Equation 4.2:

$$-\frac{d(V_{aq}[C]_{aq})}{dt} = A\{k_f^{'}[C]_{aq}^{t} - k_b^{'}[C]_{org}^{t}\} \tag{4.2}$$

The mass balance at equilibrium for a batch extraction system as used in this study will be given by Equation 4.3:

$$V_{aq}[C]_{aq} + V_{org}[C]_{org} = V_{aq}[C]_{aq}^{0} \tag{4.3}$$

Considering the initial conditions: $[C]_{aq} = [C]_{aq}^{0}$; $[C]_{org}^{t} = 0$ at t = 0, and then

$-d[C]/dt = 0$; $k_b^{'} = k_f^{'}\frac{[C]_{aq}^{e}}{[C]_{org}^{e}}$ at equilibrium.

The aluminium or sulphate disappearance rate can be expressed by Equations 4.4 and 4.5 as follows:

$$-\frac{d(V_{aq}[C]_{aq})}{dt} = k_f^{'}A\{[C]_{aq} - \frac{[C]_{aq}^{e}}{[C]_{org}^{e}}[C]_{org}\} \tag{4.4}$$

$$-\frac{d[C]_{aq}}{dt} = k_f^{'}a\{[C]_{aq} - \frac{[C]_{aq}^{e}}{[C]_{org}^{e}}[C]_{org}\} \tag{4.5}$$

The Laplace transform technique can be used to solve the above set of equations and the result is given in Equation 4.6:

$$\ln\left(\frac{[C]_{aq}^{t} - [C]_{aq}^{e}}{[C]_{aq}^{0} - [C]_{aq}^{e}}\right) = -k_f^{'}a\left(1 + \frac{[C]_{aq}^{e}V_{aq}}{[C]_{org}^{e}V_{org}}\right)t \tag{4.6}$$

By plotting the dimensionless concentration $\ln\left(\frac{[C]_{aq}^{t} - [C]_{aq}^{e}}{[C]_{aq}^{0} - [C]_{aq}^{e}}\right)$ versus time (t), a linear equation that passes through the origin can be obtained, then the forward mass-transfer coefficient $k_f^{'}$ is evaluated from the slope.

In the same way, under a mixed control extraction process, often concentrations in the bulk solution and at the interface are not equivalent. Thus both reaction kinetics and mass transfer must be considered.

By defining an apparent overall rate constant as in Equation 4.7:

$$\frac{1}{k_{app}} = \left(\frac{1}{k_{aq}} + \frac{1}{k_f^{'}} + \frac{C_{aq}^{e} \big/ C_{org}^{e}}{k_{org}} \right) \tag{4.7}$$

After rearrangement of Equation 4.5, the overall rate expression can be formulated as in 4.8 Equation:

$$\frac{d([C]_{aq})}{dt} = -k_{app} a \left\{ [C]_{aq} - \frac{[C]_{aq}^{e} V_{aq}}{[C]_{org}^{e} V_{org}} \left([C]_{aq}^{0} - [C]_{aq} \right) \right\} \tag{4.8}$$

Integrating (4.8) with an initial condition similar to Equation 4.5, the final equation is expressed as follows:

$$\ln\left(\frac{[C]_{aq}^{t} - [C]_{aq}^{e}}{[C]_{aq}^{0} - [C]_{aq}^{e}} \right) = -k_{app} a \left(1 + \frac{[C]_{aq}^{e} V_{aq}}{[C]_{org}^{e} V_{org}} \right) t \tag{4.9}$$

where $\frac{d([C]_{aq})}{dt}$ is the change in concentration of Al(III) or $[SO_4^{2-}]_{tot}$ in the solution over time.

From Equation 4.9, by plotting $\ln\left(\frac{[C]_{aq}^{t} - [C]_{aq}^{e}}{[C]_{aq}^{0} - [C]_{aq}^{e}} \right)$ versus mixing time (t), a linear equation that passes through the origin is obtained, then, the apparent mass-transfer coefficient (k_{app}) is evaluated from the slope. Thus, the plots of $\ln\left(\frac{[C]_{aq}^{t} - [C]_{aq}^{e}}{[C]_{aq}^{0} - [C]_{aq}^{e}} \right)$ versus mixing time (t) in the aluminium and sulphate extraction using 0.02 to 0.05 M Aliquat 336 in Kerosene, gave straight lines passing through the origin (Figure 4.1). This implies that the overall rate of reaction for aluminium and sulphate extraction were first-order with respect to the aluminium and sulphate concentration in the aqueous phases, as had been assumed in the Section 4.1 of this study. Table 4.1 below shows the apparent mass-transfer coefficients calculated from the experimental results.

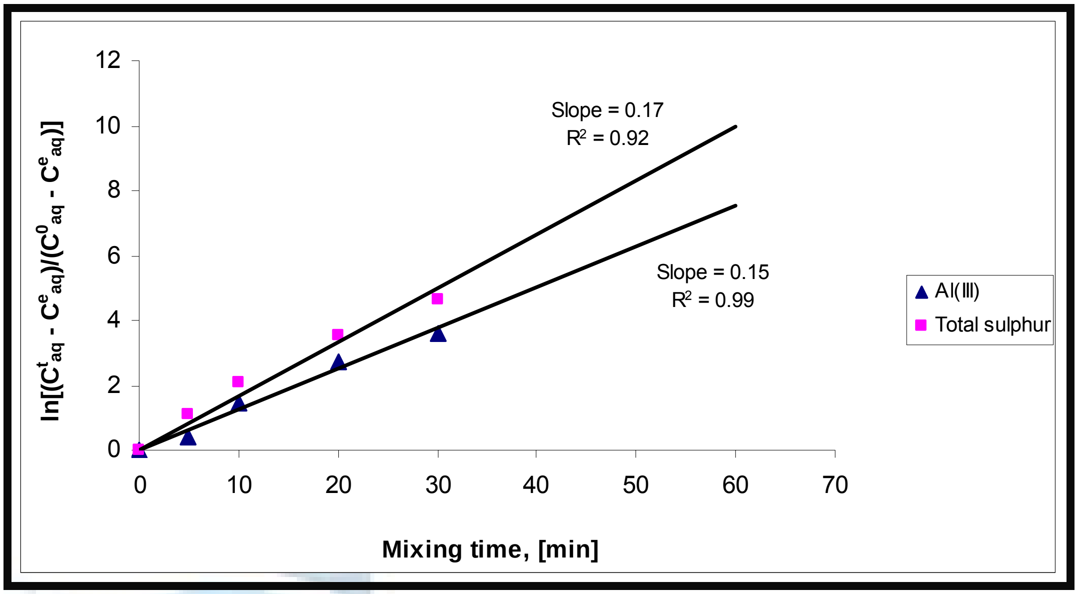


Figure 4.1: First-order rate expression for the forward reaction as a function of mixing time in the $Al(OH)_4^-$ and $[SO_4^{2-}]_{tot}$ extraction from NaOH solution with 25% (v/v) Aliquat 336 in Kerosene, separately studied

Table 4.1: Apparent mass-transfer coefficients for various operating conditions

Trial	pH	$[Al(OH)_4^-]$ (ppm)	$[SO_4^{2-}]_{tot}$ (ppm)	[Aliquat 336] (% v/v)	Temperature (°C)	Interfacial area (m^2/m^3)	$k_{app}^{Al(III)}$ (m/min)	$k_{app}^{[SO_4^{2-}]_{tot}}$ (m/min)
1	10	9.92	61	10	40	19.64	0.00252	0.00449
2	10	9.92	61	25	40	10.56	0.00454	0.00680
3	10	19.84	121	25	25	10.56	0.00827	0.00926
4	11	19.84	121	10	40	10.56	0.00652	0.0114
5	11	9.92	61	25	25	19.64	0.00298	0.00498
6	11	9.92	61	10	25	10.56	0.00529	0.00607
7	11	19.84	121	25	40	19.64	0.00468	0.00755
8	10	19.84	121	10	25	19.64	0.00214	0.00540

4.3 CORRELATION BETWEEN THE OBTAINED RATE CONSTANT AND THE OPERATING CONDITIONS

As can be seen, the obtained rate constant changes with operating conditions. The overall correlation can be obtained by non-linear regression analysis on the basis of the eight different k_{app} values summarized in Table 4.1. Due to its substantial deficiencies (Cryer, 2001), MS Excel® was not employed for statistical analysis. More specialized software such as Design-Ease Version 3 was used to develop Equations 4.10 and 4.11.

$$k_{app} = f\,(pH, Aqueous\ concentration, Aliquat336\ concentration, Temperature, Interfacial\ area)$$

$$\begin{aligned} k_{app}^{Al(III)} &= 65.10^{-5} + 50.10^{-5}\,pH + 19.10^{-5}[Al(III)] - 16.10^{-5}[Aliquat] - 1.10^{-5}\,Tempreature \\ &\quad - 4.10^{-5}\,Interfacial\ area + 2.10^{-5}\,[Al(III)][Aliquat] - 2.10^{-5}[Al(III)][Interfacial\ area] \end{aligned} \tag{4.10}$$

$$\begin{aligned} k_{app}^{[SO_4^{2-}]_{tot}} &= -1261.10^{-5} + 101.10^{-5}\,pH + 12.10^{-5}[SO_4^{2-}]_{\text{tot}} + 8.10^{-5}[Aliquat] + 8.10^{-5}\,Temperature \\ &\quad + 5.10^{-5}\,Interfacial\ area - 0[SO_4^{2-}]_{\text{tot}}[Aliquat] - 0[SO_4^{2-}][Interfacial\ area] \end{aligned} \tag{4.11}$$

The regression coefficients were estimated acceptable (R^2 = 0.93 and 0.99 respectively for aluminium and sulphate) indicating a good agreement between the experimentally obtained values and those calculated from the correlation. It implies that 93 and 99% of the variability in the response could be explained by the model.

4.4 ATTAINMENT OF STEADY STATE

In order to observe kinetics of aluminium and sulphate extraction, both aqueous and organic phases were contacted for different time intervals of up to 60 minutes. It was found that metal extraction percentage increases with increasing phase contact time of up to 30 minutes and, thereafter the extraction percentage remains nearly the same until 60 minutes. However, in subsequent extraction experiments, 60 minutes of contact time was selected to ensure that the equilibrium was reached (complete extraction).

As can be seen from Figure 4.2, the dimensionless concentration of the metal in the aqueous phase had been plotted in order to remove the effect of the initial concentration of the metal (sulphate) on the kinetic curves. It is evident that the extraction of sulphate is comparatively fast for the first 10 minutes, and then gradually slows down.

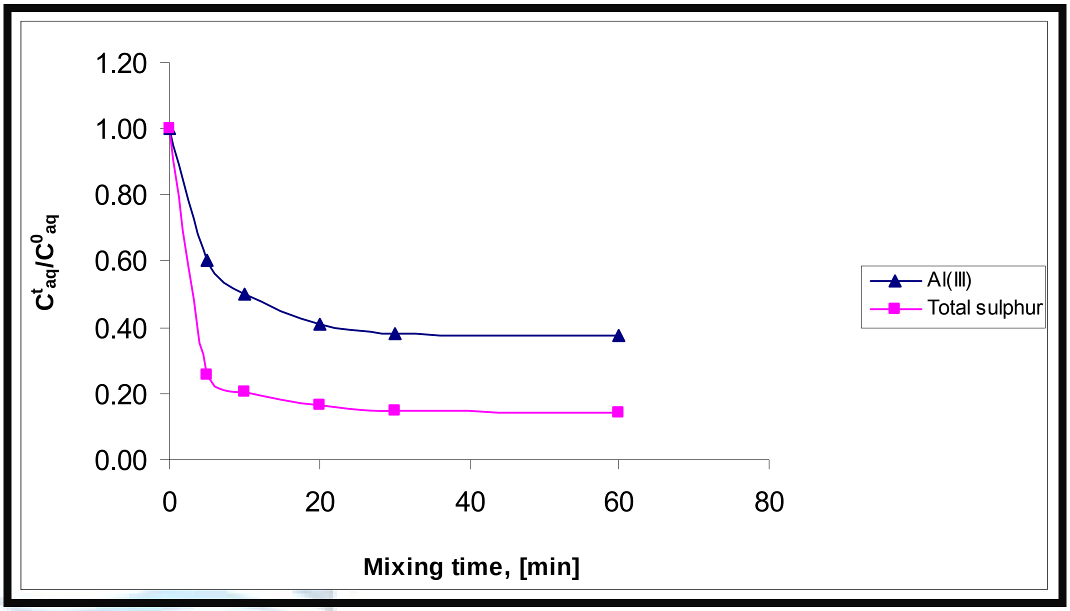


Figure 4.2: Kinetic of $Al(OH)_4^-$ and $[SO_4^{2-}]_{tot}$ concentration in the feed solution {[Aliquat 336] = 10% (v/v), mixing speed = 70 rpm, temperature = 25°C, $[Al(OH)_4^-]$ = 9.92 ppm, $[SO_4^{2-}]_{tot}$ = 61 ppm, pH = 10}

4.5 SUMMARY

The extraction behaviour of Al(III) and $[SO_4^{2-}]_{tot}$ from alkaline medium by Aliquat 336 in Kerosene has been investigated as a function of contact time. It was found that extraction percentage increases with increasing phase contact time of up to 30 minutes and, thereafter, it remains almost constant. In subsequent experiments, 60 minutes of contact time was adopted to ensure complete equilibration.

The reaction order with respect to aqueous phase concentrations has also been investigated as shown in Figure 4.1. In all cases (factorial design), results indicated that the extraction rate of aluminium and sulphate were first-order dependent on the concentration in the aqueous phase. These data will be useful in the design of the extraction processes.

CHAPTER 5 : EFFECT OF OPERATING PARAMETERS ON THE EXTRACTION

In order to elucidate the extraction process of aluminium and sulphate ions, the following parameters, namely pH, initial aluminium and sulphate concentrations, temperature and interfacial area, were systematically investigated. The factors studied and their levels are shown in Table 3.2. The parameter which was kept constant during experimentation is the stirring speed of 70 rpm. The main responses under this research were the percentage recovery of aluminium and sulphate at the end of the 60 minute experiment. A minimum of three readings with a standard deviation of less than 5% was taken and the mean value was reported as listed in Table 5.1.

5.1 DATA TREATMENT

In this study, two types of experimental methods, namely slope analysis method and fractional factorial design, were used for interpreting experimental data. Both methods were applied successively, and then were found to be resourceful and effortless to determine important operating parameters, the interaction between them, as well as optimum conditions.

As shown in Table 5.1, quite high extraction recovery of aluminium and sulphate were obtained in 60 minute periods during all runs of the factorial design, demonstrating the applicability of Aliquat 336-Kerosene system for the extraction of aluminium and sulphate from alkaline solutions.

Table 5.1: Aluminium and sulphate extraction from alkaline solutions by Aliquat 336 in Kerosene

Trial	pH	[Al(III)] (ppm)	$[SO_4^{2-}]_{tot}$ (ppm)	Aliquat 336 concentration (% v/v)	Temperature (°C)	Interfacial area per unit volume of aqueous phase $\left(m^2/m^3\right)$	%Al(III) recovered	$\%[SO_4^{2-}]_{tot}$ recovered
1	10	9.92	61	10	40	19.64	50.10	67.21
2	10	9.92	61	25	40	10.56	49.70	60.66
3	10	19.84	121	25	25	10.56	59.68	71.90
4	11	19.84	121	10	40	10.56	54.13	79.34
5	11	9.92	61	25	25	19.64	57.56	72.13
6	11	9.92	61	10	25	10.56	45.06	55.74
7	11	19.84	121	25	40	19.64	62.70	85.95
8	10	19.84	121	10	25	19.64	51.46	75.21

5.1.1 Influence of equilibrium pH

The pH of the aqueous solution is one of the most important controlling parameters on metal ions extraction process. It not only affects the metal speciation but also the surface charge of the extractant system. Therefore, metal extraction is mainly pH dependent and a function of metal complex formation and ionic strength (Kabra *et al.,* 2007).

Using the slope analysis method, Al(III) and $[SO_4^{2-}]_{tot}$ were extracted in the pH range of 10 to 12 in the presence of sodium hydroxide. An evaluation of the number of protons released for each extracted Al(III) or $[SO_4^{2-}]_{tot}$ can be made by plotting the experimental values of the distribution factor (*D*) as a function of the pH, at a constant value of Aliquat 336 concentration and other parameters. Figure 5.1 shows the dependency of $\log D_{[Al(III)]}$ and $\log D_{[SO_4^{2-}]_{tot}}$ versus equilibrium pH.

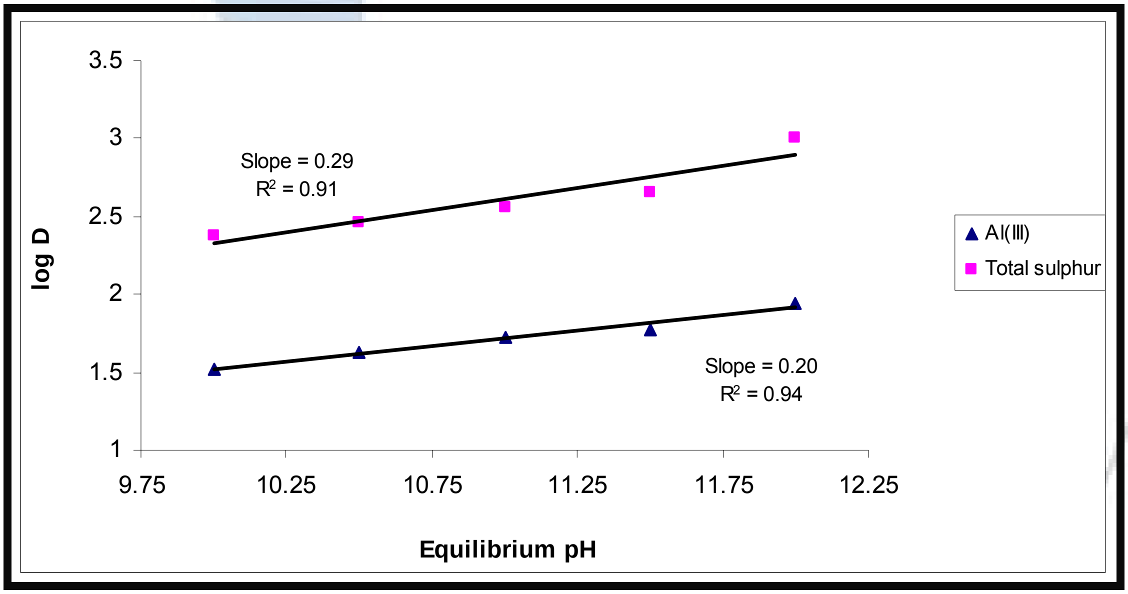


Figure 5.1: Effect of pH on the distribution coefficient of aluminium and total sulphur separately studied {Operating conditions: [Al(III)] = 2.09x10^{-4}M, $[SO_4^{2-}]_{tot}$ = 1.26x10^{-3}M, [Aliquat 336] = 0.05 M, O/A phase ratio = 1/9 and temperature = 25°C}

In general, the plots $\log D_{[Al(III)]}$ and $\log D_{[SO_4^{2-}]_{tot}}$ vs. equilibrium pH were linear, with a correlation coefficient of > 0.90, and have a slope of < 1, which indicates that no protons were involved in exchange for Al(III) ion [or $(SO_4^{2-})_{tot}$] during the extraction. It should be recognised that no precipitation in these groups of experiments was observed under the concentration and pH condition studied.

Moreover, aluminium and sulphate extraction increases when pH increases, therefore, the feed, Al(III) and $[SO_4^{2-}]_{tot}$, must be adequately alkalised with NaOH prior the extraction, so that $Al(OH)_4^-$ and SO_4^{2-} anions will be formed. Nevertheless, the initial concentration of NaOH in feed aqueous phase should not be excessively elevated because the yield of extraction of Al(III) from alkaline solutions depends on initial ionic strength of feed solutions and the solubility of Aliquat 336 increases (Barbara & Apostoluk, 2005).

5.1.2 Effect of initial aluminium and sulphate concentrations

The effect of initial feed concentration on the Al(III) and $[SO_4^{2-}]_{tot}$ distribution was investigated by changing the Al(III) concentration from $1.04x10^{-1}$ to $2.09x10^{-1}$M and from $6.35x10^{-4}$M to $1.26x10^{-3}$M for $[SO_4^{2-}]_{tot}$, keeping the NaOH and Aliquat 336 concentrations constant. Extraction tests were conducted by contacting the same organic and aqueous volumetric phase ratio (O/A = 1/9). The results indicated strongly that aluminium and sulphate ions extraction took place.

The plots of Equations 4.6 and 4.9 against the mixing time gave straight lines passing through the origin (Figure 4.1). This confirms that the forward reaction rate for $Al(OH)_4^-$ and $[SO_4^{2-}]_{tot}$ extraction is first-order with respect to the aluminium and sulphate concentration in the aqueous phase, as previously assumed in the Section 4.1 of this study. This indicates that film diffusion remains the primary mechanism of mass transfer, and then the overall apparent rate constant k_{app} was evaluated from the slope.

In addition, it is acknowledged that cationic extractants, as well as other extractants, such as amines and solvating extractants, are polymerised or self-associated in organic diluents (Tsakiridis & Agatzini, 2004). Thus, the plot of the equilibrium organic phase anionic concentration {$\log[Al(OH)_4^-]_{org}$ or $\log[(SO_4^{2-})_{tot}]_{org}$} against the aqueous anionic concentration {$\log[Al(OH)_4^-]_{aq}$ or $\log[(SO_4^{2-})_{tot}]_{aq}$} gives the degree of polymerisation of the extracted species. If only a monomeric or a dimeric species was extracted, the plot must be a straight line with a slope of 1 or 2, respectively. If both are extracted, the plot should be a curve (Wang & Nagaosa, 2002).

It can be seen (Figure 5.2) from over the range of the experimental study, that only monomeric species were involved for the metal (sulphate) ions investigated.

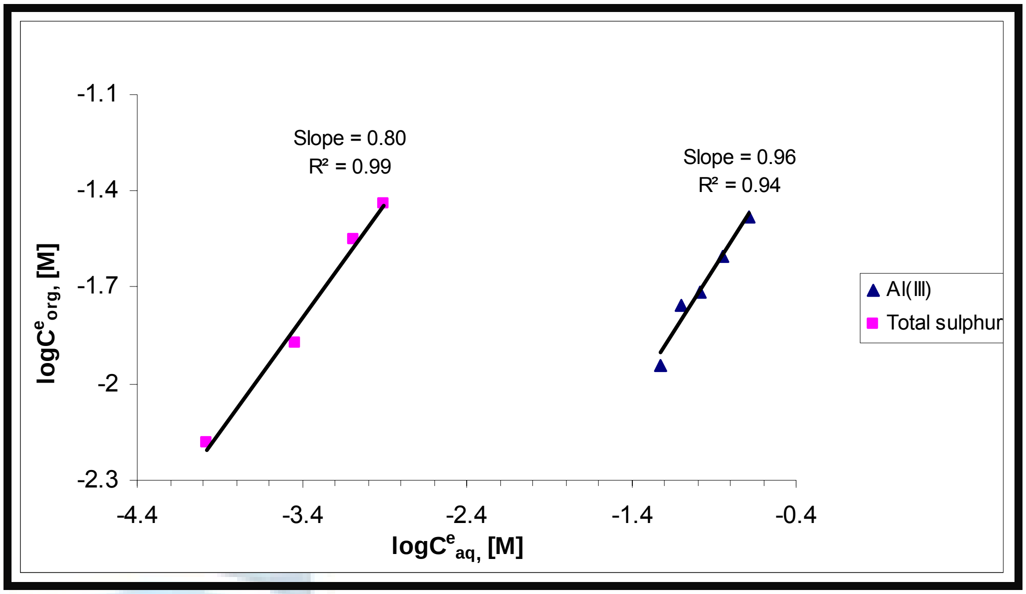


Figure 5.2: Effect of concentration of metal (sulphate) ion on the extraction of Al(III) and $[SO_4^{2-}]_{tot}$ (separately studied) from NaOH using [Aliquat 336] = 0.05 M; pH = 11, O/A phase ratio = 1/9 and temperature = 25 or 40°C for aluminium and sulphate respectively

Finally, saturation loading capacity of Aliquat 336 for the extraction of Al(III) and SO_4^{2-} from 10^{-3}M NaOH was determined by investigating the distribution of Al(III) and SO_4^{2-} over the aqueous ion concentration range of 1.044×10^{-1} to 2.088×10^{-1}M for Al(III) and 6.35×10^{-4} to 1.26×10^{-3}M for SO_4^{2-}, employing 0.05 M Aliquat 336. Linear plots (Figure 5.2) were obtained up to 3.35×10^{-2}M Al(III) and 3.76×10^{-2}M SO_4^{2-}, indicating that the distribution ratio and species does not change with an increase in metal ion concentration in the said range. Beyond these Al(III) and SO_4^{2-} concentrations, the extractant becomes saturated (the loading of the extractant is complete). The saturated loading capacities were found to be attained in 5 contacts with the same organic feed and fresh aqueous feed.

It was concluded that 0.05 M Aliquat 336 can hold-up as much as 3.35×10^{-2}M Al(III) and 3.76×10^{-2}M SO_4^{2-}, which indicates that the saturation loading capacity of Aliquat 336 for aluminium and sulphate are respectively 127 g $Al(OH)_4^-$ and 144 g SO_4^{2-} per litre of Aliquat 336. The corresponding extraction percentage with respect to saturation loading capacity (loading ratio, Z) was 66.99% for aluminium and 75.17% for sulphate ions, respectively, indicating that the extractant used was not in a pure form.

5.1.3 Extractant Aliquat 336 effect

The importance of extractant concentration dependence is of prime importance to evaluate the extraction mechanism (Saleh, Bari & Saad, 2002). The effect of Aliquat 336 concentration on the extraction percentage of aluminium and sulphate was studied in the range of 0.02 to 0.05 M.

It is usually acknowledged that in perfect extraction systems, the extraction has to increase, with an increase in the initial concentration of the extractant. However it was observed for aluminium extraction that the percentage recovery decreased with the increase of extractant concentration at high temperature (Figure 5.8). Explanation to this observation is given in Section 5.1.5.

Interpreting the experimental data of the distribution coefficient (D) as a function of the extractant concentration at the constant value of other factors, allows an evaluation of the number of extractant moles associated with the extracted metal complex; and therefore the possible mechanism. The linear relationships between Aliquat 336 concentrations with the corresponding distribution factor (Figure 5.3) were found to be approximately one or two in the investigated systems, which indicates the involvement of one or two molecule (s) of Aliquat 336 in the extracted Al(III) or $[SO_4^{2-}]_{tot}$ species, respectively.

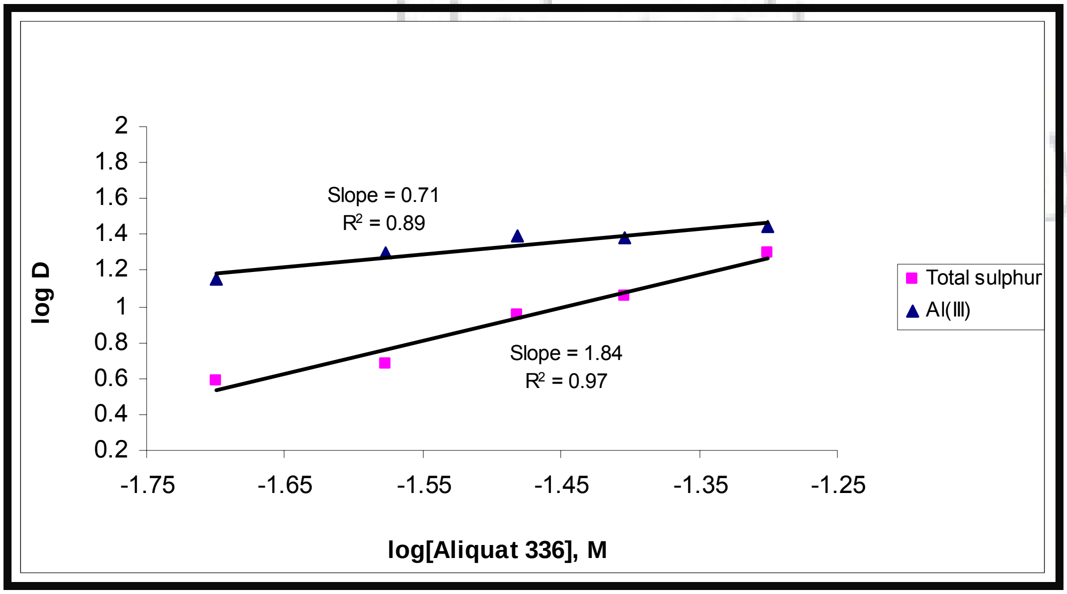


Figure 5.3: Result of extractant concentration on the distribution coefficient of aluminium and sulphate separately studied {Operating conditions: equilibrium pH = 11, [Al(III)] = 2.09×10^{-4}M, $[SO_4^{2-}]_{tot}$ = 1.26×10^{-3}M, O/A phase ratio = 1/9 and temperature = 25°C}

5.1.4 Determination of the nature of extracted metal-organic complexes

Considering the results of Al (III) and [SO$_4^{2-}$]$_{tot}$ extraction as a function of pH, extractant and aqueous phase concentrations previously obtained by slope analysis method, the extraction mechanisms can be proposed as in Equations 5.1 and 5.2 below.

$$R_4NCl_{(org)} + Al(OH)^-_{4(aq)} \rightleftarrows R_4N\,Al(OH)_{4(org)} + Cl^-_{(aq)} \tag{5.1}$$

$$2R_4NCl_{(org)} + SO^{2-}_{4(aq)} \rightleftarrows (R_4N)_2SO_{4(org)} + 2Cl^-_{(aq)} \tag{5.2}$$

In order to ascertain the composition of the extracted aluminium and sulphate species, the variation in the partition of Al(III) and [SO$_4^{2-}$]$_{tot}$ were observed as a function of chloride ion concentration in aqueous phase using Aliquat 336 as the source of Cl$^-$ ions.

As mentioned in Section 2.4 of this study, the aqueous chemistry of aluminium is dominated by the interaction of Al^{3+} with water to form hydrolytic species via the reaction shown in Equation 5.3 (Benezeth, Palmer & Wesolowski, 1997):

$$n\,Al^{3+} + y\,H_2O \rightleftarrows Al_n(OH)_y^{3n-y} + y\,H^+ \tag{5.3}$$

The presence of polynuclear species with n values up to 13 in concentrated solutions at intermediate pH range of approximately 6 to 8.5 has been reported, although in natural water, the important species are the monomeric $Al(OH)_y^{3-y}$ $(y = 0\ to\ 4)$.

On this basis, assuming that these anionic monomers prevail in solutions at pH exceeding 10, and that ionic pairs formed in the organic phase contain ammonium cations and mononuclear hydroxoaluminate anions, and knowing that all extractant molecules are not present as dimmers in Kerosene, the reaction for the extraction of the metal ion may be expressed by Equation 5.4 as follows (Barbara & Apostoluk, 2005):

$$(x-3)R_4NCl_{(org)} + Al(OH)^{(x-3)-}_{x(aq)} \rightleftarrows (R_4N)_{(x-3)}Al(OH)_{x(org)} + (x-3)Cl^-_{(aq)} \qquad (x \geq 4) \tag{5.4}$$

The equilibrium constant K_{ex}, can be given as a function of molar concentration by:

$$K_{ex} = \frac{[(R_4N)_{(x-3)}Al(OH)_x]_{org}[Cl^-]^{(x-3)}_{aq}}{[R_4NCl]^{(x-3)}_{org}[Al(OH)_x^{(x-3)-}]_{aq}} \tag{5.5}$$

Substitution of the distribution coefficient D, and considering V_{org} and V_{aq}, Equation 5.5 becomes:

$$K_{ex} = \frac{V_{aq} D [Cl^-]_{aq}^{(x-3)}}{V_{org} [R_4NCl]_{org}^{(x-3)}} \tag{5.6}$$

Using the logarithms of Equation 5.6, one obtains:

$$\log D = \log K_{ex} + (x-3) \log \frac{V_{aq}[R_4NCl]_{org}}{V_{org}[Cl^-]_{aq}} \tag{5.7}$$

The equilibrium concentration of free quaternary ammonium salt $\left[R_4NCl\right]_{org}$ in the organic phase is determined as for Equation 2.41. The coefficient $(x-3)$ in Equation 5.7 is determined by plotting $\log D$ against $\log \frac{V_{aq}[R_4NCl]_{org}}{V_{org}[Cl^-]_{aq}}$. Therefore, substituting x in Equation 5.4, one can obtain the simplified stoichiometric equation for the extraction reaction. Thus, the plot of $\log D$ vs. $\log \frac{V_{aq}[R_4NCl]_{org}}{V_{org}[Cl^-]_{aq}}$ (Equation 5.7 above) gave a straight line with a slope $(x-3)$ of $\cong 1$ (Figure 5.4), meaning that ionic pairs containing one Trioctylmethylammonium cation (TOMA$^+$) and one tetrahydroxoaluminate anion are the main species in organic phases. Consequently, the extraction equilibrium of Al(III) from alkaline solutions with Aliquat 336 at concentration ≤ 0.05 M, can be represented by Equation 5.1.

Sulphate extraction under the conditions used in this investigation, can be represented by the general reaction described by Equation 5.8:

$$(2-x)R_4NCl_{(org)} + H_xSO_{4(aq)}^{(2-x)-} \rightleftarrows (R_4N)_{(2-x)}H_xSO_{4(org)} + (2-x)Cl^-_{(aq)} \qquad (x=0\ or\ 2) \tag{5.8}$$

The equilibrium constant K_{ex}, can be given as a function of molar concentration as follows:

$$K_{ex} = \frac{[(R_4N)_{(2-x)}H_xSO_4]_{org}[Cl^-]_{aq}^{(2-x)}}{[R_4NCl]_{org}^{(2-x)}[H_xSO_4^{(2-x)-}]_{aq}} \tag{5.9}$$

Developing 5.9 expression as in Equation 5.7, the coefficient $(2-x)$ in Equation 5.9 is determined by plotting $\log D$ against $\log\frac{V_{aq}[R_4NCl]_{org}}{V_{org}[Cl^-]_{aq}}$. This gave a straight line with a slope $(2-x)$ of $\cong 2$ as illustrated in Figure 5.4, which is in good agreement with SO_4^{2-} extraction, because substituting x in Equation 5.8, the simplified stoichiometric equation for the extraction reaction can be expressed by Equation 5.2.

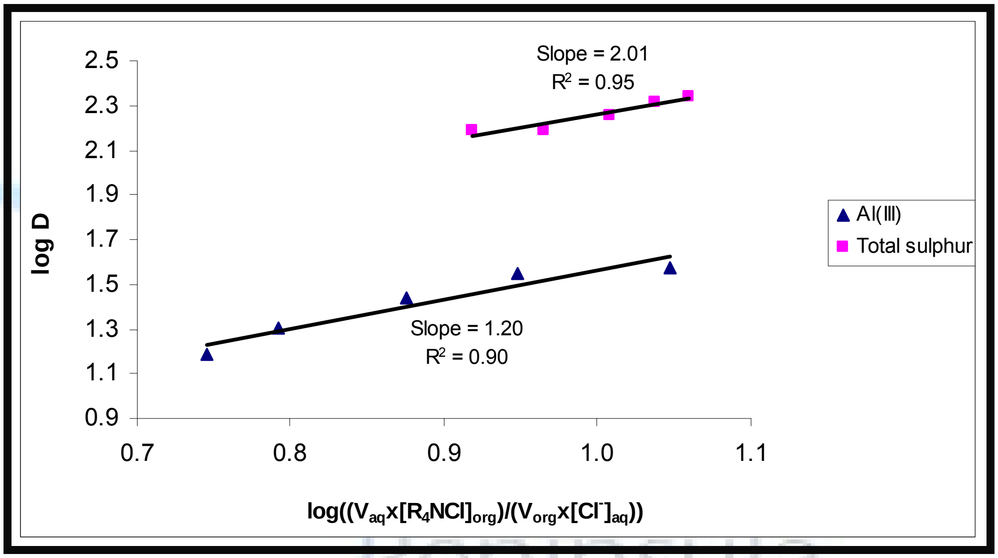


Figure 5.4: Plot of $\log D\ vs.\ \log\frac{V_{aq}[R_4NCl]_{org}}{V_{org}[Cl^-]_{aq}}$ {operating conditions: equilibrium pH = 11, [Al(III)] = 2.09x10^{-4}M, [SO_4^{2-}]$_{tot}$ = 1.26x10^{-3}M, O/A phase ratio = 1/9, [Aliquat] = 25 or 10% (v/v) and temperature = 25 or 40°C for aluminium and total sulphur, respectively}

5.1.5 Effect of the temperature

Temperature effect is a complex parameter influencing the equilibrium in extraction procedures. A rise in temperature could augment the metal complex extraction due to the enhanced dehydration of the species (Kislik & Eyal, 2003); but a rise in temperature could also diminish the extraction, owing to the decreased stability of the complex at higher temperatures (Kumar *et al*., 2008). This negative interaction was found for aluminium extraction in the present study.

To study the temperature effect on Al(III) and $[SO_4^{2-}]_{tot}$ extraction, experiments were performed in a thermostated bath water for 60 minutes. Temperature was varied in the range of 298 to 313 K.

From the Van't Hoff equation: $\log D = \frac{-\Delta H}{2.303RT} + C^{st}$ (Equation 5.10), the ΔH values for Al(III) and $[SO_4^{2-}]_{tot}$ were calculated.

C^{st} is an integration constant which includes the equilibrium constant for the extraction reaction, and activity coefficient for other components that are assumed to be constant under the experimental conditions (Mohapatra *et al*., 2007).

The plot of $\log D = \frac{-\Delta H}{2.303RT} + C^{st}$ vs. $\frac{1}{T}$ (Equation 5.10 above) should give a straight line with a slope of $\frac{-\Delta H}{2.303R}$, so that the value of ΔH can be calculated (Figure 5.5). The free energy (ΔG) and entropy change (ΔS) can be determined using Equations 5.11 and 5.12:

$$\Delta G = -RT \ln D = -2.303RT \log D \tag{5.11}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{5.12}$$

From the thermodynamics point of view, the magnitude of the Gibbs free energy change ΔG is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature if the value of ΔG is negative; thus the extraction of Al(III) and $[SO_4^{2-}]_{tot}$ by Aliquat 336 from alkaline medium occurred spontaneously in all cases (factorial design).

From the calculated values of ΔH at each run for Al(III) and $[SO_4^{2-}]_{tot}$ extraction using Aliquat 336, it will also be noticed that the extraction reactions were endothermic, and then positive ΔH values suggested that the dehydration process predominates (Cestari, Vieira & Mota, 2008; Weiwei, Xianglan, Shulan, Hongfei & Deqian, 2006; Kislik & Eyal, 2003). The dissociation of water molecules into ions is bond breaking and is therefore an endothermic process; energy must be absorbed to break the bonds (Murry & Fay, 1995). The positive values of the entropy of activation in the system indicated that the extraction reaction was thermodynamically favourable and entropy driven. On other hand, the extraction process was dominated by entropic, rather than enthalpic, changes; ΔH < TΔS within the temperature range of 298 to 313 K.

The solvation effect dominates the entropy of activation, where charged ions are involved. Low positive values of the entropy of activation represent the fact that solvent molecules are loosely attached around the metal ions (Biswas & Begum, 1999).

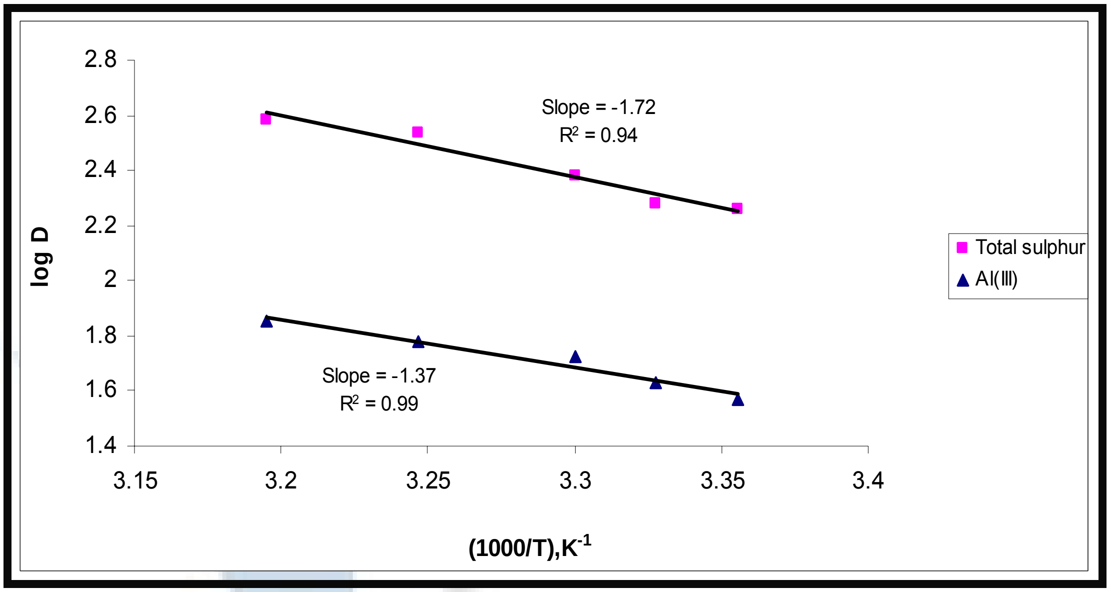


Figure 5.5: Temperature effect on Al(III) and [SO$_4^{2-}$]$_{tot}$ extraction separately studied {10% (v/v) extractant, aqueous phase: Al(III) = 19.84 ppm, [SO$_4^{2-}$]$_{tot}$ = 121 ppm, equilibrium pH = 11}

Statistical analysis also revealed that, when temperature was considered individually, there was a positive influence on the rate of aluminate and sulphate ions extraction. Kinetic parameters increased with increasing temperature from 298 to 313 K. The corresponding extraction percentage increases were from 53.59 to 54.47% and from 70.34 to 73.36% for aluminate and sulphate ions, respectively (Figures 5.15 and 5.20).

5.1.6 Determination of the activation energy

An important part of the kinetic analysis of a chemical reaction is to determine the activation energy (E_a). This latter can be defined as the indispensable energy to initiate a spontaneous chemical reaction so that it will continue to react without the need for additional energy. It is the smallest possible quantity of energy necessary for a specific chemical reaction to take place; in other words, it is the energy that must be overcome in order for a chemical reaction to take place (Murry & Fay, 1995).

From Equations 4.10 and 4.11, the calculated $\ln k_{app}$ values were plotted against 1/T (not shown graphically) to find activation energies from the slopes. Activation energies were underestimated, and this could be attributed to the method used (pseudo first-order rate constant), which ignores the basics of heterogeneous kinetics (Biswas & Mondal, 2003).

Therefore, activated complex theory has been employed to obtain a thermodynamically consistent formulation of the activation energy that is in agreement with experimental data as described by Moore (1983b). Considering the calculated thermodynamic parameters of aluminium and sulphate extraction in Appendix A, a quantitative approach was considered essential for activation energy determination. Details of the calculations made by means of Equation 2.55 can be found in Appendix A.

A process is chemically controlled if the reaction is slow in comparison to the rate of diffusion. It is diffusion controlled if the reaction is fast, the rate of extraction increases with increasing the stirring speed while there is no effect on the extraction rate governed by chemical reaction (Naglaa, 2007). If the process takes place under mixed control, both reaction and diffusion must be taken into account. It is well-known that the rate-determining step will be the diffusion process when E_a < 20 kJ/mol and will be the chemical reaction when E_a > 50 kJ/mol (Biswas & Hayat, 2002).

The calculated activation energies varied within 28.40 to 39.62 and 32.52 to 39.51 kJ/mol over the temperature region 298 to 313 K, for aluminium and sulphate respectively, indicating a mixed diffusion and chemically controlled mechanism which take place either in the aqueous bulk phase or at the interface.

5.1.7 Interfacial area

Interfacial area as a parameter in a given system is typically studied to make a distinction regarding whether a chemical reaction is taking place in the bulk phase or at the interface. The extraction rate is independent of the interfacial area in the first case, while it increases with the increase in the interfacial area in the second case (Naglaa, 2007).

In order to define the driving mechanism behind the extraction of $[SO_4^{2-}]_{tot}$ and $Al(OH)_4^-$, experiments were conducted at different interfacial areas, using two reactors with different internal diameters (Figures 3.1 and 3.2), while keeping the volume of each phase constant. From the tests, it was evident that aluminium and sulphate ion concentrations increased fast (Figures 5.16 and 5.21). This was a first indication that film diffusion might take part in a central role of the extraction mechanism. The dependence of the rate constant on interfacial area is a strong indicator that the mass transfer step is a controlling step in aluminium and sulphate ions extraction. The reason behind this is that the increase in interfacial area reduces the film layer thickness, therefore decreasing the transfer time, which is approximately estimated by Tai, You and Chen (2000) from 5.13 Equation.

$$Transfer\ time = \frac{(Film\ thickness)^2}{(Diffusion\ coefficient)} \tag{5.13}$$

The final results indicated that the interfacial area positively affects the transport rate of aluminate (sulphate) ions through the liquid interface. Kinetic parameters increased with increasing interfacial area. The corresponding extraction percentage increased from 52.41 to 55.50% (aluminium extraction), and from 66.82 to 75.80% (sulphate extraction) for 110 and 150 mm internal diameters, respectively (Figures 5.16 and 5.21).

5.2 DATA ANALYSIS

5.2.1 Statistical analysis

The data analysis was performed using Design-Ease Version 3 statistical software (Stat Ease Inc., Minneapolis, MN, USA). In order to interpret the combined interactions, it is preferable to construct interaction plots. When lines are non-parallel to each other, therefore, the factors are interacting. This means that any change in the mean response from a low to a high level of a factor depends on the rank of the other parameters. The interaction effect is strong if the degree of departure from being parallel is large (Figures 5.8, 5.9, 5.10 and 5.11).

The determination of interactions could only be obtained using statistical designs of experiments. Thus, the normal probability method is particularly valuable for analysing the effects in experiment without replicates. All the effects that lie along the line were negligible, whereas large effects were far from the line (Figures 5.6 and 5.7). The design indicates which parameters have significant effects on the response as well as how the effect of one parameter varies with the level of the other parameters.

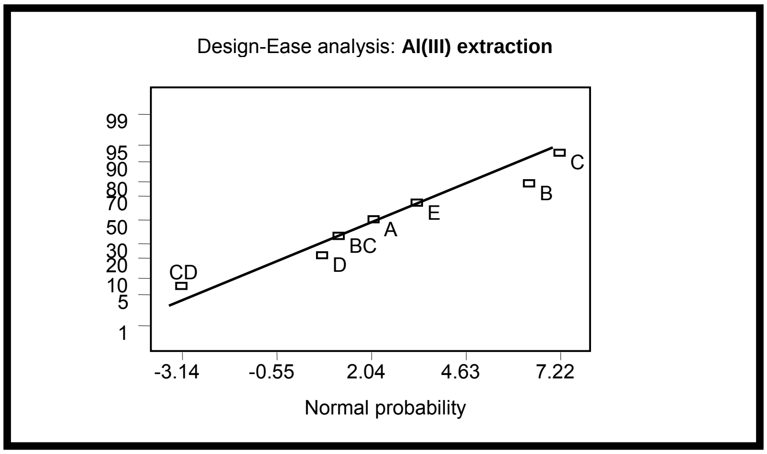


Figure 5.6: Normal probability plot of average effects for aluminium extraction percentage response (studied alone) from 2^3 fractional factorial designs

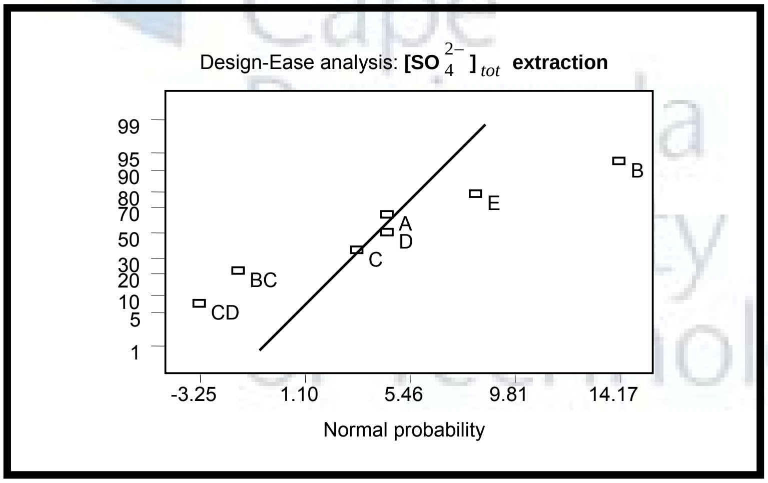


Figure 5.7: Normal probability plot of average effects for sulphate extraction percentage response (studied alone) from 2^3 fractional factorial designs

From Figure 5.8, increasing the Aliquat 336 concentration from 10 to 25% (v/v) causes an increase in extraction percentage of 10.58% when the relative temperature is 25°C. The same increase in Aliquat concentration causes an increase in extraction percentage of 4.40% if the relative temperature is 40°C.

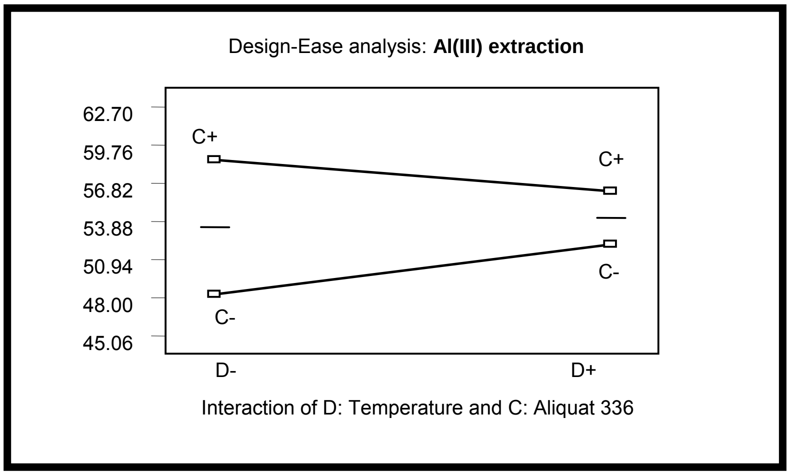


Figure 5.8: Combined interactive effect of temperature and initial Aliquat 336 concentration on aluminium extraction percentage (studied alone)

Increasing the relative Aliquat 336 concentration from 10 to 25% (v/v), increases the extraction percentage by 5.88% if the Al(III) concentration is 9.92 ppm. The same increase in Aliquat 336 concentration increases the extraction percentage by 7.94% when the Al(III) concentration is 19.84 ppm (Figure 5.9). The total aluminium extraction percentage varies from 45.06 to 65.12% within the operating range of the extraction experiments.

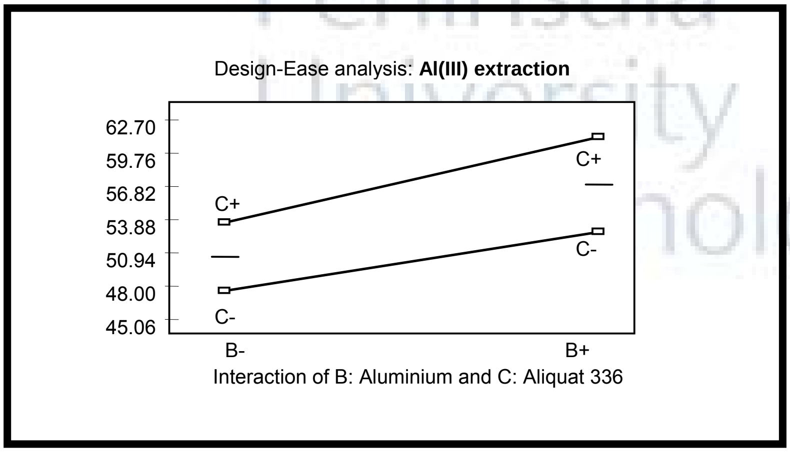


Figure 5.9: Combined interactive effect of initial aluminium and Aliquat 336 concentration on aluminium extraction percentage (studied alone)

Figure 5.10 shows the relationship of sulphate extraction with an increase of Aliquat 336 concentration from 10 to 25% (v/v). It was observed that the increase of Aliquat 336 causes an increase in the extraction percentage by 5.03%, if the relative temperature is maintained at 25°C. The same increase in Aliquat 336 concentration has no effect the on extraction percentage if the relative temperature is 40°C.

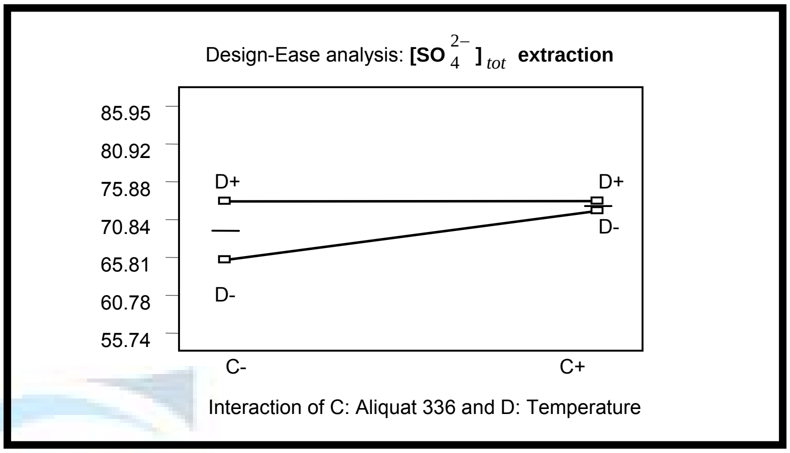


Figure 5.10: Combined interactive effect of initial Aliquat 336 concentration and temperature on sulphate extraction percentage (studied alone)

While increasing the relative Aliquat 336 concentration from 10 to 25% (v/v) increases the extraction percentage by 5.03% when the sulphate concentration is 61 ppm. The same increase in Aliquat 336 concentration increases the extraction percentage by 1.03% if the sulphate concentration is 121 ppm (Figure 5.11). Within the operating range of the process, the total sulphur extraction percentage varies from 55.74 to 85.95%.

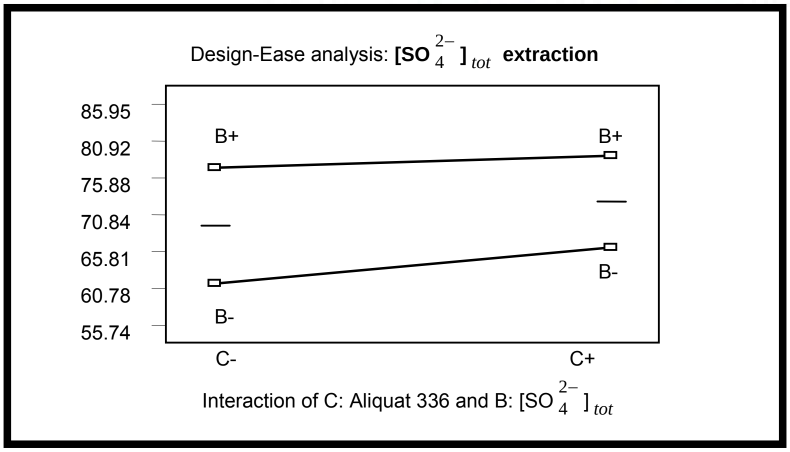


Figure 5.11: Combined interactive effect of initial sulphate and Aliquat 336 concentration on sulphate extraction percentage (studied alone)

Table 5.2: Standardised effect on aluminium and sulphate extraction percentages

Item of effect	Standardised effect	
	Al(III)	$[SO_4^{2-}]_{tot}$
Average	53.80	71.02
A = pH	2.13	4.55
B = Aqueous concentration	6.39	14.17
C = Aliquat 336 concentration	7.22	3.29
D = Temperature	0.72	4.55
E = Interfacial area	3.31	8.22
BC	1.17	-1.64
CD	-3.14	-3.26

From Table 5.2, it will be noticed that the initial concentration of Al(III), $[SO_4^{2-}]_{tot}$, Aliquat 336 and the interfacial area are the controlling parameters for aluminium and sulphate extraction under the experimental conditions used in this study. They had the main effects on the extraction process. A high level of aluminium and sulphate concentration is preferred because its effects are positive. The positive values of the effects mean that an increase in their respective levels lead to an increase in the Al(III) and $[SO_4^{2-}]_{tot}$ uptake by the extractant Aliquat 336. On the other hand, the negative values of the effects, lead to a reduction in the response (percentage recovery), when their levels were increased (Figures 5.12 to 5.21).

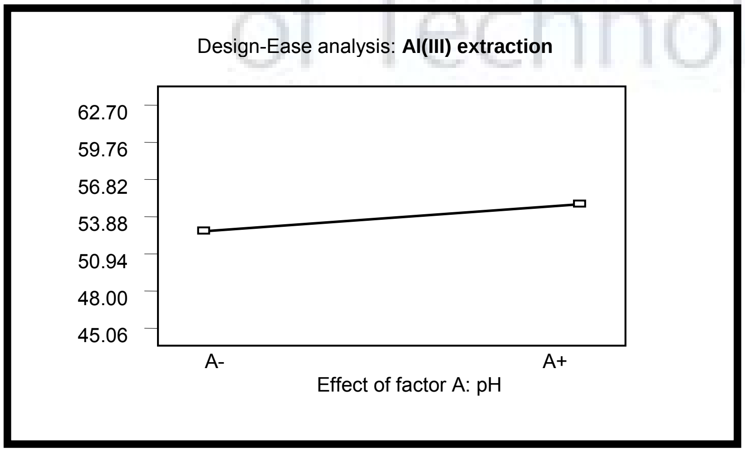


Figure 5.12: Interactive effect of pH on aluminium extraction percentage (studied alone)

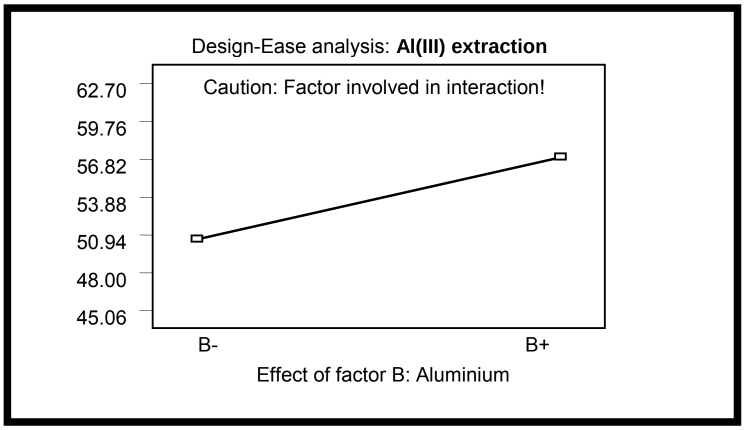


Figure 5.13: Interactive effect of initial aluminium concentration on its extraction percentage (studied alone)

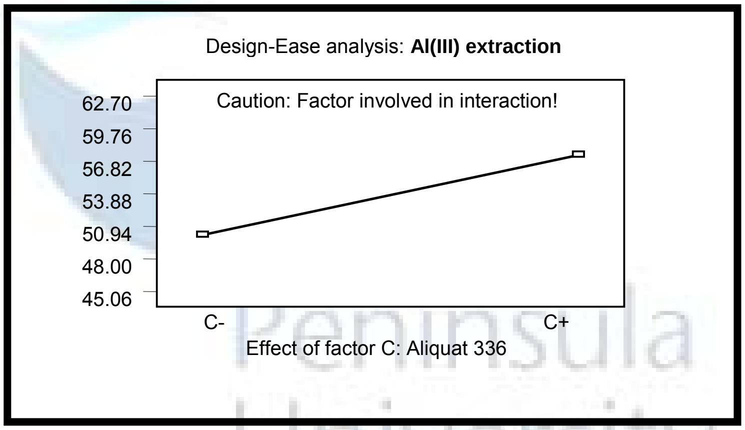


Figure 5.14: Interactive effect of Aliquat 336 concentration on aluminium extraction percentage (studied alone)

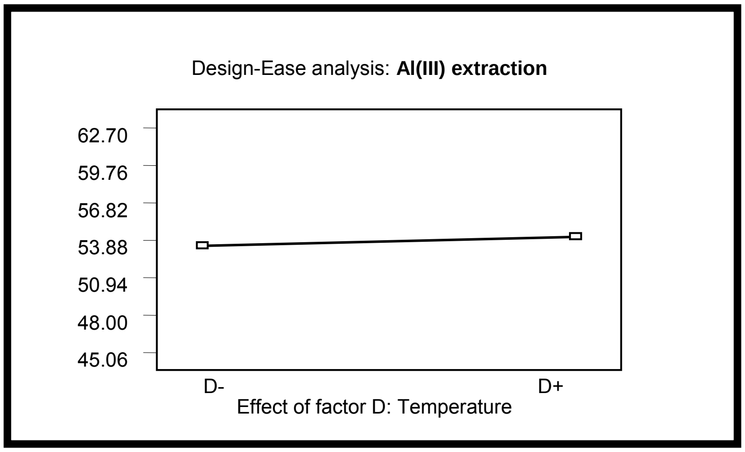


Figure 5.15: Interactive effect of temperature on aluminium extraction percentage (studied alone)

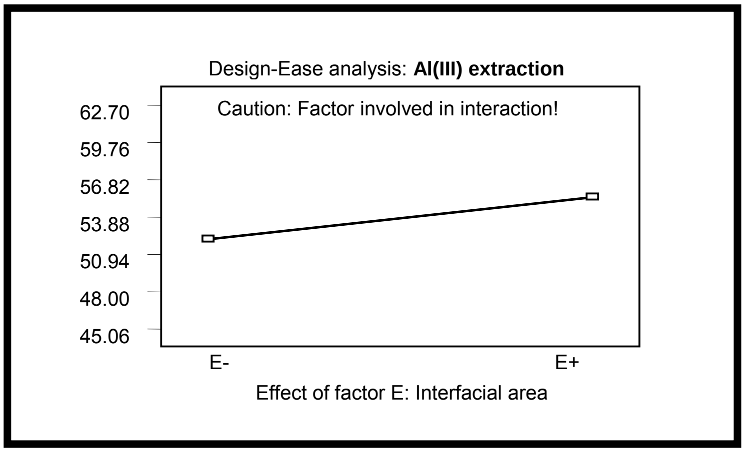


Figure 5.16: Interactive effect of interfacial area on aluminium extraction percentage (studied alone)

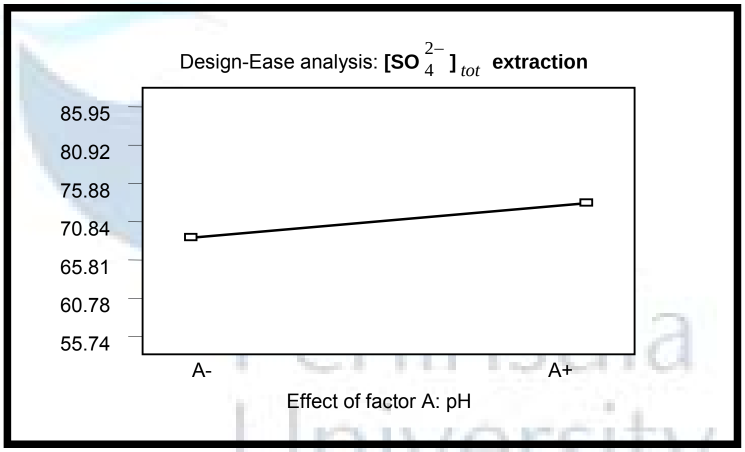


Figure 5.17: Interactive effect pH on sulphate extraction percentage (studied alone)

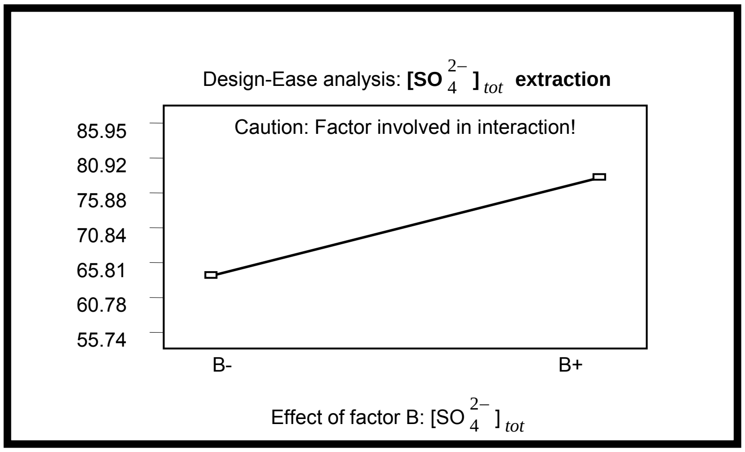


Figure 5.18: Interactive effect of initial sulphate concentration on its extraction percentage (studied alone)

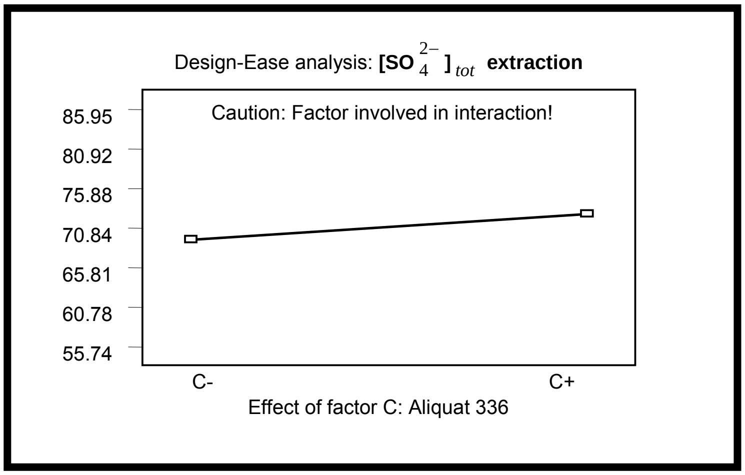


Figure 5.19: Interactive effect of Aliquat 336 on sulphate extraction percentage (studied alone)

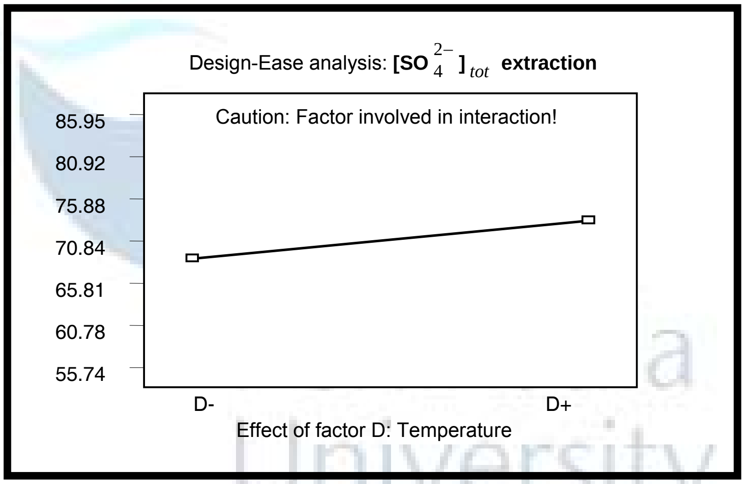


Figure 5.20: Interactive effect of temperature on sulphate extraction percentage (studied alone)

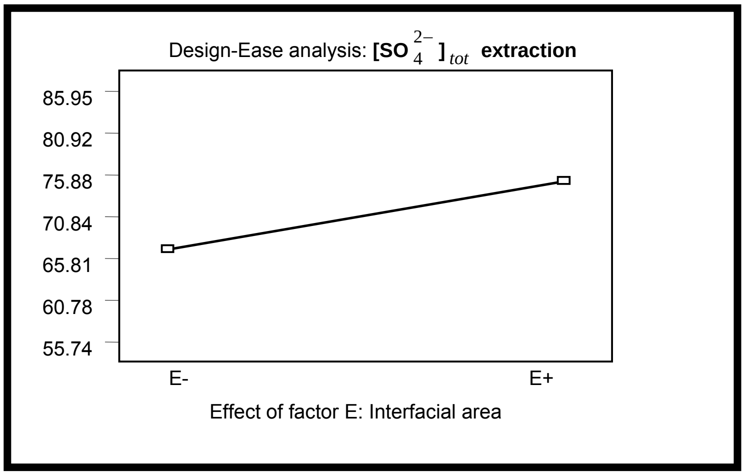


Figure 5.21: Interactive effect of interfacial area on sulphate extraction percentage (studied alone)

5.2.2 Sensitivity analysis

The fundamental objective of a factorial design is to originate a predictive model, because the existence of statistically significant interactions means that a model based on the main effects only would not be suitable (Tsakiridis & Leonardou, 2005).

Sensitivity analysis is the first and the most useful step in the optimisation of processes, because it yields information about the relative effects of model parameters on model results. The sufficiency of the models and the impact of coefficients were evaluated by applying an analysis of variance technique. Correlation coefficient (R^2) was found to be 0.99 (See statistical details given in Appendix B), which means that the model could explain 99% of the total variations in the system. It is therefore concluded that all models were satisfactory. Thus, the regression equations with interactive terms can be described by Equations 5.14 and 5.15 below:

$$Y_1 = -5.370 + 2.128\text{*pH} + 0.368\text{*[Al(III)]} + 1.153\text{*[Aliquat]} + 0.536\text{*Temperature} + 0.365\text{*Interfacial area} + 0.016\text{*[Al(III)]*[Aliquat]} - 0.028\text{*[Aliquat]*Temperature} \tag{5.14}$$

$$Y_2 = -47.740 + 4.545\text{*pH} + 0.480\text{*}[SO_4^{2-}]_{tot} + 0.550\text{*[Aliquat]} + 0.303\text{*Temperature} + 1.992\text{*Interfacial area} - 0.004\text{*}[SO_4^{2-}]_{tot}\text{*[Aliquat]} - 0.012\text{*}[SO_4]_{tot}\text{*Interfacial area} \tag{5.15}$$

where Y_1 and Y_2 are the predicted values of the percentage of aluminium and sulphate extracted respectively. To certify the accuracy of the developed equations, it is important to identify the outliers; because they can considerably influence the model, thereby providing potentially inaccurate results. The plot of actual values vs. predicted values indicates the possible existence of outliers: if a point lies far from the majority of points, it may be an outlier. The predicted value thus obtained using Design-Ease software has been found close to the experimental value indicating the applicability of the model. The estimated regression Equations 5.14 and 5.15 fit the experimental data adequately.

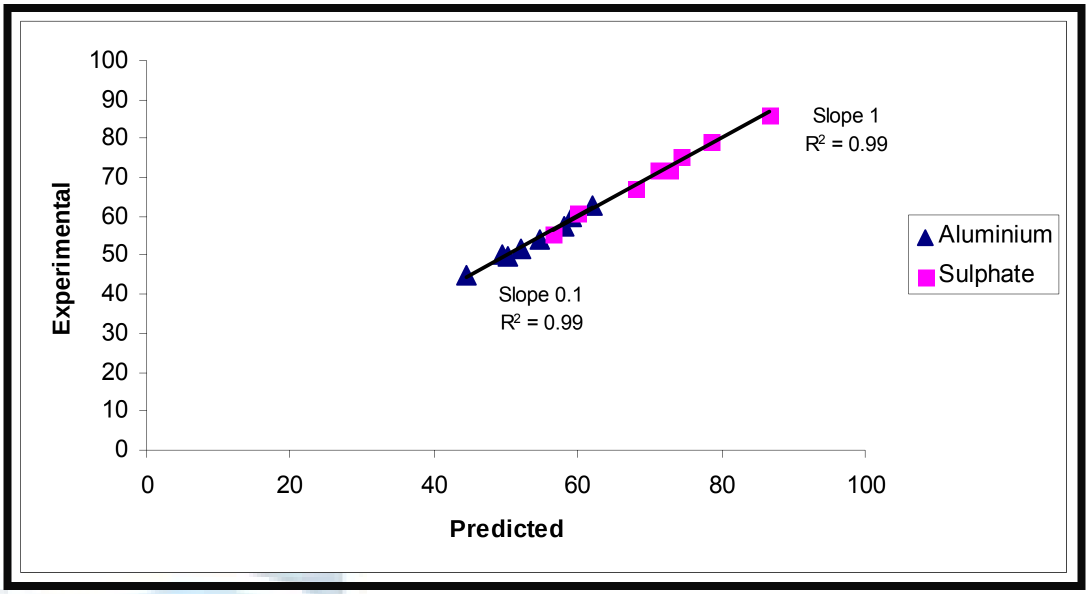
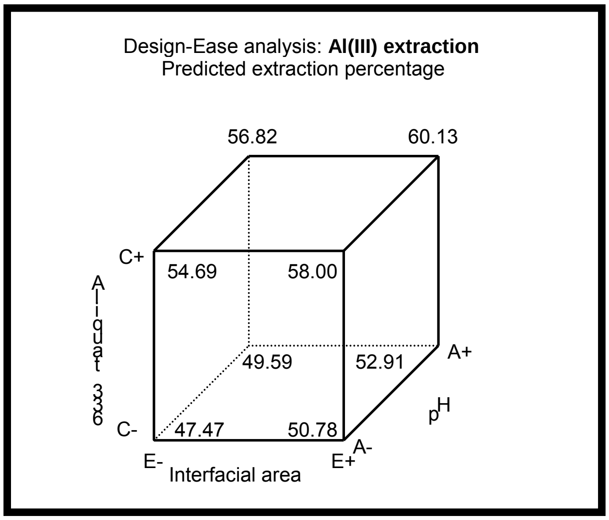


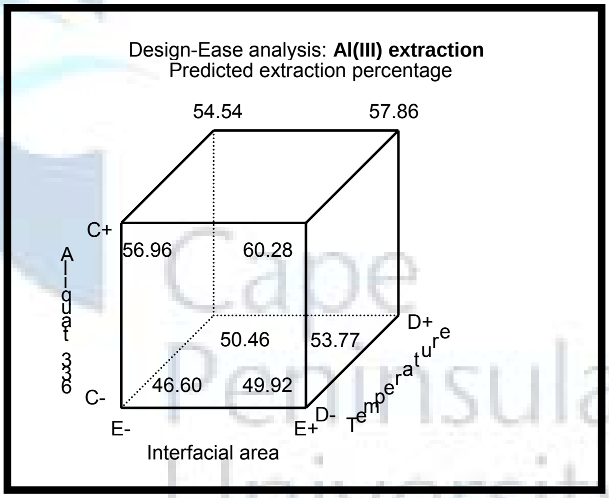
Figure 5.22: Fitting of calculated experimental data of aluminium and sulphate recovery in the organic phase to those predicted

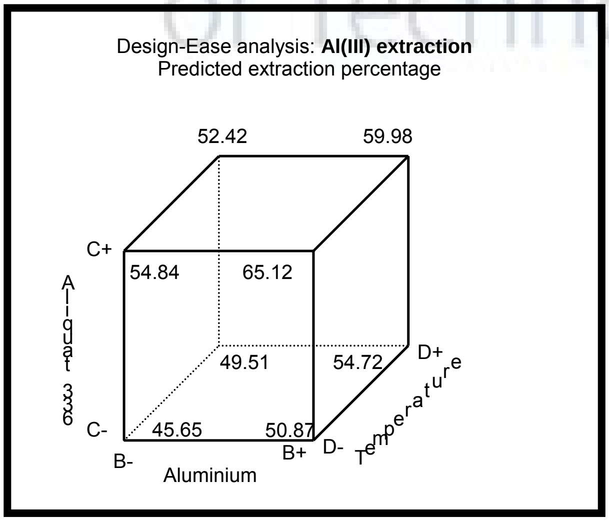
Figure 5.22 shows the dependencies for experimental extraction percentage versus modelled extraction percentage. It is a straight line for all concentrations of Aliquat 336, indicating that there is not much variation in both the results. It can also be seen that all residuals lie on a straight line, which shows that residuals were distributed normally. Reliability of the model is therefore verified.

5.2.3 Optimisation strategy

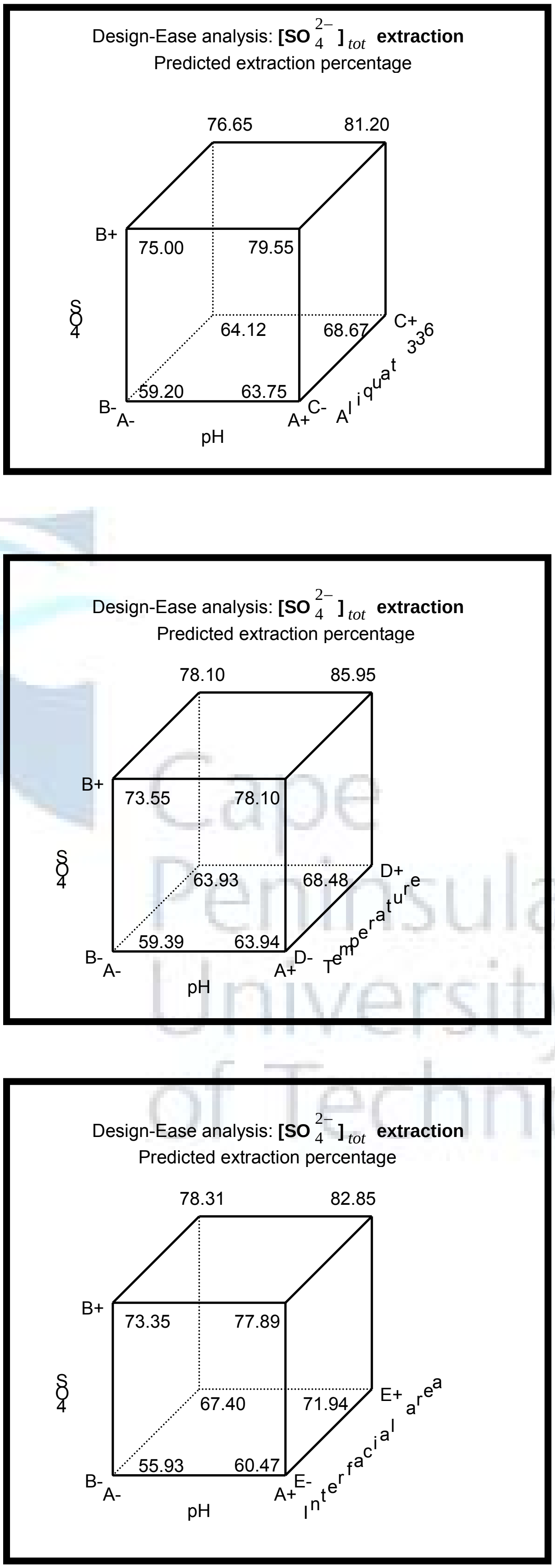
In order to determine the optimum values of each variable involved in the system for maximum response, cube plots were used (Figures 5.23 and 5.24). To substantially improve total aluminium and sulphate extraction percentage, the following should be increased: the equilibrium pH, the interfacial area, the initial aqueous phases and the Aliquat 336 concentrations. The temperature should be decreased for aluminium and increased for sulphate. By making these changes, an increase of approximately 65.12 and 85.95% in aluminium and sulphate extraction recovery respectively will be achieved.







Figures 5.23: Cube plots for optimum operational conditions determination: Case of aluminium extraction studied alone



Figures 5.24: Cube plots for optimum operational conditions determination: Case of sulphate extraction studied alone

CHAPTER 6 : CONCLUSIONS AND RECOMMENDATIONS

Solvent extraction is one of the practised methods of concentrating and separating different metal species, as well as aluminium and sulphate, from aqueous solutions. In this work, alkaline synthetic solutions of $Al(OH)_4^-$ and SO_4^{2-} were separately used for studying their extractability by the Aliquat 336-Kerosene system.

A factorial design was carried out in order to study the effects of the following variables: pH, initial aqueous feed and extractant concentrations, the temperature and the interfacial area. To carry out the experimental design, eight tests were performed for each element [$Al(OH)_4^-$ and SO_4^{2-}] separately studied. The responses were the aluminium and sulphate percentages recovered. The main effects and interactions controlling the extractability were determined from the effect analysis, normal probability plot, and visualised through the interaction diagrams.

The extraction thermodynamic parameters, namely ΔH , ΔG and ΔS , were determined for all the factorial design results. Endothermic values (positives) were found in relation to ΔH . The negative values of Gibbs free energy change (ΔG) denoted the thermodynamical spontaneity of the extraction process. The positive ΔS values showed that entropy was a motivating force for extraction.

Under the established conditions, and based on the experimental results obtained, the subsequent conclusions can be drawn:

1) Technically, it is feasible to remove aluminium and sulphate from an alkaline solution using the solvent extraction route. The optimum conditions determined for aluminium extraction from the alkaline solution by Aliquat 336-Kerosene system, were as follows: pH of 11, aluminium feed concentration of 19.84 ppm, extractant Aliquat 336 concentration of 25% (v/v), temperature of 25°C and interfacial area of 19.64 m^2/m^3. As for sulphate, the optimum conditions were found to be: pH of 11, initial sulphate concentration of 121 ppm, temperature of 40°C, interfacial area of 19.64 m^2/m^3 and extractant Aliquat 336 concentration of 25% (v/v).

2) The Aliquat 336-Kerosene system extracted aluminium with an extraction percentage of 65.12%, while sulphate was extracted with a percentage of 85.95% at the optimum operating conditions.

3) The rate of extraction was found to increase by increasing the interfacial area for either Al(OH)$_4^-$-[SO$_4^{2-}$]$_{tot}$/Aliquat 336-Kerosene system.

4) Saturation loading capacity of the solvent Aliquat 336 was determined as approximately 127 g Al(OH)$_4^-$ and 144 g SO$_4^{2-}$ per litre, respectively.

5) The stoichiometry and the degree of polymerisation of the extracted species were determined from the experimental studies using the slope analysis method. The results showed that the extracted species in both cases are monomeric species in Aliquat 336. The extracted aluminium or sulphate is solvated with one/two molecule (s) of Aliquat 336, respectively. The extraction reactions with Aliquat 336 were suggested to be as follows:

$$R_4NCl_{(org)} + Al(OH)^-_{4(aq)} \rightleftarrows R_4N\,Al(OH)_{4(org)} + Cl^-_{(aq)}$$

$$2\,R_4NCl_{(org)} + SO^{2-}_{4(aq)} \rightleftarrows (R_4N)_2SO_{4(org)} + 2Cl^-_{(aq)}$$

6) The calculated values of activation energy indicated a mixed diffusion and chemically controlled mechanism that take place either in the aqueous bulk phase or at the interface.

7) The extraction process was dominated by entropic, rather than enthalpic, changes.

8) A regression model with interactive terms was developed to predict the response as a function of independent variables and their interactions.

9) Experimental design technique and slope analysis method are an exceptionally economic approach; it is a very simple and fast method for extracting the greatest amount of complex information in a short period of time.

RECOMMENDATIONS

1) The recycling of the organic phase is a critical step in the solvent extraction process. A study will therefore have to be performed on stripping investigations of the loaded organic

phase to ensure the effective recovery of $Al(OH)_4^-$ and SO_4^{2-} and the subsequent reuse of the organic phase.

2) This study has been carried out on a bench scale, to build up an entire technology various pilot scale tests need to be done.

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APPENDICES

APPENDIX A

TABULATION OF EXPERIMENTAL DATA

1. THERMODYNAMIC FUNCTIONS FOR THE EXTRACTION OF Al(III) AND $[SO_4^{2-}]_{tot}$ USING ALIQUAT 336 IN KEROSENE

EXPERIMENT 1				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 32.38 kJ/mol ΔG = -9.02 kJ/mol ΔS = 138.93 J/mol. K E_a = 34.98 kJ/mol	ΔH = 36.64 kJ/mol ΔG = - 10.58 kJ/mol ΔS = 158.45 J/mol. K E_a = 39.20 kJ/mol	447.3	3690

EXPERIMENT 2				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 31.89 kJ/mol ΔG = -6.70 kJ/mol ΔS = 129.49 J/mol. K E_a = 34.49 kJ/mol	ΔH = 36.91 kJ/mol ΔG = -7.64 kJ/mol ΔS = 149.50 J/mol. K E_a = 39.51 kJ/mol	177.5	1332

EXPERIMENT 3				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 31.43 kJ/mol ΔG = -7.88 kJ/mol ΔS = 131.90 J/mol. K E_a = 33.91 kJ/mol	ΔH = 32.48 kJ/mol ΔG = -9.08 kJ/mol ΔS = 139.46 J/mol. K E_a = 34.96 kJ/mol	426.2	3132

EXPERIMENT 4				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 35.60 kJ/mol ΔG = -9.33 kJ/mol ΔS = 150.78 J/mol. K E_a = 38.20 kJ/mol	ΔH = 34.68 kJ/mol ΔG = -12.45 kJ/mol ΔS = 158.15 J/mol. K E_a = 37.28 kJ/mol	966.6	8640

EXPERIMENT 5				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 31.53 kJ/mol ΔG = -7.50 kJ/mol ΔS = 131.0 J/mol. K E_a = 34.01 kJ/mol	ΔH = 34.96 kJ/mol ΔG = -8.96 kJ/mol ΔS = 147.40 J/mol. K E_a = 37.44 kJ/mol	205.6	1584

EXPERIMENT 6				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 25.92 kJ/mol ΔG = -9.09 kJ/mol ΔS = 117.49 J/mol. K E_a = 28.40 kJ/mol	ΔH = 32.60 kJ/mol ΔG = -9.73 kJ/mol ΔS = 142.28 J/mol. K E_a = 35.08 kJ/mol	402.3	3060

EXPERIMENT 7				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 37.02 kJ/mol ΔG = -7.87 kJ/mol ΔS = 150.64 J/mol. K E_a = 39.62 kJ/mol	ΔH = 29.92 kJ/mol ΔG = -11.52 kJ/mol ΔS = 139.07 J/mol. K E_a = 32.52 kJ/mol	447.8	3744

EXPERIMENT 8				
Extractant	**Thermodynamic aspects (activation parameters)**		**Loading capacity (mg/L)**	
	Al(III)	$[SO_4^{2-}]_{tot}$	Al(III)	$[SO_4^{2-}]_{tot}$
Aliquat 336	ΔH = 35.79 kJ/mol ΔG =-9.03 kJ/mol ΔS = 150.41 J/mol. K E_a = 38.27 kJ/mol	ΔH = 33.53 kJ/mol ΔG = -12.02 kJ/mol ΔS = 152.85 J/mol. K E_a = 36.01 kJ/mol	918.9	8190

EXPERIMENT 1

PARAMETERS

Alkalinity level (pH): 10
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $1x10^{-5}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 10
Temperature of the solution (°C): 40
Interfacial area (m^2/m^3): 19.64

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	9.92	6.97	6.05	5.63	5.28	4.95
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	61	34	27	23	21	20
Al(III) loading (mg/L)	0	265.5	348.3	386.1	417.6	447.3
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	2430	3060	3420	3600	3690

EXPERIMENT 2

PARAMETERS

Alkalinity level (pH): 10
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $25x10^{-6}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 25
Temperature of the solution (°C): 40
Interfacial area (m^2/m^3): 10.56

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	9.92	7.01	6.01	5.76	5.33	4.99
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	61	38	32	29	25	24
Al(III) loading (mg/L)	0	104.8	140.8	149.8	165.2	177.5
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	828	1044	1152	1296	1332

EXPERIMENT 3

PARAMETERS

Alkalinity level (pH): 10
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $25x10^{-6}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 25
Temperature of the solution (°C): 25
Interfacial area (m^2/m^3): 10.56

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	19.84	11.9	10.1	8.5	8.2	8
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	121	58	45	40	36	34
Al(III) loading (mg/L)	0	285.8	350.6	408.2	419.0	426.2
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	2268	2736	2916	3060	3132

EXPERIMENT 4

PARAMETERS

Alkalinity level (pH): 11
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $1x10^{-5}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 10
Temperature of the solution (°C): 40
Interfacial area (m^2/m^3): 10.56

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	19.84	13.4	11.6	9.8	9.4	9.1
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	121	45	39	32	26	25
Al(III) loading (mg/L)	0	579.6	741.6	903.6	939.6	966.6
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	6840	7380	8010	8550	8640

EXPERIMENT 5

PARAMETERS

Alkalinity level (pH): 11
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $25x10^{-6}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 25
Temperature of the solution (°C): 25
Interfacial area (m^2/m^3): 19.64

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	9.92	6.31	5.21	5.07	4.55	4.21
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	61	30	23	20	18	17
Al(III) loading (mg/L)	0	130.0	169.6	174.6	193.3	205.6
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	1116	1368	1476	1548	1584

EXPERIMENT 6

PARAMETERS

Alkalinity level (pH): 11
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $1x10^{-5}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 10
Temperature of the solution (°C): 25
Interfacial area (m^2/m^3): 10.56

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	9.92	6.91	6.5	5.67	5.63	5.45
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	61	39	35	32	28	27
Al(III) loading (mg/L)	0	270.9	307.8	382.5	386.1	402.3
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	1980	2340	2610	2970	3060

EXPERIMENT 7

PARAMETERS

Alkalinity level (pH): 11
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $25x10^{-6}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 25
Temperature of the solution (°C): 40
Interfacial area (m^2/m^3): 19.64

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	19.84	11.91	9.89	8.18	7.55	7.4
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	121	31	25	20	18	17
Al(III) loading (mg/L)	0	285.5	358.2	419.8	442.4	447.8
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	3240	3456	3636	3708	3744

EXPERIMENT 8

PARAMETERS

Alkalinity level (pH): 10
Aqueous volume (m^3): $9x10^{-4}$
Organic volume (m^3): $1x10^{-4}$
Solvent volume (m^3): $1x10^{-5}$

Stirring speed (rpm): 70
Organic concentration (% v/v): 10
Temperature of the solution (°C): 25
Interfacial area (m^2/m^3): 19.64

Extraction time (min)	0	5	10	20	30	60
$Al(OH)_4^-$ in aqueous phase (ppm)	19.84	13.92	12.93	11.26	10.84	9.63
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	121	50	48	34	32	30
Al(III) loading (mg/L)	0	532.8	621.9	772.2	810.0	918.9
$[SO_4^{2-}]_{tot}$ loading (mg/L)	0	6390	6570	7830	8010	8190

2. ADDITIONAL TESTS

EXPERIMENT 1 (pH effect)

PARAMETERS

Al(III) = 19.84 ppm
$[SO_4^{2-}]_{tot}$ = 121 ppm
Stirring speed (rpm): 70
Temperature of the solution (°C): 25
Organic concentration (% v/v): 25

Solvent volume (m^3): $25x10^{-6}$
Organic volume (m^3): $1x10^{-4}$
Interfacial area (m^2/m^3): 10.56
Aqueous volume (m^3): $9x10^{-4}$
Extraction time (min): 30

pH	10	10.5	11	11.5	12
$Al(OH)_4^-$ in aqueous phase (ppm)	11.9	8	7.5	6.72	5.73
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	56	37	32	26	11

EXPERIMENT 2 (Temperature effect)

PARAMETERS

Al(III) = 19.84 ppm
$[SO_4^{2-}]_{tot}$ = 121 ppm
Stirring speed (rpm): 70
Aqueous volume (m^3): $9x10^{-4}$
Organic concentration (% v/v): 10
Solvent volume (m^3): $1x10^{-5}$
Organic volume (m^3): $1x10^{-4}$
Interfacial area (m^2/m^3): 10.56
Extraction time (min): 30
Alkalinity level (pH): 11

Temperature of the solution (°C)	25	28	30	35	40
$Al(OH)_4^-$ in aqueous phase (ppm)	10.01	9.2	8.32	7.51	6.7
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	42	41	35	31	25

EXPERIMENT 3 (Extractant Aliquat 336 concentration effect)

PARAMETERS

Al(III) = 19.84 ppm
$[SO_4^{2-}]_{tot}$ = 121 ppm
Stirring speed (rpm): 70
Extraction time (min): 30
Organic volume (m^3): $1x10^{-4}$
Interfacial area (m^2/m^3): 10.56
Aqueous volume (m^3): $9x10^{-4}$
Alkalinity level (pH): 11

[Aliquat 336] (% v/v)	10	12.5	15	20	25
$Al(OH)_4^-$ in aqueous phase (ppm)	9.2	8.43	8.32	7.51	6.7
$[SO_4^{2-}]_{tot}$ in aqueous phase (ppm)	54	34	29	23	17

EXPERIMENT 4 (Determination of the metal-organic complexes nature)

PARAMETERS

Al(III) = 19.84 ppm
$[SO_4^{2-}]_{tot}$ = 121 ppm
Stirring speed (rpm): 70
Extraction time (min): 30
Organic volume (m^3): $1x10^{-4}$
Interfacial area (m^2/m^3): 10.56
Aqueous volume (m^3): $9x10^{-4}$
Alkalinity level (pH): 11

Extraction time (min)	0	5	10	20	30	60
$[Cl^-]$ in $Al(OH)_4^-$ aqueous phase (ppm)	0	480	600	630	710	756
$[Cl^-]$ in $[SO_4^{2-}]_{tot}$ aqueous phase (ppm)	0	470	495	530	585	665

APPENDIX B

TABULATION OF STATISTICAL DATA

DESIGN SUMMARY

1/4 Replicate of 5 factors in 8 experiments

5 Factors: A, B, C, D, E

Factor Generator

D = AB

E = AC

Defining Contrast

I = ABD = ACE = BCDE

Word Lengths of Contrast

1	2	3	4	5
0	0	2	1	0

Resolution III

ALIASES

A = BD = CE

B = AD = CDE

C = AE = BDE

D = AB = BCE

E = AC = BCD

BC = DE = ABE = ACD

BE = CD = ABC = ADE

Effects Lost from Blocking Options:

2 Blocks of 4 Experiments Each

Blocking generator: BC

BC = DE = ABE = ACD

Table B.1: Statistical data of regression model with interactive terms predicting aluminium extraction response

R-squared	0.99
Adjusted R squared	0.92
Pred R-squared	0.27
Dependent mean	53.80

Table B.2: Statistical data of regression model with interactive terms predicting sulphate extraction response

R-squared	0.99
Adjusted R squared	0.94
Pred R-squared	0.49
Dependent mean	71.02

Table B.3: Multiple regression statistics for $k_{app}^{Al(III)}$ determination

Summary output of k_{app} value of aluminium	
R squared	0.93
Adjusted R squared	0.83
Pred R-squared	0.49

Table B.4: Multiple regression statistics for $k_{app}^{[SO_4^{2-}]_{tot}}$ determination

Summary output of k_{app} value of sulphate	
R squared	0.99
Adjusted R squared	0.97
Pred R-squared	0.85