Purification of $VOSO_4.5H_2O$ using solvent extraction

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“Education is the most powerful weapon which you can use to change the world.” – Nelson Mandela.

ABSTRACT

Vanadium (V), which is found in over 50 minerals usually in combination with other elements is used in a variety of applications including cladding for titanium to steel, material in nuclear fusion reactors, ceramics, glass coatings, catalysts, automobiles, rubbers, plastics, chemicals, spacecraft and airplane industries and submarine pipes. Apart from these existing applications, a novel application of V is in the all vanadium redox flow battery, which has shown promise as a future energy storage system. All these applications have given rise to an increased V demand and the subsequent opportunity for the development of new or improved purification methods. In view thereof, the aim of this M.Sc. study was to develop an improved solvent extraction (SX) based purification method for the recovery of $VOSO_4.5H_2O$ (V(IV)) from a multicomponent electrolyte solution containing $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $Co_2(SO_4)_3.7H_2O$, $NiSO_4.6H_2O$ and $K_2Cr_rO_{7.}$ After optimisation of the SX variables, the suitability of membrane-based solvent extraction (MBSX) was investigated.

The research presented can be divided into three parts. In a first step two preliminary experiments were conducted, where i) the extraction of V from different H_2SO_4 feed concentrations using eight extractants and ii) the effect of the impurities in the synthetic solution on V(IV) extraction was investigated. In the second step, the SX process was optimised in terms of i) the extractant concentration, ii) the effect of contact time, iii) the effect of diluent, iv) the effect of organic and aqueous volume phase ratios, v) the effect of acid concentrations, vi) the effect of the stripping agents and vii) stripping agent concentrations. In the third part, MBSX experiments were done using the optimised SX conditions.

From the preliminary experiments, it became apparent that of all of the eight extractants that were tested, the oxime based extractant, LIX-84-IC and the tertiary amine based extractant, Alamine 336 gave the highest extraction of V(IV), specifically at low acid concentrations (0.1 mol/dm^3). The results from the single salt extractions confirmed the complexity of the V-speciation in aqueous solutions as well as the influence of the impurities on extraction. Since both LIX-84-IC and Alamine 336 showed promising results, the SX process was optimized for both the extractants as discussed in Chapter 3 and 4 respectively.

For LIX-84-IC, the highest V extraction was attained when extracting for 15 minutes using a 30 % (v/v) LIX-84-IC containing organic phase consisting of cyclohexane and 1-octanol as the diluent and modifier. For this extraction the O/A volume ratio was 1:1. While under these conditions the co-extraction of Cr(VI) was observed, little to no-co-extraction of the other salts occurred. The selective stripping of V(IV), without any co-extraction fo Cr(VI), was achieved using a 0.05 mol/dm^3 NaOH solution. When using MBSX significantly higher equilibrium times were required while the selectivity decreased in terms of the V(IV) extracted. The delayed time suggests mass transfer limitations when using LIX-84-IC.

When using Alamine 336, optimal extraction was obtained from low H_2SO_4 feed concentrations (0.0002 mol/dm^3), confirming a metal complex anion exchange extraction mechanism due to the presence of metal anions in the feed solution. Optimal extraction was achieved when using 20 % (v/v) Alamine 336 with a contact time of 90 minutes using ShellSol 2325 and 1-octanol as the diluent and modifier and an O/A volume phase ratio of 1:1. While the co-extraction of Cr(VI) was again observed, selective V(IV) recovery from the loaded organic was achieved when using a 0.03 mol/dm^3 HCl solution. Additionally, scrubbing with 7 mol/dm^3 HCl can be used to first remove Cr(VI) from the loaded organic prior to the stripping of the V(IV). When using MBSX, both the selectivity for V(IV) as well the recovery increased compared to SX, which is contrary to the results obtained when using the oxime-based extractant, while no significant change in the equilibrium time was observed.

The results for the batch extraction experiments showed that, when using the oxime based extractant LIX-84-IC, the purity of V(IV) increased from 15.02 % to 99.98 % in a single extraction and stripping stage with a yield of 88 %. When using the amine based extractant Alamine 336, the V(IV) purity increased from 15.26 % to 95.3 % with a significantly lower yield of 27.1 %, also in a single extraction/scrubbing and stripping stage. Hence while high purities of V(IV) were attained using both the extractants when using SX, the higher yield attained favours the oxime based extraction. Contrariwise, in the MBSX studies, Alamine 336 outperformed LIX-84-IC in terms of recovery and extraction time.

Keywords: vanadium purification, solvent extraction, membrane-based solvent extraction.

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CHAPTER 1 – INTRODUCTION

1.1 Background

In this section, a brief background of vanadium (V) will be given, including its applications such as the novel developments regarding the vanadium redox flow battery (VRFB). From this the problem statement follows, leading to the aim and objectives of this study. This is followed by a brief overview of the outlay of the dissertation.

Andrés Manuel del Rio, a Mexican scientist, discovered V in the early 1800s as a co-constituent in a lead vanadite ore ($Pb_5[VO_4]_3Cl$). Since V was initially mistaken for chromium (Cr), this transition metal was only named thirty years after its discovery, as V concentrations present in iron (Fe) converter slags, by Swedish chemist Nils Gabriel Sefstrom (Moskalyk and Alfantazi, 2003). The first separation of V was achieved by Sir Henry Roscoe in 1867, while the successful purification of V metal (99.7 %) was obtained in 1925 by two American chemists, J.W. Marden and M.N. Rich, who reduced vanadium pentoxide (V_2O_5) using calcium metal (Moskalyk and Alfantazi, 2003). V, a first row transition element, is 22nd most abundant of all the elements with a molecular weight of 50.945 g/mol, specific gravity of 5.96 and a melting point of 1929 °C (Moskalyk and Alfantazi, 2003).

Due to its distinctive physical and chemical properties, V has numerous applications, including its use as cladding for titanium to steel (Gummow, 2011, Chu *et al.*, 2017), in nuclear fusion reactors (Palacios *et al.*, 2016), ceramics (Cuff, 1996), glass coatings (Lyons, 2010), catalysts (Agrawal, 2005), automobiles, rubbers, plastics, chemicals (Gummow, 2011), spacecraft and airplane industries (Moskalyk and Alfantazi, 2003), and submarine pipes. Of all the numerous applications, the steel industry accounts for 85 % of the V consumption (Moskalyk and Alfantazi, 2003). More recently, V has drawn attention due to its possible use in alternative energy storage systems. The increased demand for alternative energy storage systems has created the opportunity for the development of novel or improved energy storage devices such as the redox flow battery (RFB).

The possibility of integrating RFBs with the current electricity grid have, due to several advantages, become feasible (Galloni *et al.*, 2015, Ponce de León *et al.*, 2006). Common RFBs have the problem of cross-contamination of the respective metal species through the separating membrane, resulting in shorter lifespans. However, this problem of cross-contamination is minimised when using VRFBs where V, in different oxidation states, is the only element present in both electrolytes of the cell, resulting in longer lifespans (Joerissen *et al.*, 2004). According to

Lucas and Chondrogiannis (2016) vanadium-based energy storage systems such as the VRFB can therefore, at least theoretically, last for decades. VRFBs also have other advantages over conventional RFBs, which include increased charge cycles, flexibility in the assembly and operation of the battery and suitability for industrial-sized applications. According to Arbabzadeh *et al.* (2015), cost efficiency due to increased energy density and efficiency also makes the VRFB a worthy competitor for integration with alternative energy systems. A generic diagram of the VRFB is shown in Figure 2-1. During discharge on the anode side of the cell, V^{2+} is oxidised to V^{3+} with the release of an electron. On the cathode side of the battery V^{5+} (VO_2^{+}) is reduced to V^{4+} (VO^{2+}). The V species both in the anode and cathode are dissolved in a sulphuric acid (H_2SO_4) solution where the pH of the solution is maintained by exchanging protons between the two half cells (Lucas and Chondrogiannis, 2016).

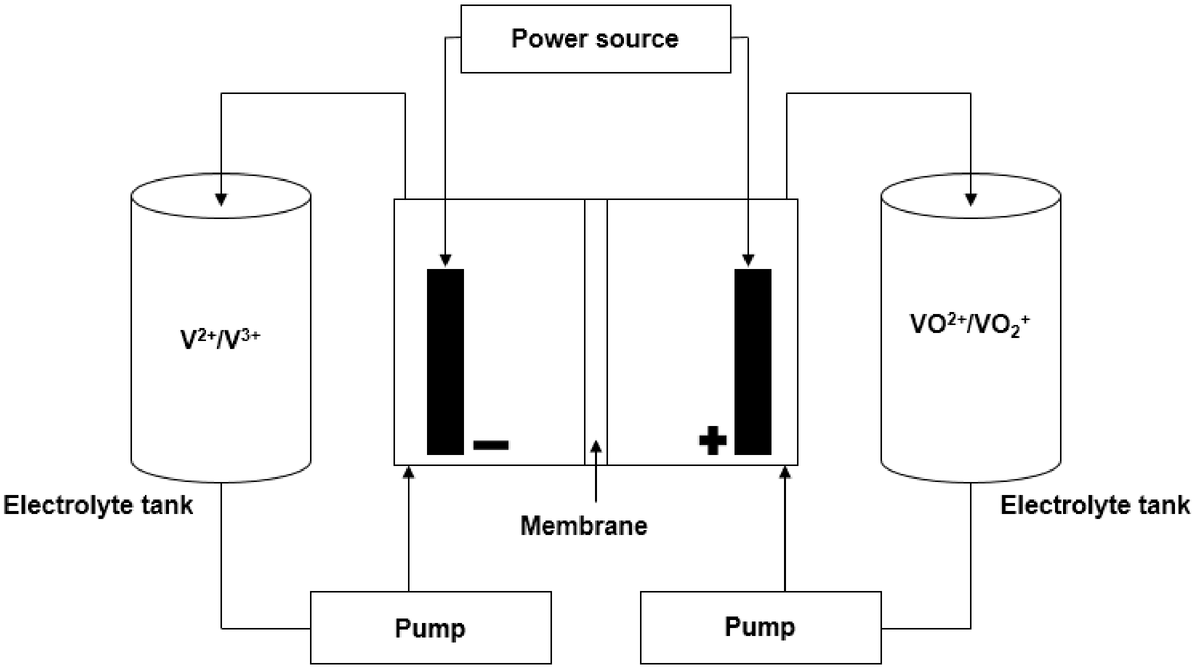

Figure 2-1: **A simplified diagram of the VRFB with the positive electrolyte consisting of V(IV)/V(V) and the negative electrolyte containing V(II)/V(III) (Lucas and Chondrogiannis, 2016).**

The two half reactions are presented below.

$$\mathbf{VO^{2+} + H_2O \leftrightarrow VO_2^{+} + e^{-} + 2H^{+}} \text{ (Positive half-cell)}$$

$$\mathbf{V^{3+} + e^{-} \leftrightarrow V^{2+}} \text{ (Negative half-cell)}$$

1.2 Problem statement

In view of the existing as well as the new possible applications, an increased demand for specifically pure V is expected (Okudan *et al.*, 2015). According to Zhao *et al.* (2012), the current primary sources are insufficient to meet the increasing demand and thus the recovery of V from both primary and secondary resources are essential. While various methods exist for the recovery and purification of V, high purity V remains highly expensive.

1.3 Aim and objectives

The aim of the research presented in this dissertation is to propose a feasible separation method for V from a multicomponent synthetic solution. From the various hydrometallurgical separation processes, and based on the composition of the chosen synthetic solution, SX was selected as the most suitable purification technique. A comprehensive discussion as to why SX was selected is given in the Literature Chapter (Chapter 2) of this dissertation. To achieve the abovementioned aim, the following three objectives were set.

- The first objective was to conduct a preliminary screening study. The purpose of this was threefold; i) to confirm the suitability of the chosen extractants, ii) to gain an understanding as to which V species are present based on known extraction mechanisms for the various extractants and iii) to discuss the correlations and differences of the experimental data generated and the results reported in literature.

- The second objective was to systematically investigate the effect of key operating variables in a SX process using a series of batch experiments. Based on the available literature of the SX of V, the following variables were investigated: i) the extractant concentration, ii) the effect of contact time, iii) the effect of diluent, iv) the effect of organic and aqueous volume phase ratios, v) the extraction isotherms, vi) the effect of acid concentrations, and vii) the effect of the stripping agents and stripping agent concentrations.

- The third and final objective entailed the application of the optimised conditions as determined in objective two to a MBSX system. This task entailed an equilibrium study as well as a study on the effect of carrier concentration, thereby determining the feasibility of MBSX for the purification of V.

1.4 Layout of this dissertation

This dissertation is divided into five chapters. Chapter 1 commences with a general introduction. Subsequently, the problem statement is specified, followed by a systematic outline regarding the aims and objectives of this study and the outline of the dissertation.

In Chapter 2, which is the Literature study, a comprehensive literature survey in relation to this study is given, focussing on V and its purification using, amongst others, SX and MBSX.

Chapters 3 and 4 contain the experimental work of this M.Sc. project. Both these chapters are divided into the four typical research sections: Introduction, experimental methods and reagents, results and discussion and the conclusions and recommendations. While both deal with the SX of V, the effect of an oxime extractant, LIX-84-IC was investigated in Chapter 3, while the extractant studied in Chapter 4 was the amine-based extractant Alamine 336.

The dissertation concludes with Chapter 5 entitled Evaluation and Recommendations. This chapter gives an overview of all the results, including the important conclusions drawn from this dissertation, and evaluates to which extent the goal of the study was achieved. The chapter ends with recommendations for future work.

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CHAPTER 2 – LITERATURE CHAPTER

2.1 Introduction

In Section 2.1.1 of this literature survey a general background of V is presented focussing on its sources, applications, physical and chemical properties including a brief discussion on V solution chemistry. While recovery processes (Section 2.1.2) of V can either follow a hydrometallurgical or a pyrometallurgical route, a discussion on the advantages and disadvantages of hydro- and pyrometallurgy (Section 2.1.3) was also included to motivate as to why a hydrometallurgical route was chosen for this study. This is followed by a general discussion on the primary hydrometallurgical leaching process (Section 2.1.4), including a discussion on general purification methods for the recovery of various metals from leaching solutions (Section 2.1.5) thereby showing the suitability of SX for V recovery. In Section 2.2, a review of SX is given including, operating variables involved in extraction (Section 2.2.1), stripping from specific ligands (Section 2.2.2) and a short review about scrubbing (Section 2.2.3). A novel process adapted from SX, called MBSX, will be reviewed (Section 2.2.4) focussing on the process itself and the motivation behind the choice of the membrane materials used in this study. Herewith the general principles and theory of SX will be discussed (Section 2.2.5) concluding with a summary of the chapter, which is Section 2.3.

2.1.1 Vanadium

V is defined as a rare metal and is found in over 50 minerals (Moskalyk and Alfantazi, 2003). Similar to most other metals, V is found in a compound form (Wiberg *et al.*, 2001) ranging from iron ores, clays, basalts and soils (Wiberg *et al.*, 2001). Of all the different V containing mineral ores, V is most abundant in patronite (VS_4), vanadinite ($Pb_5(VO_4)_3Cl$, which is very similar to apatite ($Ca_5(PO_4)_3Cl$), roscoelite ($K(Al,V)_2(OH,F)_2$ [$AlSi_3O_{10}$]) and finally carnotite which is also known as the uranium ore ($K(ClO_2)(VO_4))1.5H_2O$). According to Wiberg *et al.* (2001), the main deposits of V are found in RSA, China, Russia and USA with RSA currently contributing 40 % of the global V_2O_5 production (Polyak, 2016a). The V from the RSA is found in the Highveld region of Mpumalanga, Witbank (Rohrman, 1985) and is recovered from a Fe – Ti ore (magnetite) that typically contains 1 – 2 % V_2O_5 (Polyak, 2016a).

Most of the produced V is consumed by the steel industry in the form of ferrovanadium, which is used to produce steel alloys where the amount of V in the alloys can range from < 0.2 % (construction steels) to 5 % (high speed drill steels). When adding V to steel, the V combines with the C to form V_4C_3, which results in a decrease in the grainsize of the steel thereby increasing the resistance against wear and elevated temperatures. This property makes these alloys suitable for tools that must bear significant mechanical stresses. Apart from steel, V can be combined with a range of other metals, such as, V – Ti alloys which are used when working at high temperatures, or V – Fe – Co alloys which are used as magnet steels. Finally, V_2O_5 is used as a heterogeneous catalyst for the production of H_2SO_4, through an oxidation reaction where SO_2 is transferred to SO_3 using a V_2O_5 catalyst at 400 °C (Riegel and Kent, 1974). The absorption of the SO_3 into the 96 % concentrated H_2SO_4, results in a further increase of the H_2SO_4 concentration to 98 % (Habashi, 1999).

V has a high melting point (1915 °C) that can be even further increased by adding minor amounts of H, C, N or O. For example, 10 % C containing V has a melting point of 2700 °C. Similar to Ti, V has a boiling point of 3350 °C. V has four different oxidation states, +5, +4, +3 and +2, of which the oxidation states +5 and +4 are the most stable V species. However, V can freely change oxidation states, explaining its suitability as catalyst in oxidation reactions (Wiberg *et al.*, 2001) and in the VRFB. In addition, it has been reported that V can have a valence of +1, 0 and -1 (Crans and Smee, 2003).

The different species of V in solution depend on three factors; i) the valence of V, ii) the concentration of V and iii) the pH of the solution (Zhou *et al.*, 2011). With its many oxidation states, V displays complex speciation in aqueous solutions (Zeng and Yong Cheng, 2009). When Zhou *et al.* (2011) investigated the speciation of V in V – H_2O and V – H_2SO_4 systems for all four of the oxidation states, they found that V(V) is present as a VO_2^+ cation (pervanadyl cation) between a pH of 1 and 2. This was confirmed by Wiberg *et al.* (2001) who stated that V(V) displays a colourless solution containing $[V^{V}O_2(H_2O)_4]^+$ cations, also commonly known as VO_2^+ ions. Between a pH of 1.4 and 3, the solubility of V(V) decreases forming the less soluble V_2O_5. When considering the speciation of V(IV), Zhou *et al.* (2011) showed that at low pH, V(IV) is present in the form of a vanadyl cation ($[V^{IV}O(H_2O)_4]^{2+}$ or VO^{2+}), which precipitates as vanadium-tetra-oxide ($V_2O_{4(s)}$) in the pH range of about 3. The blueish VO^{2+} has a higher solubility than that of V(V). Above a pH of 3, the solid vanadium-tetra-oxide will dissolve forming the $(HV_2O_5)^-$ metalate anion (Zhou *et al.*, 2011).

In the (III) and (II) oxidation state, the V cations $[V^{III}(H_2O)_6]^{3+}$ and $[V^{II}(H_2O)_6]^{2+}$ display green and grey-violet coloured solutions respectively (Wiberg *et al.*, 2001). Similar to the other oxidation states discussed previously, Zhou *et al.* (2011) showed that V(III) forms readily when dissolved in an acid (pH < 3), displaying a blue-green colour. From the above discussion it can be concluded that the solution chemistry of V can be intricate due to the formation of numerous complex metal cations and anions. For this study, the speciation effects of V are important and accordingly, will be discussed in more detail in Section 2.2.1.1 of this chapter.

2.1.2 Current recovery processes of vanadium

The discovery of V in U-containing ores and the successful leaching and separation using SX made V available for industrial applications. The V can be recovered from this U-containing ores using a synergistic extraction with dodecyl orthophosphoric acid (DDPA), heptadecyl orthophosphoric acid (HDPA) and tri-alkylamine (Habashi, 1999). The V can subsequently be selectively stripped using a 2 mol/dm^3 HCl before stripping the U using a 10 mol/dm^3 HCl solution. Na_2CO_3 has also been used to strip both V and U yielding a concentrated solution, where the U can be precipitated selectively using NaOH with sodium vanadate remaining in the aqueous solution (Habashi, 1999).

For the recovery of aluminium using the Bayer Process (Figure 2-1) (Klauber *et al.*, 2011), both the V and aluminium are dissolved at 150 – 200 °C using NaOH. The aluminium is precipitated as $Al(OH)_3$ (gibbsite), while the V remains in solution. The subsequent evaporation, which concentrates the alkaline solution, results in the precipitation of V fluorocomplexes. To recover these complexes, the solution is filtered before dissolving the precipitates in dilute acid (pH = 5). With SX the V can be recovered from this solution using an organic phase consisting of 10 % secondary aliphatic amines, 30 % alcohol and 60 % diluent (aliphatic hydrocarbons). After extraction, the loaded organic phase is stripped using a 0.02 mol/dm^3 ammonia solution at an equal O/A volume phase ratio. This stripped solution contains 30 – 35 g/L V_2O_5. The V_2O_5 is recovered by precipitation using ammonium salts and high purity ammonium metavanadate is formed (≤ 98 %).

As mentioned in Section 2.1.1, V can also be recovered from magnetite ore. A typical composition of such V – containing ore found in South Africa is shown in Table 2-1. Due to the high Ti content, two additional steps are required during V recovery in SA. Firstly, an initial reduction step is required using powdered coal, followed by reduction to the metallic state in an electric furnace (Moskalyk and Alfantazi, 2003).

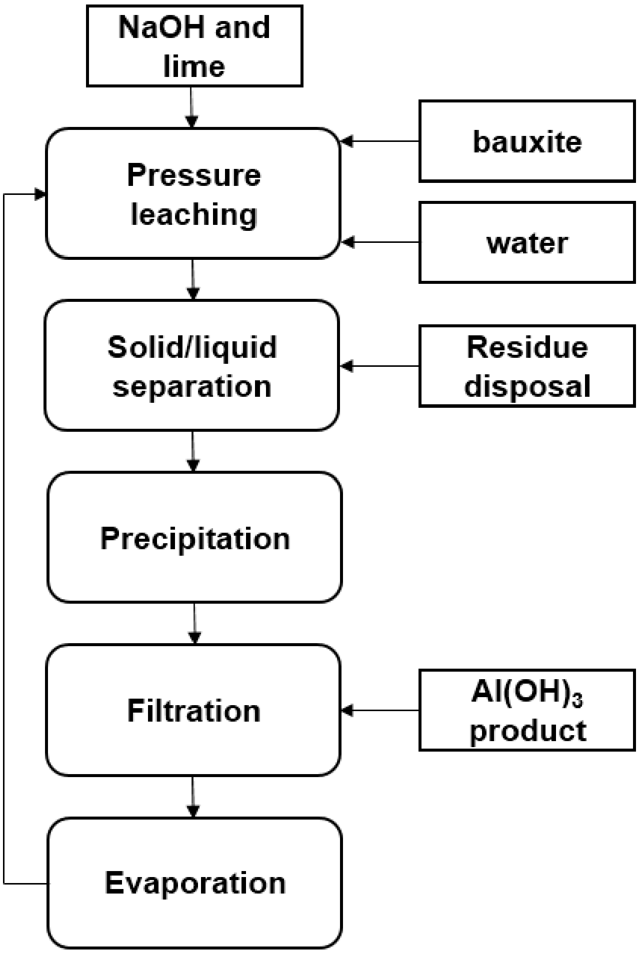

Figure 2-1: **Schematic presentation of the Bayer process (Klauber *et al.*, 2011)**

Table 2-1: **The typical composition of V-containing ore (magnetite) from South Africa (Rohrman, 1985).**

Composition	Concentration % (v/v)
$Fe_20_3 + Fe_30_4$	53 % – 57 %
TiO_2	12 % – 15 %
V_2O_5	1.4 % – 1.9 %
SiO_2	1.0 % – 1.8 %
Al_2O_3	2.5 % – 3.5 %
Cr_2O_3	0.15 % – 0.6 %

2.1.3 Pyrometallurgy and Hydrometallurgy

The aim of this section is to draw a brief comparison between pyrometallurgical and hydrometallurgical processes and accordingly confirm the suitability of the hydrometallurgical technique chosen for this study which will subsequently be discussed in more detail in Sections 2.1.4 and 2.1.5.

The most important steps involved in pyrometallurgy and hydrometallurgy (Wilson *et al.*, 2014) are shown in Figure 2-2 and Figure 2-3 respectively. As can be seen from Figure 2-2, pyrometallurgical processes can be divided into four main steps i) calcination, which entails the thermal decomposition of the ore, ii) roasting, which involves gas-solid reactions under elevated temperatures, iii) smelting, which separates the products generated from the roasting step and iv) refining, which is essentially the purification of the desired product. From Figure 2-3, which shows the main steps in a hydrometallurgical process, it can be seen that the mineral ore or material from secondary sources are leached before concentrating and separating the metal salts using a suitable technique. Finally, the metal in the purified aqueous solution is reduced for metal recovery (Wilson *et al.*, 2014).

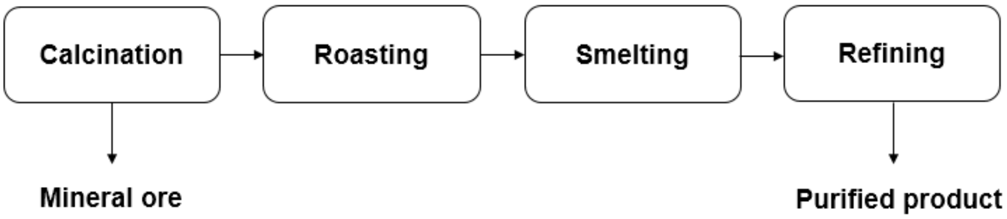

Figure 2-2: The main process flow in pyrometallurgy for the recovery of metals from the mineral ore (Hiskey, 2000)

Although the reaction rates in hydrometallurgical processes are usually lower than those found in pyrometallurgical processes, the lower fuel consumption due to the more favourable process conditions, such as the low temperatures required (100 °C as opposed to 1200 °C required for the pyrometallurgical processes), is advantageous. Furthermore, the generation of dust from pyrometallurgical processes contributes to the cost of the process due to the processes and equipment required to recover the dust, whereas no dust generation is involved using hydrometallurgical processes, being a wet process (Habashi, 1999). Similarly, hydrometallurgical processes are more suitable for the separation of metals from complex ores where separation is more readily achieved. Similarly, hydrometallurgical processes are also preferable when recovering elements from low grade ores again due to the high-energy requirements during the heating of the gangue minerals in the pyrometallurgical processes.

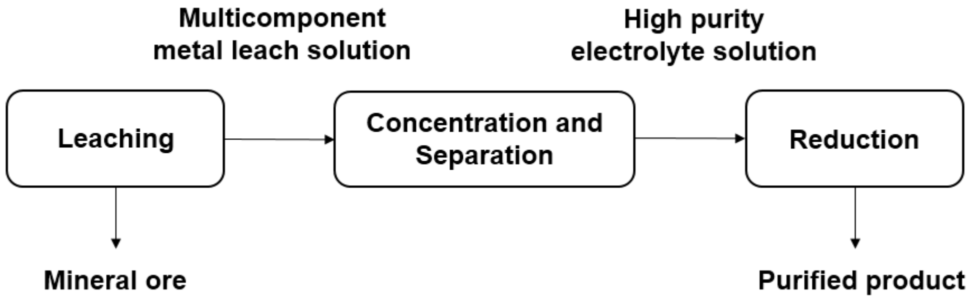

Figure 2-3: The main process flow in hydrometallurgy for the recovery of metals from primary and secondary sources (Wilson *et al.*, 2014)

The waste disposal for hydrometallurgical processes have a smaller environmental impact than that of pyrometallurgy while hydrometallurgical processes are cheaper for small scale operations where lower capital investments are required. For large scale operations, pyrometallurgical processes become more suitable with similar capital investments required for both processes.

An example of an industrial metal recovery process where the hydrometallurgical route was favoured, despite the fact that pyrometallurgy was used as the initial recovery method, is the production of Al_2O_3 from bauxite. The pyrometallurgical method, entailed heating the bauxite with Na_2CO_3 at 1200 °C, treating the formed sodium aluminate with H_2O before precipitating $Al(OH)_3$ by bubbling the solution with carbon dioxide (Habashi, 1999). The hydrometallurgical route however, entails the leaching of bauxite using NaOH under high (relative to hydrometallurgical scale) temperatures and pressures. The product, (sodium aluminate) is filtered and precipitated to ultimately produce pure $Al(OH)_3$. Due to the advantages involved in the hydrometallurgical route, it was favoured and the pyrometallurgical route was cast aside. Similarly, the hydrometallurgical process for producing zinc was also preferred to the pyrometallurgical route (Habashi, 1999).

Based on the discussion above, it is clear that the recovery of precious metals using a hydrometallurgical route has several advantages over the pyrometallurgical route. More importantly, with higher selectivity achievable via a hydrometallurgical route, and since the aim of this research is the separation of V from various other elements, a process in which higher selectivity is attainable is imperative and hence a hydrometallurgical route was selected for the research conducted in this dissertation.

2.1.4 Leaching

In the subsequent sections the leaching (Section 2.1.4) and the purification (Section 2.1.5) of the hydrometallurgical process will be discussed. The leaching of copper form pyrite, using heap leaching was recorded as early as the sixteenth century (Habashi, 2005). Only in 1892, the pressure leaching of bauxite with NaOH was introduced. During leaching, the elemental content from a primary (ore) or secondary (recycle) source is dissolved using a suitable lixiviant. During leaching from mineral ore deposits (primary source), the choice of lixiviant is usually based on the nature of the ore. There are basically three different types of ores including low grade ore, direct leaching ores and high grade ores (Gupta and Mukherjee, 1990). Once the grade of an ore has been identified, a suitable leaching method and leaching reagent is chosen. According to Habashi (1999) leaching agents should be selective, act rapidly and yield optimal recovery. Furthermore, a suitable leaching lixiviant should be affordable, easily accessible in substantial volumes and recyclable for continuous use. There are various leaching methods that can be considered for metal recovery depending on the composition of the source, including in situ leaching, heap leaching, dump leaching as well as agitated leaching. Leaching agents can consist of acids, bases, salts and even water. Most common is H_2SO_4 (diluted and concentrated), for the recovery of CuO and ZnO, sulphides of Cu, Ni and Zn, as well as uranium oxide ore (Gupta and Mukherjee, 1990). Usually V is extracted from ores using an oxidative leaching method with alkali earth-metals (NaCl or $NaCO_3$) at elevated temperatures (850 °C) resulting in the formation of vanadates. These can then be recovered with H_2O followed by the addition of H_2SO_4 to adjust the pH of the solution to between pH = 2 – 3 where $V_2O_5.XH_2O$ subsequently precipitates. The excess of water is thermally removed producing the pure V_2O_5 product (Wiberg *et al.*, 2001). The leaching of metals from secondary sources such as lithium ion batteries (Ku *et al.*, 2016), spent V catalysts and spent Mo and V hydrodesulphurisation catalysts have also been reported where various methods and extractants have been proposed (Zeng and Yong Cheng, 2009).

2.1.5 Recovery of metals from leaching solutions

The metal rich leaching solution can be purified using a variation of purification techniques. Some of these purification methods date back to as early as the 1940's in the case of the large-scale purification of U during the Manhattan Project (US) (Venkatachalam, 1998). There are currently various purification techniques used of which the most common include (Habashi, 2005):

- ion exchange (IE),
- adsorption using activated carbon,
- electrowinning,
- precipitation and
- solvent extraction

All these purification techniques are well developed and have been successfully utilized in the hydrometallurgy industry. Since the use of either of the aforementioned purification methods can be used for the purification of V, a discussion of each is included in this section to motivate the method of choice for this study. The criteria under which the purification methods were evaluated were related to environmental issues and the suitability of the method for the purification or separation of V from other contaminants. The combination of contaminants was again related to the envisaged purification in this study such as the separation of V from Cr.

2.1.5.1 Ion exchange

The reversible interchange of ions between a solution phase and a solid phase, commonly known as ion exchange (IE), dates back to the 1940's (Harland, 1994). The development of a variation of resins and solvents formed the basis for the use of IE in the purification of for example U as well as the separation of other lanthanides (Habashi, 2005). Since the running costs for IE are lower and if well maintained the resin beds can last for long periods of time, IE became preferable to fractional distillation for the separation of rare earth metals and accordingly replaced the latter as purification method (Habashi, 2005). However, IE has various disadvantages including resin fouling while the loading capacity of ion exchange resins have shown to be very low, which implies that ion exchange would be preferable for the purification of metals from aqueous solutions of low metal concentrations (Nguyen and Lee, 2014). While IE has for example been used to remove V and Mo from spent hydroprocessing catalysts bearing high concentrations of Mo and lower concentrations of V (Zeng and Yong Cheng, 2009), it was shown that SX, which is specifically suited for the purification of metals with similar chemical properties (Venkatachalam, 1998), has some advantages over ion exchange (Li *et al.*, 2013) specifically for the purification of V species (Zeng *et al.*, 2009, Nguyen and Lee, 2014, Guo and Shen, 2016, Fan *et al.*, 2013).

2.1.5.2 Precipitation

Purification by precipitation from leach solutions is a well-known and accomplished technique in hydrometallurgy and dates back to the precipitation of copper by iron as early as the sixteenth century (Habashi, 2005). Currently hydroxides are widely used ranging from the precipitation of iron from leaching solutions, Ni and Co from sulphate solutions and the recovery of metals from waste waters. Apart from hydroxides other salts are also used including arsenates and phosphates (Burkin, 2001). In spite of the already wide use, precipitation methods using hydroxides are continuously being developed for example, when studying the effect of magnesia for mixed hydroxide precipitation during the recovery of Ni and Co from Ni-laterite deposits, where Ni and Co were recovered with high purity and low recovery of impurities (Harvey *et al.*, 2011). According to Zeng and Yong Cheng (2009), the main precipitation methods for V from spent catalysts include sulphide precipitation and ammonium salt precipitation. The latter entails the addition of $(NH_4)_2SO_4$ to the leachate after roasting of the aqueous solution at pH = 8.6.

Precipitation is usually inexpensive and straightforward to operate. However, the complete separation of V cannot be achieved (Zeng and Yong Cheng, 2009). Furthermore, the addition of extra chemicals to the already complex metal anion and cation environment (five other impurities in the synthetic solution) will only add to the uncertainties of speciation as well as increasing the environmental impact during purification.

2.1.5.3 Adsorption using activated carbon

The purification of specifically precious metals using activated carbon is well-recognized. For the purification of V, the metalate anions are replaced by the hydroxyl ions on the surface of the activated charcoal using an exchange process (Zeng and Yong Cheng, 2009). To recover the metal, the anions are mixed with suitable alkaline solutions. Although it has been shown that the production of pure V_2O_5 from the sludge generated from the Bayer process is a feasible purification method and could be advantageous to industrial application, the loading capacity of activated charcoal is moderately low when separating V and Mo (Zeng and Yong Cheng, 2009). Hence, purification using activated carbon was not considered for this study.

2.1.5.4 Electrowinning

Electrowinning is a purification method dating back to 1912 where it substituted precipitation of Co from diluted H_2SO_4 leached oxide ores four years before the electrolytic refining process of Zinc (Zn) was developed. Electrolytic refining has also been used in combination with SX for the purification of metals such as indium (In) (Kang *et al.*, 2011) and copper (Cu) (Sueros Velarde *et al.*, 2005). Today, electrolytic refining is used for the purification of V using V and Ta or Mo anodes and cathodes with heated NaCl as the electrolyte solution (Wiberg *et al.*, 2001). Since the combination of SX and ER has shown to be successful it would seem advisable to first purify the desired metal using SX while concentrating the feed generated from the SX process using EW. This latter step however falls beyond the scope of this study.

2.1.5.5 Solvent extraction

SX have been used as a purification technique since the 1940s, where SX replaced IE with the first SX plant introduced in the USA (Mountain Pass) for the purification of rare earths (Habashi, 2005). The purification of Cu using SX dates back to the 1960s, and the process is still being used today (Habashi, 2005). However, the purpose of SX can vary ranging from purification, enrichment, separation to analysis (Venkatachalam, 1998). High purity requirements were set by the atomic energy program for the Manhattan project, where U was purified (< 1 mg/L impurities). Other examples of metals that are recovered commercially using SX include: Beryllium (Be), Cobalt (Co), Cu, Hafnium-Zirconium (Hf/Zr), Molybdenum (Mo), Nickel (Ni), Platinum (Pt) group metals, Thorium (Th), Trans-uranium elements, Tungsten (W), U and V (Venkatachalam, 1998).

2.1.5.5.1 SX process overview

In Figure 2-4, a representation of a typical SX process flow in solvent extraction from the impregnated leaching solution to the regenerated solvent is presented. As discussed previously (Section 2.2), SX can be subdivided into extraction and stripping where both processes are driven by the distribution (D) of a solute between two immiscible phases. The aqueous phase typically contains some sort of aqueous component (loaded leachate), while the organic phase (solvent) typically contains the extractant, modifier and diluent.

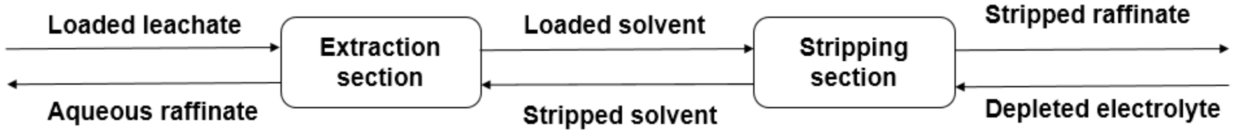

Figure 2-4: A typical process diagram for the leaching, SX, stripping and electrowinning of metals adapted from Cuevas *et al.* (2015) and Venkatachalam (1998)

The aqueous solute can be either an acidic or alkali aqueous metal containing solution – typically the leachate that consists of two or more metals dissolved in a suitable solvent. Distress (agitation) is applied to the system containing the two phases in order for the metal to be transferred or extracted from the aqueous phase into the organic phase. After agitation for a certain time the two phases are allowed to separate. The residual aqueous solution after extraction is called the “raffinate” and the organic phase is typically referred to as the metal loaded organic phase. Once equilibrium between the two phases has been obtained, the metal is distributed between the two phases in a specific ratio known as the distribution coefficient or the distribution ratio which will be discussed in Section 2.2.5. After the metal is extracted into the organic phase the metal is stripped back into an aqueous solution (Section 2.2.2) for further downstream processing. Subsequently the stripped solvent may be recycled to be reused for extraction (Venkatachalam, 1998).

Due to advantages such as ease of operation, fast kinetics and a wide range of possibilities with relatively simple equipment (Kislik, 2012a), this purification method is suitable for various applications. In addition, significant literature has been presented on the suitability of SX for the purification of V making this the choice method to be used in this study.

2.1.5.5.2 MBSX

The primary focus of this study is the purification of V using dispersive SX, however, SX, with its advantages, also has some limitations such as the formation of third phases, the need of large scale equipment (mixer-settlers, column contactors and centrifugal contactors) occupying large spaces and the health hazards due to exploitation of volatile solvents (Meerholz, 2015). Furthermore, as briefly discussed, the combination of leaching-solvent extraction-electrowinning operation for the purification of Ni from low grade ores is a well accomplished combination of techniques, however, impurity (Co) build-up during the regeneration of the electrolyte (EW) for the stripping process (SX) remains a problem (Soldenhoff *et al.*, 2005). This created the opportunity for the development of new technologies to be explored. One such is the use of either flat sheet or hollow fibre membrane (HFM) modules. The effect of impurity build-up can be minimalized by using non dispersive membrane-based solvent extraction (NDMBSX), still attaining the selectivity obtained with dispersive SX (Soldenhoff *et al.*, 2005), with increased surface area. A more in depth discussion on MBSX will be presented in Section 2.2.4, of this literature survey.

2.2 Solvent extraction

In this section a more in depth discussion on SX is presented emphasizing where possible its application on V purification and separation, while elaborating on extraction (Section 2.2.1), stripping (Section 2.2.2), scrubbing (Section 2.2.3) and MBSX (Section 2.1.5.5.2) before concluding with a section on the chemistry of extraction and stripping (Section 2.2.5).

2.2.1 Extraction

2.2.1.1 Extractants

In recent years the extraction of both pentavalent (V(V)) and tetravalent (V(IV)) V with a wide variety of extractants has been reported (Al-Ghouti *et al.*, 2011, Li *et al.*, 2015, Li *et al.*, 2011a, Cheraghi *et al.*, 2015, Navarro *et al.*, 2007, Nguyen and Lee, 2015, Ning *et al.*, 2014, Sun *et al.*, 2016, Tavakoli and Dreisinger, 2014, Zhu *et al.*, 2015, Zeng *et al.*, 2015). As discussed in Section 2.1.1, the speciation of V in aqueous solutions is complex, and accordingly several authors have attempted to determine the multiple possible V species in aqueous solutions (Chagnes *et al.*, 2010, Zhou *et al.*, 2011, Li *et al.*, 2012a). The speciation of metals play an important role in SX due to its direct influence on the affinity of the extractant to the metal which in turn determines the extraction efficiency from the aqueous solution. Thus, the extractant should be chosen based on the speciation of the desired metal which again, depends on the concentration of the metal and the pH of the aqueous solution. Hence a brief introduction is given on the speciation before further discussing the extractants.

Since it is known from speciation studies that only the +5 and +4 oxidation states of V are relevant under typical SX conditions (Zeng and Yong Cheng, 2009), the speciation of V(III) and V(II) in aqueous solutions will be excluded from this discussion. Furthermore, in view of the scope of this dissertation, the discussion will focus mainly on the speciation of V from sulphuric media (V – H_2SO_4 systems) and not for example, chloride media. The reason for choosing H_2SO_4 as the aqueous component will be discussed in Section 2.2.1.4. The role of important V anions, cations as well as neutral and solid species relevant to SX can be summarized as follows:

When Yang *et al.* (2015) investigated the speciation of V(V) and V(IV) in sulphate systems in the pH range of 0 – 4, they found that the speciation distribution of V(V) is considerably more complex than that of V(IV). In pH solutions ranging from 2 – 4, V(IV) exists solely in the form of the neutral $VOSO_4$. When the pH decreases to 0, the fraction of the neutral species decreases slightly with the amount of the vanadyl cation (VO^{2+}) increasing with the decrease in the pH of the solution (Yang *et al.*, 2015). For V(V), the fractions of anionic species $VO_2SO_4^-$, $V_{10}O_{27}OH^{5-}$ and $V_{10}O_{26}(OH)_2^{4-}$ are higher in higher pH solutions (2 – 4). In accordance with Wiberg *et al.* (2001) and Zhou *et al.* (2011) the fraction of the pervanadyl cation (VO_2^+) increases significantly as the pH decreases. The formation of V_2O_5 in solutions of pH > 2 was confirmed by Yang *et al.* (2015). According to Zeng and Cheng (2009), both V(IV) and V(V) species can be present at a low pH, while only V(V) is present in solutions of higher pH values. They also reported on the presence of the polyanions $V_{10}O_{28}^{6-}$ and $V_4O_{12}^{4-}$, which can be partially protonated while existing over the entire pH range of 2 – 12. Additionally, V is known to polymerize which, according to Zeng and Yong Cheng (2009), is dependent on the concentration of the transition metal and the pH of the solution. Finally, in accordance with previous findings discussed above, V(V) cations are dominant in acidic solutions (pH < 2), whereas polynuclear anionic species dominate in solutions of a pH ranging from 2 – 9. The presence of mononuclear V anions are evident in solutions of pH > 9 (Zeng and Yong Cheng, 2009). However, since only aqueous solution of pH values below 4 were considered in this SX study only the V species present in the applicable pH ranges were included in the results and discussion sections of this dissertation.

With a deeper understanding of the solution chemistry of V, the extractants required for optimal extraction efficiency are briefly discussed. Venkatachalam (1998) listed a few requirements that should be considered when selecting extractants, including selectivity, ease of stripping, solubility in aqueous solutions (which should be low), differences in the density compared to water (low viscosities with fairly high interfacial tensions), purity, cost, formation of third phases/emulsions, high compatibility with the diluent, high loading isotherms and high solubility’s both in aromatic and aliphatic diluents. Kislik (2012a) added additional requirements that extractants should adhere to including high extraction and stripping reaction rates, low environmental impact and high recyclability (Kislik, 2012a).

Generally, extractants can be subdivided into four categories:

- organic acids,
- solvating extractants,
- ion pair extractants (anion exchangers) and
- chelating extractants

In the following sections, these four types will be further discussed in terms of their properties as well as advantages and disadvantages thereby demonstrating the suitability of each of the extractants from the four categories for the extraction of V.

2.2.1.1.1 Organic acids

These extractants include carboxylic acids, phosphorus acids, phosphoric acids (e.g. D2EHPA) (Li *et al.*, 2012a), phosphonic acids (e.g. PC88A), phosphinic acids (e.g. Cyanex 272) (Li *et al.*, 2012a) and dithiophosphininc acids (e.g. Cyanex 301). While several studies have been conducted investigating the extraction of V with organic acids, three examples will be briefly discussed in this section.

Fast extraction kinetics were reported by Zhu *et al.* (2015) during the separation of Mo and V from impurities using Cyphos IL 101 (trihexyl(tetradecyl)phosponium chloride) with the industrial solvent ShellSol A150. The optimal pH range for the extraction of V was 1.8 and 0.5 for the effective separation of Mo and V, while the extraction equilibrium was reached after only 0.5 minutes (Zhu *et al.*, 2015).

Cheraghi *et al.* (2015) investigated the extraction of V(V) using D2EHPA and TBP synergistically. The optimum extraction was achieved using an extractant to metal ratio of 1:1, where the association of VO^{2+} metal cations with the P-O-H functional group of D2EHPA via a cationic exchange extraction mechanism was observed (Cheraghi *et al.*, 2015).

Chen *et al.* (2015) designed an extraction process for the recovery of V from a low grade magnetite ore using D2EHPA (di-(2-ethylhexyl)phosphate), and tri-n-butylphsophate (TBP) with kerosene as the solvent. The leaching solution was HCl based and contained low concentrations of V and high concentrations of Fe and other impurities. According to their results, the initial pH value of the solution and the phase ratio had a significant influence on the extraction efficiency of

V. Under optimum conditions a selective extraction of V was obtained with a recovery of 85.5 % (Chen *et al.*, 2015).

While fast extraction kinetics are attainable using acidic extractants, the selectivity of these extractants is for example lower than that obtained with oxime extractants. Furthermore, the undesirable formation of emulsions from basic solutions has been observed (Kislik, 2012e).

2.2.1.1.2 Solvating extractants

These extractants are typically neutral. The extraction is usually attained by stabilizing the metal anion or neutral species with a weakly hydrated sphere to create a more favourable solvating environment. Examples of these include certain phosphine oxides, ketones and certain amines (Wilson *et al*., 2014).

As mentioned previously Zhou *et al.* (2011) showed that V(IV) can be present in the neutral $VOSO_{4(aq)}$ species when in an H_2SO_4 aqueous environment and accordingly, solvating extractants such as tributyl phosphate (TBP) could be considered (Zhou *et al.*, 2011). Solvating extractants have also been used as co-extractants during synergistic extractions or as phase modifiers (Tasker *et al.*, 2003). Although these extractants display fast extraction and stripping kinetics (Kislik (2012e), these extractants are not that selective, and since the synthetic solution in this study contains many impurities, the requirement of high selectivity of the extractant is crucial.

2.2.1.1.3 Ion pair extractants

An example of ion pair extractants are the amine extractants which have been successfully used for the selective extraction from both basic as well as acidic aqueous feed solutions. According to Section 2.2.1.2 and Section 2.2.1.3, the diluents and modifiers influence the stability of both the amine-acid, as well as the amine-metal complexes. The amine extractants can be classified as either primary **(RNH_3^+)**, secondary **($R_2NH_2^+$)** tertiary **(R_3NH^+)** or quaternary amines **(R_4N^+)** (Kislik, 2012b). A few examples of each type are presented in Table 2-2.

It is clear from literature (and Table 2-2) that there is a wide variety of amines available to choose from, which is one of their advantages (Kislik (2012e). The extraction rate using amines as extractants is fast while the selectivity increases in the order: tertiary/quaternary > primary/secondary (Kim *et al.*, 2015). It is accordingly sensible to investigate extraction with either quaternary or tertiary amines. When Ning *et al.* (2014) investigated the effect of the primary amine LK-N21 on the extraction of V(V) and Cr(VI), they found that extractant concentrations above 15 % v/v resulted in a decreased extraction due to the association of the extractant with other extractant molecules via H - bonding that could result in slower phase separation and crud formation (Ning *et al.*, 2014). Based on additional lower selectivities (Kim *et al.*, 2015) and phase separations that could be problematic (Ning *et al.*, 2014), the suitability of primary amines for V extraction is questionable. Additionally, Kim *et al.* (2015) reported that the extraction with tertiary amines, specifically Alamine 336, is higher than that of quaternary amines making these potentially more advantageous for industrial applications (Kim *et al.*, 2015). The suitability of Alamine 336 for the extraction of V(V) from sulphate solutions was confirmed by Kurbatova *et al.* (2015). In view of these studies it seems clear that Alamine 336 should be included.

Table 2-2: Examples of amine ion pair extractants and their structures

Extractant	Example	Side chains	References
Primary **RNH_2**	Primene 81R	R = $C_{12-14}H_{26-30}$	(Lozano, 2003, Navarro *et al.*, 2007, Ning *et al.*, 2014)
	Primene JMT	R = $C_{16-22}H_{34-46}$	
Secondary	Amberlite	$R_1 = C_{12}H_{25}$	(Navarro *et al.*, 2007)
	Adogen 283	$R_1 = R_2 = C_8H_{17}$	
Tertiary **$R_1R_2R_3N$**	Alamine 336	R = C_8H_{17} and $C_{10}H_{21}$ (2:1)	(Kurbatova *et al.*, 2015, Lozano, 2003, Navarro *et al.*, 2007)
	Alamine 308	R = C_8H_{17}	
	Alamine 304	R = $C_{12}H_{25}$	
Quaternary **$R^1R^2N(CH_3)^+Cl^-$**	Aliquat 336	R = C_8H_{17} and $C_{10}H_{21}$ (2:1)	(Navarro *et al.*, 2007)

2.2.1.1.4 Chelating extractants

Presently, chelating extractants are commonly used for the recovery of for example Cu, Ni and Pd. These extractants can readily extract from both acidic and basic leaching solutions (Kislik, 2012e), while showing higher selectivities than ion exchange or organic acid extractants, albeit at the cost of slower extraction kinetics. While phase disengagement is unproblematic with good phase separation, the synthesis of the extractants can be difficult (Kislik, 2012e). An example of a typical phenolic oxime chelating extractant is shown in Figure 2-5.

Two classes of oxime extractants, i.e. aldoximes and ketoximes, are suitable for metal cation extractions. While aldoximes are strong extractants with rapid extraction kinetics, the stripping from aldoximes is challenging. Ketoximes, which have a moderate strength and hence moderate extraction kinetics, display good stripping ability. However, both extractants are considered strong enough to selectively extract the preferential metal in the presence of ferric iron (Fe(III)) cations. Since V naturally co-exists with Fe (Section 2.1.1), Fe(III) was added to the synthetic solution used in this study, making the oximes possibly suitable for this study.

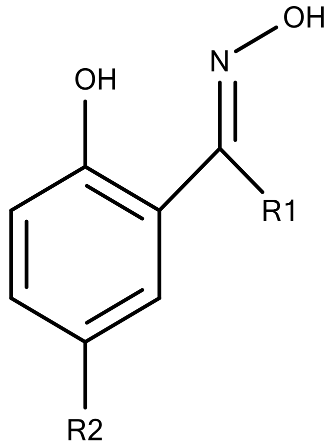

Figure 2-5: The general structure of phenolic oxime extractants (Kordosky, 2002, Wilson *et al.*, 2014)

According to a review done by Kordosky (2002), the strength of aldoximes and ketoximes are comparable and the author established that although the extractive strength of ketoximes are lower than that of aldoximes, stripping is effective, while the selectivity toward Cu and Fe is high. In addition, the extraction kinetics for copper recovery are high, while fast phase separation is attainable with excellent stability and low crud formation. In Table 2-3, a few examples of both are presented.

While it has been shown that oxime extractants may undergo hydrolysis when present in low pH solutions, the presence of $–NR_3$ prevents hydrolysis if the solubility of the oxime in water is low enough. Accordingly, the resistance to hydrolysis is higher for ketoximes than for aldoximes (Wilson *et al.*, 2014). In fact, phenolic ketoximes such as LIX-84-IC are less susceptible to hydrolysis than aliphatic hydroxyoximes such as LIX 63. As far as the reaction mechanism for oxime extractants is concerned, the extraction takes place via a cationic exchange mechanism which will be discussed in more depth in Section 2.2.5. The previously discussed predominance of V cations in the acidic range of V - H_2SO_4 systems confirms the suitability of oxime extractants for V extraction. Finally, the presence of both V(V) and V(IV) cations in acidic and basic media confirm the specific suitability of the oxime based extractant, LIX-84-IC.

Table 2-3: Examples of chelating extractants and structures (Kislik, 2012e, Kordosky, 2002)

Oxime type	Example	Side chain*	
Ketoxime	LIX 65	C_6H_5	$C_{12}H_{25}$
Ketoxime	LIX 65N	C_6H_5	C_9H_{19}
Ketoxime	SME 529 & LIX-84-	CH_3	C_9H_{19}
Aldoxime	LIX860-I, LIX 622	H	$C_{12}H_{25}$
Aldoxime	P1, LIX 860N-I	H	C_9H_{19}

* R1 and R2 according to Figure 2-5

2.2.1.2 Diluents

Diluents are typically volatile aromatic or aliphatic hydrocarbons or mixtures thereof and are added to the organic mixture primarily to decrease the density and viscosity of the extractants and although it can influence the extraction it does not necessarily contribute to the extraction itself (Venkatachalam, 1998). According to Habashi (1999), the diluents can affect the polymerization of the extractant. Similarly, there is sometimes a correlation between the solvent and the dielectric constant of the diluent. For instance, when an extraction reaction follows a cationic exchange mechanism, diluents with lower dielectric constants produce higher extraction efficiencies, which is attributed to the ability of the diluents to favour polymerization of the extractant by hydrogen bonding (Habashi, 1999). This was confirmed in a recent study conducted by El-Nadi (2010) when investigating the extraction of praseodymium and samarium from acidic media using Cyanex 923. An increase in the dielectric constant of the diluent resulted in a decrease in extraction while the separation efficiency remained constant. Furthermore, it was shown that the extraction kinetics and selectivity can be influenced by the nature of the diluent – solvent system (Kislik, 2012a).

Similar to the extractants, the diluents should also comply with certain requirements such as a compatibility with the extractant and the extractant – metal complex (high solubility of the extractant), the avoidance of emulsion or crud formation with low density and viscosity, affordability, ease of access, the minor release of volatiles, a high stability and no negative effect on the extraction and stripping chemistry (Kislik, 2012e). Mishra *et al.* (2011) investigated the extraction of Fe(III) from an HCl medium using the quaternary amine Aliquat 336 and found that the extraction efficiency increased as the dielectric constants of the diluents increased in the order cyclohexane < xylene < benzene < toluene < diphenyl ether < diethyl ether < hexanol < butanol < cyclohexanol. In this series kerosene, which is a mixture of aromatic and aliphatic substituents, gave contradictory results as to what had been predicted (Mishra *et al.*, 2011). Finally, Habashi (1999) found that the effect of the diluents on the extraction using specifically amines is highly complex due to the polymerization of the amines which can differ depending on the type and structure of the amine. Accordingly, the exact effect of the diluent on the extraction efficiency is not clear in view of the complex interactions between the diluents and the extractants and its possible influence on the polymerization of the extractants. According to literature, further work is required to further elucidate this effect and gain a deeper understanding of diluent chemistry.

Diluents can be categorized into aliphatic or aromatic ketones and alcohols. According to Lofstrom-Engdahl *et al.* (2010), aliphatic diluents can be sub-divided according to their distribution ratio or separation factor and their simple management and production.

2.2.1.3 Modifiers

As previously discussed the formation of a third phase in extraction remains a challenge adding to the SX process complexity and cost. According to Habashi (1999) extractants, particularly tertiary amines, form insoluble salts when interacting with acidic aqueous solutions, which results in the formation of a third phase that can be in either a liquid or solid form. This formation of third phases can be avoided by the addition of a suitable modifier (Habashi, 1999). For example, Habashi (1999) found that the addition of 3 % alcohol was enough to avoid the formation of a third phase.

During SX, modifiers that are soluble in the diluent can donate and or accept a hydrogen bond and typically contain alcohols, esters or ketone functional groups. Modifiers are also known to increase the solubility of amine extractants and amine extractant metal complexes in the organic phase (Al-Siddique *et al.*, 1980). This was confirmed by Lozano (2003) who investigated the extraction efficiencies of a primary (Primene 81R) and a tertiary amine (Alamine 336) finding that a modifier was necessary to avoid third phases and crud formation.

Modifiers were also shown to assist in Cu stripping from oximes with lower acid concentrations (Kislik, 2012e). However, a study conducted by Chagnes *et al.* (2012) showed that a structural change in the modifier can result in the degradation of the extractant and accordingly, influence the extraction efficiency. Hence it is important for the modifier to not only be compatible with the solvent system, but also be stable in the specific environment. V(V) for example, can oxidize the modifier 1 – tridecanol, which can result in the formation of free radicals causing the extractant, Alamine 336, to degrade. Furthermore, V(V) and molecular O_2 can oxidize the extractant leading to the conversion of the extractant from tri-n-octylamine to n-octylamine (Chagnes *et al.*, 2012). The authors concluded that the presence of alcohols with long aliphatic chains as phase modifiers instead of 1-tridecanol may lower the degradation rate of the extraction solvent. Since it has been shown that V(V) can oxidize components in the solvent, it is thus wise to consider using V(IV) rather that V(V) to avoid the oxidation of the modifier or extractant.

2.2.1.4 Acids

According to Habashi (1999) who investigated the extraction efficiency of H_2SO_4 using the tertiary amine Alamine 336, found that acids can also be extracted into the organic phase along with the metal species, which should hence always be considered when extracting a metal solution from an acidic environment. While the extraction of H_2SO_4 from ketones, ethers and esters has not been reported as yet, it is possible with alcohols, which extract HNO_3 and small amounts of HCl. The extraction of acids also occurs when using amines and organophosphorus extracts. Due to the availability of species distribution diagrams of both V(IV) and V(V) in H_2SO_4 systems (Zhou *et al.*, 2011), and the fact that the VRFB electrolyte is H_2SO_4 based, sulphuric acid was chosen as the acid in this study.

2.2.1.5 Phase ratio

The effect of the phase ratio plays a significant role in extraction. While low O/A volume phase ratios can be advantageous from an economic perspective, they are undesirable due to possible solvent losses. During the extraction of metals, the O/A volume ratio's change, which can be attributed both to the miscibility of the two phases and the migration of metals from one phase to the other. However, this effect can be reduced by pre-conditioning the solvent (Habashi, 1999).

2.2.2 Stripping

The extraction of metal cations or anions from an aqueous phase by a water insoluble extractant to form neutral organic soluble complexes is a reversible chemical reaction (Kislik, 2012c). While the principles for stripping are similar to those of extraction (Figure 2-6), the distribution ratio's should ideally be less than unity (Kislik, 2012c).

Usually traces of the extracted metal will remain in the loaded organic after stripping where these trace amounts result in impurity build-up and finally lower extraction efficiencies in the first stages of extraction. This problem can be reduced using one of two approaches. Firstly, the solvent can be treated with a more aggressive stripping agent, removing the impurities for optimal conditions to be maintained using a side stream in the process to remove the stripped impurities, or, secondly the impurities can be allowed to build up in the organic phase before regenerating the solvent using an additional batch extraction step. However, since the regeneration of the organic phase can be a costly process, this approach is only suitable if the value of the impurities or product is high enough (Kislik, 2012d).

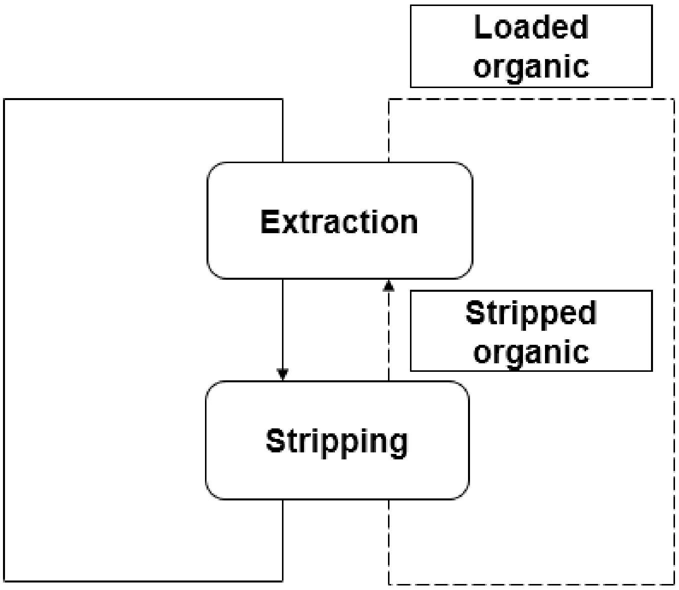

Figure 2-6: A typical process diagram for the regeneration of the extractant using SX (Venkatachalam, 1998)

2.2.3 Scrubbing

In order to further remove impurities from the system, scrubbing is commonly used which uses the same principle as extraction, i.e. to transfer unwanted extracted components in this case to the scrubbing raffinate. While this could result in the loss of desired components from the extract, the scrub raffinate is reused as part of the aqueous feed in first stage extractions, in order to recover the minor loss in desired components from the scrubbing solution (Kislik, 2012b).

2.2.4 MBSX

As discussed, the aim of the study was to develop separation and or purification techniques via both dispersive and non-dispersive solvent extraction. While batch shake out tests were used for the dispersive SX, MBSX was investigated as the non-dispersive SX technique. The general principles and theory concerning MBSX can be summarised as follows.

Membrane technology is currently used in a wide range of separation processes due to its various advantages such as continuous separation, low energy requirements, integration with other separation processes (hybrid processing), easier industrial applications and the ease of membrane property alterations (Mulder, 1996). These advantages have to be weighed against their disadvantages including concentration polarization and membrane fouling (which could be an advantage depending on the process), limited lifespans, low selectivity and flux (Mulder, 1996). Membranes can be categorized according to their membrane configurations including tubular, plate-and-frame, spiral-wound, capillary and HFMs, which should be selected based on the application of the membrane process. For example, HF modules are typically used in seawater desalinisation, gas separation and pervaporation (Mulder, 1996).

Research conducted during the 1960’s on the reverse osmosis membranes created the opportunity for the development of HFM technology. There are important advantages that HFM’s hold over flat sheet (FS) or tubular membranes, including the high efficiency and productivity attainable due to the high packing density and surface area leading to exceptional mass-transfer capabilities, which in turn has resulted in several novel applications (Tasker *et al.*, 2003, Moch, 1991). HFM’s are also self-supporting, which simplifies the use of HFM technology on industrial scale. For example, the hardware required using FS membranes for the operation of ultrafiltration or reverse osmosis are diverse and must be assembled whereas HFMs can simply fit into a tube. Finally, high purity products are attainable using HFM technology (Moch, 1991). However, like all membrane processes HF modules are susceptible to fouling and clogging (pore plugging), which is attributed to the small passages for the matter to transfer through as well as the small inside diameters of the fibres (Moch, 1991). To remove this clogging these HF Modules require laborious cleaning processes (Mulder, 1996). Fouling can however be reduced by including a pre-treatment step before actual operation.

For the application of this study, Manuel *et al.* (1997) investigated the extraction efficiency of a supported HFLM on the extraction of V(V). The authors reported the successful concentration and separation using the quaternary amine extractant Aliquat 336. Additionally, Rout and Sarangi (2014) conducted a comparative study investigating the extraction of V(V) from chloride solutions using the oxime extractant LIX-84-I as the extractant and carrier for mixer-settler and HFLM extractions respectively. Higher recovery of V(V) was obtained in the HF studies and no indication of third phases were observed compared to the emulsions and crud formation observed in the mixer-settler studies (Rout and Sarangi, 2014).

Based on the advantages that HFMs hold and the available literature for both amine and oxime extractants, the HFM was selected as the most suitable for the investigation in this study.

2.2.5 Extraction and stripping equilibria

Based on the conclusions drawn from Section 2.2.1, the most suitable extractants for the purification of V(IV) were the ion exchange extractants LIX-84-IC and Alamine 336. In this section a review of the most important principles and calculations involved in solvent extraction will be provided, followed by a discussion on the general metal extraction and stripping chemistry found in oxime and amine based extraction.

Extraction efficiency can be measured by the extraction percentage (E). If the mass of the solute in the aqueous phase is $\mathbf{M_i}$ and the mass after extraction of that same solute in the other phase is $\mathbf{M_f}$, the following equation can be deduced (Habashi, 1999)

$$\mathbf{E = \frac{(M_i - M_f)/V_{org}}{M_f/V_{aq.}}}$$

where **V** is the volumes of the aqueous and organic phases respectively. Hence,

$$\mathbf{\frac{M_f}{M_i} = \frac{V_{aq.}}{V_{org.}E+V_{aq.}}}$$

And,

$$\mathbf{\%\ Extraction = \frac{(M_i - M_f)}{M_i}\ x\ 100\ \%}$$

The efficiency of an extractant can be evaluated using the distribution coefficient $\mathbf{(D_x)}$ and the separation factor (β).

$$\mathbf{D_x = \frac{[Metal\ x]org}{[Metal\ x]aq}}$$

Accordingly, the distribution coefficient refers to the distribution of the solute between two immiscible phases. Alternatively, the selectivity of an extractant can be measured using the separation factor, which is expressed as the ratio of the distribution coefficients of two metals x and y.

$$\boldsymbol{\beta}_{\frac{x}{y}} = \frac{\mathbf{D}_x}{\mathbf{D_y}}$$

High separation factors imply highly selective extractants. An increase in the distribution constant coefficient is expected once the extractant concentration is increased.

The purity (∝) of

$$\% \text{ purity } (\propto) = \frac{[V(IV)]}{\Sigma [M_i]} \times 100 \%$$

$$\% \text{ yield } (\propto) = \frac{[V(IV)]_{product}}{[V(IV)]_{feed}} \times 100 \%$$

2.2.5.1 Metal cation exchangers (oximes)

When extracting with oximes an ionisable hydrogen on the extractant (LH) is replaced by a metal cation (M), giving rise to the metal-cation exchange reaction (Wilson *et al.*, 2014).

$$nLH_{(organic)} + M^{n+}{}_{(aqueous)} = LnM_{(organic)} + nH^{+}{}_{(aqueous)}$$

Metal cation extractants can be classified as either strong or weak (Wilson *et al.*, 2014). The strength of the extractant is determined by measuring the ability of the extractant to load 50 % of the metal in the aqueous solution at a certain pH value ($pH_{1/2}$). Strong extractants can, for instance, load metals from low pH solutions whereas weak extractants load metals from pH solutions that are more basic. The disadvantage of weak extractants however is the additional step required for the required conversion of the extractant to associate with the desired metal cation. The interest in phenolic oximes arises from the nature of their coordination chemistry (Wilson *et al.*, 2014). The combination of leaching, extracting with, and stripping Cu(II) from oxime reagents with electrolytic refining was shown to be highly efficient with excellent material balances, while back extraction is attained using acidic strippants:

$$LnM + HX = MX + nLH$$

Ni(II) was selectively stripped with LIX-84-IC from a multi-metal loaded organic using a constant pH (Wilson *et al.*, 2014). To determine the reaction stoichiometry, a method known as slope analysis can be used to determine the ratio of the extracted metal to the amount of protons involved as well as the amount of extractants participating. Considering the general metal cation exchange reaction mechanism provided above, the equilibrium constant can be derived as follows,

$$\mathbf{K= \frac{[L_nM].[H^+]^n}{[M^{n+}].[LH]^n}}$$

After taking the logarithms,

$$\mathbf{logK = log[L_nM] + nlog[H^+] - log[M^{n+}] - nlog[LH]}$$

and rearrangement the above equation becomes,

$$\mathbf{log\frac{[L_nM]}{[M^{n+}]} = LogD = logK + nlog[LH] + npH}$$

Therefore, by plotting the LogD of the desired metal against the pH while using a constant extractant concentration, or by plotting the LogD against the extractant concentration at a constant pH the two ratios can be obtained. For V, the stoichiometry of the extractant extraction mechanism using cationic exchange extractants has been investigated by Li *et al.* (2012a), where Kislik (2012c) has shown that certain assumptions have to be made before this method can be employed.

2.2.5.2 Metal anion exchangers (amines)

Leaching processes such as oxidative leaching generates metalate anions $(MX_x)^{n-}$ (Wilson *et al.*, 2014) where the cationic element of the ion pair is produced by the protonation of the extractant. It has been shown that the hydration sphere of bigger metallic anions with smaller ionic charges makes it easier to remove them compared to metallic anions with higher ionic charges and accordingly, the selective extraction of metalate anions is obtainable when the metal in its ionic form is stable, avoiding the loss of anions which would generate lower charged, easier extractable metalate anions (Tasker *et al.*, 2003). Hence, ion pair extractants are based on the association of positively charged extractants with large metalate anions where the extraction of larger molecules with lower charges is favoured.

Tertiary amines (R_3N) are usually protonated by a suitable acid and coordinate with the metalate cation resulting in two possible ion-pairing reactions depending on whether the acid is protonated.

$$\mathbf{R_3N + HA = R_3NH^+\ A^-}$$

$$\mathbf{R_3NH^+\ A^- + M^- = R_3NH + A^-}$$

Again, the extraction efficiency depends on the extent to which the metal ions can form anionic complexes with the aqueous medium known as the speciation effect and will hence be pH dependant.

As previously mentioned the stripping from tertiary amines is more convenient than that of quaternary amines and can be accomplished by the deprotonation of the amine extractant with an alkali or base.

$$\mathbf{R_3NH^+ M^- + OH^- = R_3N + M^- + H_2O}$$

Various studies have successfully demonstrated the suitability of amines as extractants for V (Sun *et al.*, 2016, Ning *et al.*, 2014, He *et al.*, 2007, Sahu *et al.*, 2013, Chagnes *et al.*, 2010, Kim *et al.*, 2015, Kurbatova *et al.*, 2015, Yang *et al.*, 2015). Similarly studies were conducted showing the suitability of stripping agents such as, NH_4OH (He *et al.*, 2007, Sahu *et al.*, 2013, El-Nadi *et al.*, 2009), NaOH (Zhao *et al.*, 2015) and H_2SO_4 (Kim *et al.*, 2015).

2.3 Conclusion

Although often at low concentrations, V is found in more than 50 different minerals. Due to its four different oxidation states (V^{5+}, V^{4+}, V^{3+} and V^{2+}) V has complex speciation. However, the variety of applications of V created the opportunity for the development of novel recovery processes. Currently V is recovered via a hydrometallurgical route or a pyrometallurgical route from i) U – containing ores using SX, ii) Bayer sludge which is generated by the Bayer process and iii) Fe – ore (magnetite). Based on its advantages, a hydrometallurgical route was identified as the most suitable route for V purification for this research. From the various hydrometallurgical purification methods considered for this research, including i) IE, ii) precipitation, iii) adsorption using activated carbon, iv) electrowinning and v) SX, SX was selected as the most suitable technique for the purification of V for this study. According to literature, the amine based extractants and oxime based extractants showed to be most promising V extractants with Alamine 336 and LIX-84-IC as most suitable in their categories. Various operating variables should be considered during extraction including the diluent, the modifier, the O/A phase ratio and the type of acid, where H_2SO_4 was found to be most suitable. While regeneration of the extractant would have advantages, the process can be expensive.

A more recent purification technique used for the recovery of valuable metals is MBSX, which might help overcome typical SX shortcomings such as third phase formation. While HFM’s have shown to be advantageous due to excellent mass transfer capabilities, disadvantages such as membrane fouling and clogging remain a challenge. Available literature entailing the successful purification of V using MBSX confirm the suitability of this approach for this study.

2.4 References

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CHAPTER 3 – THE PURIFICATION OF $VOSO_4.5H_2O$ WITH LIX-84-IC USING SX AND MBSX

3.1 Introduction

V, which is a transition metal found in over fifty different mineral ores, has a high melting point and is mainly used in the steel industry due to its high corrosion resistance at low temperatures (Moskalyk and Alfantazi, 2003). South Africa is one of four major producers of V contributing to nearly 24 % of the global V supply (Polyak, 2016b). Magnetite (V-containing ores) found in South Africa typically contains 1.4 – 1.9 % V_2O_5, as shown in Table 2-1 (Rohrman, 1985) (Section 2.1.2). It has been reported that several reducing agents can be used to reduce pentavalent V to tetravalent V and most of these reduction reactions take place in acidic media (Bobtelsky and Glasner, 1942). While steel remains the primary application of V, an increase in V demand, due to its use in the VRFB and numerous other applications (Gummow, 2011, Chu *et al.*, 2017, Palacios *et al.*, 2016, Cuff, 1996, Lyons, 2010, Moskalyk and Alfantazi, 2003), can be expected. According to (Li *et al.*, 2013), the recovery of V using SX is preferred over ion exchange. For example, for the VO_2^+ species, which is more stable at pH ≤ 2, cationic extractants such as di-(2-ethylhexyl)phosphoric acid (D2EHPA), bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), 2-ethylexyl phosphonic acid mono-2-ethexyl ester (PC88A) and 5,8-diethyl-7-hidroxydodecane-6-oxime (LIX 63) have been shown to be suitable. At pH ≤ 2, the VO_2^+ species hydrolyse forming oxyanions (Zeng and Yong Cheng, 2009), which can be extracted with ion exchange-complex forming extractants such as trioctylamine (Alamine 336) and methyl-trioctylammonium chloride (Aliquat 336) (Wilson *et al.*, 2014). While several SX methods have been presented for the purification of V(V), limited information is available for V(IV), which in fact has a higher solubility than V(V) and as previously mentioned, is also present in the VRFB.

In this study the extraction, separation and recovery of V(IV) from electrolyte solutions containing some impurities commonly found in the South African V containing ore described above (Ni(II), Cr(VI), Al(III), Co(II) and Fe(III)) was investigated. Several experimental parameters such as the type and concentration of the extractant, the concentration of the H_2SO_4, the type of diluent, the contact time and the O/A volume ratio were investigated. Extractants that were evaluated included Alamine 336, Aliquat 336, D2EHPA, Dio-PA, Cyanex 301, Cyanex 923, Cyanex 272 and LIX-84-IC with 1-octanol as phase modifier. After optimizing the extraction, suitable stripping agents (HCl, H_2SO_4 and NaOH) were investigated to recover the extracted metal from the loaded organic phase. Even though various studies have focussed on the purification of V, the combination of V(IV) with these specific impurities using various extractants and acids has not been reported as yet.

3.2 Experimental

3.2.1 Material, reagents and solutions

The commercial extractants D2EHPA, Alamine 336 (trioctylamine), Aliquat 336 (methyltrioctylammoniumchloride), Cyanex 301 (Bis(2,4,4-trimethylpentyl) di-thiophosphinic acid), Cyanex 272 and Cyanex 923 (mixture of various 4 trialkyl-phosphine oxides) used in the screening experiment were all supplied by Sigma- Aldrich, while LIX-84-IC (2-hydroxy-5-nonyl acetophenoneoxime) was supplied by BASF South Africa and used without further purification. 1-Octanol (Sigma-Aldrich), was used as phase modifier to prevent emulsion or third phase formation (Al-Siddique *et al.*, 1980). The purities and suppliers of the diluents (used without further purification) and the metal salts in the synthetic solution used are listed in Table 3-1 and Table 3-2 respectively. Aqueous solutions for the extraction and stripping experiments were prepared with deionized water and H_2SO_4 (98 %) or HCl (32 %), both supplied by Labchem. The NaOH (25 wt. %) used in the stripping experiment was supplied by Labchem.

Table 3-1: Sources and purities of diluents used in this study

Diluent	Purity	Supplier
Kerosene	> 95.00 %	Sigma-Aldrich
Cyclohexane	99 %	Sigma-Aldrich
n-Hexane	97 %	HiPerSolv
Heptane	99 %	Sigma-Aldrich
Toluene	99.8 %	Rochelle Chemicals
Xylene	99 %	Rochelle Chemicals
ShellSol 2325 (IS)	NS*	ChemQuest
ShellSol D70 (IS)	NS*	ChemQuest

* NS = Not specified

Table 3-2: Sources and purities of metal salts for the synthetic solutions

Composition	Purity	Supplier	Concentration (g/L)
$Fe_2(SO_4)_3$	70 %	Saarchem	0.1
$Al_2(SO_4)_3$	100 %	Pal Chemicals	0.1
$Co_2(SO_4)_3.7H_2O$	99 %	Sigma-Aldrich	0.1
$NiSO_4.6H_2O$	99 %	Riedel-de haen	0.1
$K_2Cr_rO_7$	99.5 %	Minema	0.1
$VOSO_4.5H_2O$	*	Merck	0.1

* Purity is unknown

Table 3-3: The features and specifications of the membrane used in this study (Adapted from (Meerholz, 2015))

Features	Specification
Module length (cm)	20.32
Module diameter (cm)	6.35
Housing material	Polypropylene
Fibre material	Polypropylene
Potting material	Polyethylene
Number of fibres	~ 10 000
Fibre length (cm)	15.6
Fibre diameter (µm)	240
Fibre wall thickness (µm)	30
Pore size (µm)	0.03
Approximate surface area (m^2)	1.4

3.2.2 Extraction

Extraction experiments were conducted by mechanically shaking (360 rpm) the organic solvent (diluent, extractant and 5 % (v/v) 1-octanol) and aqueous (H_2O, H_2SO_4 and metal salts) phase in a shaking incubator at 25 °C unless indicated otherwise. Since certain extractants with higher viscosities may prolong the required time for sufficient extraction, all extractions (except when investigating the effect of contact time) were done for 60 minutes. The O/A volume ratio was kept at 1 unless stated otherwise while 5 % (v/v) 1-octanol was used as phase modifier (Al-Siddique *et al.*, 1980). After separating the organic and aqueous phases in separating funnels, the samples were diluted before measuring the concentrations of the V(IV) and impurities in the aqueous phase before and after extraction using ICP-OES (Thermo-Scientific iCAD 6000 Series ICP-OES, using iTEVA software and standard solutions from De Bruyn Spectroscopics). The metal concentration in the loaded organic phase was calculated from the differences between the metal concentration in the feed phase before and after extraction using a mass balance (Zhang *et al.*, 1996) and the distribution constant (D) was determined from the ratio of the metal concentrations in the organic- and aqueous phases respectively (Venkatachalam, 1998).

3.2.3 Stripping

For the stripping studies three stripping agents HCl, H_2SO_4 and NaOH were investigated. The loaded organic and stripping phases were shaken at 360 rpm (shaking incubator) for 60 min. at 25 °C. The concentration of V(IV) and other impurities in the aqueous phase before and after extraction was again determined using ICP-OES from which the metal concentration in the loaded organic phase was calculated (Zhang *et al.*, 1996).

3.2.4 MBSX

A Liqui-cel® 2.5x8 HFM (Figure 3-1) was used for the MBSX studies conducted in this research. This membrane module was subsequently integrated in manually controlled (Figure 3-2) and an automated MBSX.

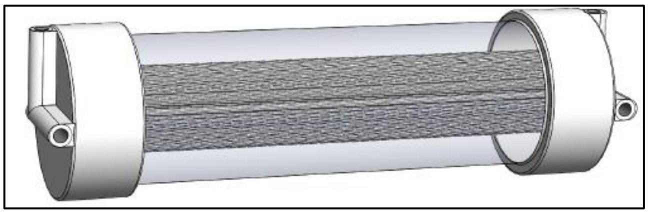

Figure 3-1: A schematic illustration of the Liqui-cel 2.5x8 HFM used for the extraction studies in this paper (Meerholz, 2015)

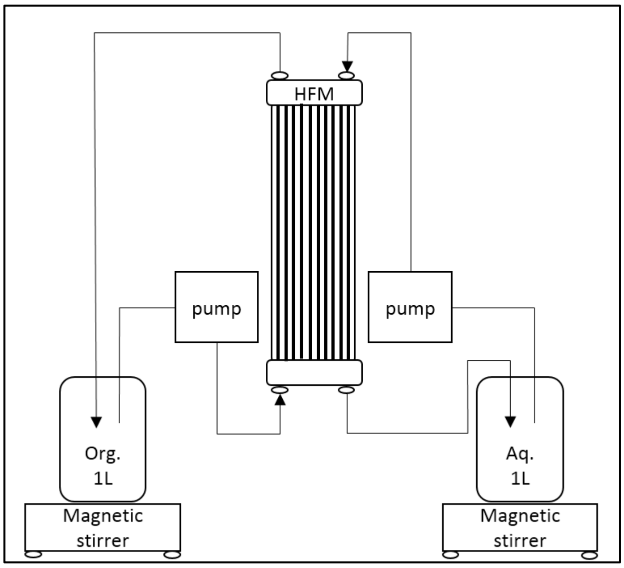

Figure 3-2: **Schematic presentation of a manually controlled counter current MBSX setup adapted from Meerholz (Meerholz, 2015)**

The HFM was saturated with the aqueous and organic solutions before starting the actual extraction or stripping experiment. Equal volumes of the feed (1 L) and organic (1 L) solutions flow at the lumen and shell sides respectively in circulating batch mode. Both the organic and aqueous phases were continuously stirred and samples of the aqueous phase were acquired at regular intervals. The concentration of V(IV) and other impurities in the aqueous phase before and after extraction was determined using ICP-OES from which the metal concentration in the loaded organic phase was calculated. The set values for the pressure and flow rates on the shell and lumen sides were 70 kPa and 35 kPa and 450 mL/min and 350 mL/min respectively.

3.3 Results and Discussion

3.3.1 Extraction

3.3.1.1 Effect of acid concentration in feed

As previously mentioned, for the screening experiments the influence of eight extractants with the effect of H_2SO_4 concentration and the effect of the impurities (Fe(III), Al(III), Co(II), Ni(II) and Cr(VI)) on the extraction of V(IV) was investigated. For the first screening experiment which was the effect of the extractant and acid type, the organic phase consisted of 10 % (v/v) extractant with cyclohexane as diluent and 5 % (v/v) 1-octanol as phase modifier. The O/A volume ratio was maintained at 1. In Figure A1 (Appendix 1), the extraction of V(IV) with various extractants is shown. Accordingly, LIX-84-IC gave the highest extraction (86.1 % in 0.1 mol/dm^3 H_2SO_4), at lower acid concentrations (pH $\approx$ 0.7). This correlates with the strong and weak metal cation extractants described by Wilson *et al.* (2014), where strong extractants preferentially form metal complexes at low pH values and weak extractants at more basic solutions. This implies that the results found in this study confirm that the phenolic oxime extractant used in this study (LIX-84-IC) is a strong enough extractant to extract V(IV) cations from the acidic water phase (pH < 1), while other cations such as Fe(III) remained in the water phase. It appears that these phenolic oxime ligands, through hydrogen bonds, can pre-organise to form macrocyclic structures (Wilson *et al.*, 2014), where a bonding cavity is formed with the phenolic oxygen and the oxime providing the bridging units to complex the metal (Smith *et al.* 2014). In the case of vanadyl sulphates, the formed V(IV) – phenolic oxime complex is neutral (Smith *et al.*, 2003). For all the other extractants tested there was some extraction at very low H_2SO_4 concentrations with the highest extraction (61 %) attained when using Alamine 336 at 0.1 mol/dm^3 H_2SO_4. The extraction of V(IV) and the chosen salts using Alamine 336 will be discussed in Chapter 4. While V(IV) extraction remained low there was a slight increase above 6 mol/dm^3 H_2SO_4 attaining 33.7 %, 23.9 %, 13.3 % and 9.8 % at 9 mol/dm^3 H_2SO_4 when using D2EHPA, Cyanex 272, DioPA and Alamine 336 respectively. While the results presented in Figure A1 focussed only on the V(IV) extraction, the results obtained for the other metals (Fe(III), Al(III), Co(II), Ni(II) and Cr(VI)) using the various extractants correlated with those presented in literature, including the selective extraction of Co and Ni with the phosphorous extractant Cyanex 301 (not shown) (Flett, 2005), the separation of V(IV) and Fe(III) with D2EHPA (not shown), as well as the selective extraction of Fe(III) with Aliquat 336 (not shown) in concentrated acidic aqueous solutions (Mishra *et al.*, 2011).

Since the other extractants did not show significant extraction of V(IV), the phenolic oxime extractant, LIX-84-IC and the amine based extractant, Alamine 336 was selected as suitable extractants for the optimization of the V(IV) purification process using SX. In this Chapter, the key operating variables in a SX system using LIX-84-IC as the extractant will be presented whereas the purification of V(IV) using Alamine 336 will be discussed in Chapter 4.

According to the extraction results of all the metals using LIX-84-IC (Figure 3-3), the extraction of both V(IV) and Cr(VI) decreased with increasing acid concentration with hardly any extraction of the other metals observed, yielding the highest extraction of 86 % and 47 % for V(IV) and Cr(VI) respectively at 0.1 mol/dm^3 H_2SO_4. While the declining extraction efficiency of V(IV) with increasing H_2SO_4 concentration may suggest that sulphate ions participated during the extraction of V(IV), Li *et al.* (2012b) reported, when investigating the effect of sulphate ions on the extraction of V(IV) with D2EHPA, EHEHPA and Cyanex 272, that it is unlikely that the V(IV) ions will coordinate with the sulphate ions in view of the small complex formation constant (Li *et al.*, 2012a). The extraction mechanism for the extraction of V(IV) with organophosphorus cationic exchange extractants like D2EHPA, EHEHPA and Cyanex 272 are known to depend on the pH of the solution with a extractant to metal ratio of 1:1 at higher pH (pH ≈ 2) (eq. 1) and 2:1 at lower pH (pH ≈ 1) (eq. 2) (Li *et al.*, 2012a) :

$$\mathbf{VO^{2+}_{(aq)}+H_2R_{2(org)}\rightarrow VOR_{2(org)}+2H^+} \quad \mathbf{(1)}$$

$$\mathbf{VO^{2+}_{(aq)}+2H_2R_{2(org)}\rightarrow VO(HR)_{2(org)}+2H^+} \quad \mathbf{(2)}$$

While the above was postulated for organophosphorus extractants, it could also hold for the extraction with oximes when considering the observed increasing extraction with decreasing proton concentration, where an increase in protons would cause an equilibrium shift to the left of eq. 1 and 2, resulting in lower metal extractions.

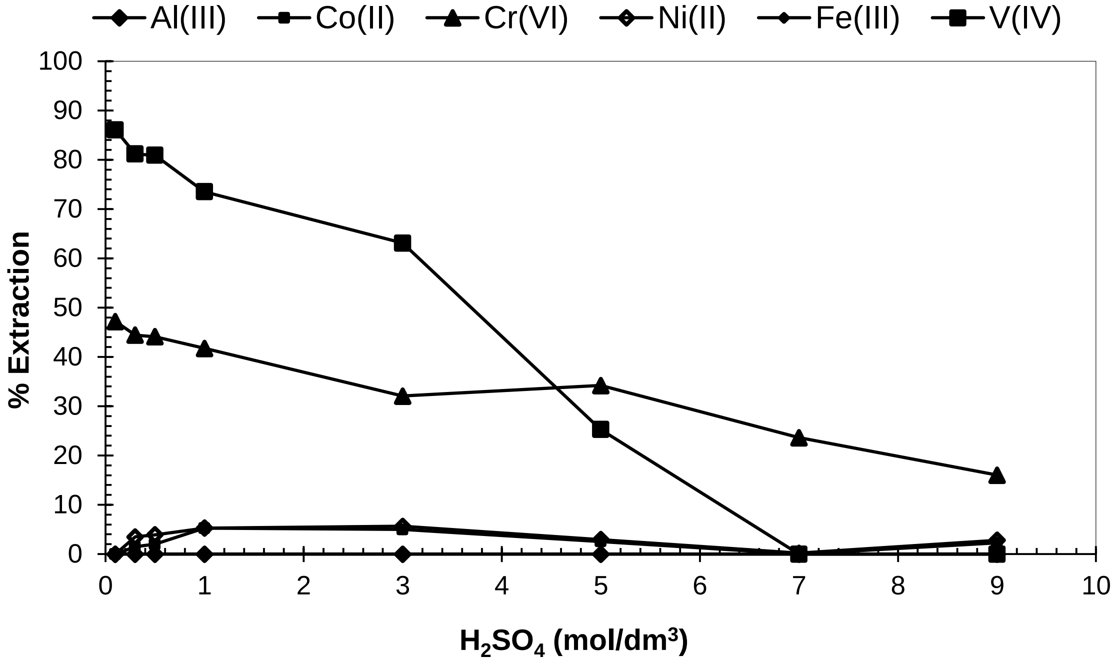

Figure 3-3: Extraction of Al(III), Co(II) Cr(VI), Ni(II), Fe(III) and V(IV) with 10 % (v/v) LIX-84-IC in cyclohexane

The effect of the chosen impurities (Al(III), Co(II), Ni(II), Fe(III) and Cr(VI)) was determined from a 0.1 mol/dm^3 feed solution containing only the $VOSO_4.5H_2O$ salt (100 mg/L), i.e. single salt extraction. The extraction was investigated as a function of LIX-84-IC concentration (1 % – 50 % v/v) and the results are shown in Figure 3-4. As can be seen, the extraction of V(IV) slightly increased from (0 % - 6.1 %) when the extractant concentration increased from 1 – 50 % (v/v). As discussed in Chapter 2, the oxime extractant, LIX-84-IC follows a metal cation exchange extraction mechanism. Hence, it can be assumed that the attainability of extraction confirms the presence of metal cations in the synthetic feed solution. However, in the single salt experiment little to no extraction was attained which, if assumed that the same V(IV) species are present in the synthetic solution of both the mixed salts and single salts studies and the same $VOSO_4.5H_2O$ salt was used throughout, is conflicting with the results obtained from the mixed salts studies(Figure 3-3).

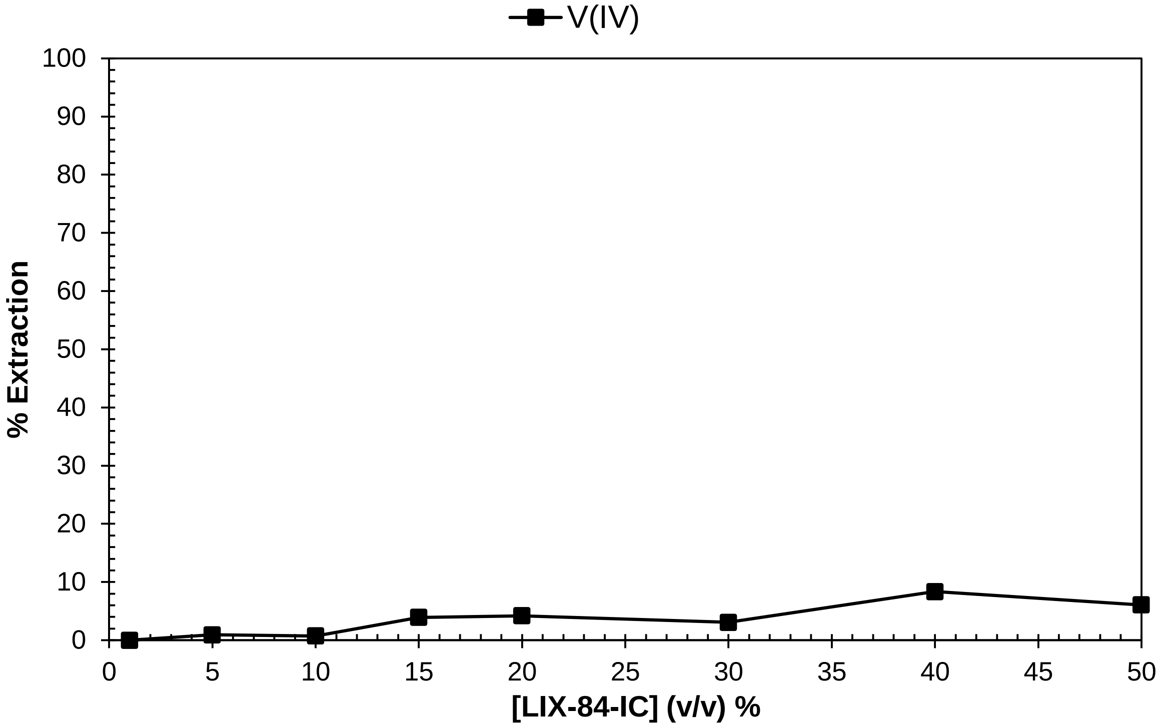

Figure 3-4: **The extraction of V(IV) from a single salt solution as a function of the LIX-84-IC concentration from 0.1 mol/dm^3 H_2SO_4**

According to speciation data available for V(IV) – H_2SO_4 systems, neutral $VOSO_4$ species will be the dominant species in this specific aqueous environment Yang *et al.* (2015), contradictory to the results obtained in the screening experiment (Figure A1 and Figure 3-3) which could explain the low extraction attained (0 % - 3.1 %) using lower extractant concentrations (0 % (v/v) – 30 % (v/v)). Nonetheless, extraction, although still low, is obtained with increased extractant concentrations (8.3 % using 40 % (v/v) LIX-84-IC) suggesting the presence of V(IV) (VO^{2+}) cations, which previously has been reported (Yang *et al.*, 2015). While the fraction of each of the neutral- and cationic species for this system is unknown, based on the result for the single salts study, the fraction of cations in the synthetic solution was significantly lower compared to the fraction of cations in the mixed salts study. This gives rise to the idea that a speciation effect between V(IV) and the impurities (Al(III), Co(II), Ni(II), Fe(III) and Cr(VI)) could have arisen increasing the fraction of metal cations in this specific synthetic feed solution and as a result increasing the extraction. Based on literature the dominant species for V cations in this specific pH environment is a VO_2^+ (V(V)) cation which is a derivative of V_2O_5. Due to the presence of a strong oxidizing agent such as Cr(VI) in the synthetic solution, an environment is created where the oxidation of V(IV) to V(V) can take place, resulting in the presence of V(V) metal cations VO_2^+ which would explain the high extraction obtained in the mixed salt studies. However, while a study of the extent of this effect falls beyond the scope of this study, the assumption can safely be made that both V(V) and V(IV) species (including neutral- anionic and cationic species) would probably have been present in the synthetic feed solution. Although this will be considered when discussing the results, for the purpose of the discussion, V will be referred to as V(IV), (assuming that both V(V) and V(IV) species can be present) since the V-salts used for the synthetic solution is in the tetravalent oxidation state. From studies conducted to determine if ageing of the synthetic solution had an effect on the extraction of V(IV) (data not shown) it seems that the extraction remained constant regardless of the ageing times which means that if these redox reactions occur, they reach equilibrium instantaneously.

3.3.1.2 Effect of contact time

The effect of contact time was determined using 30 % LIX-84-IC (v/v) (which was the optimal concentration for V(IV) extraction according to Section 3.1.4), in cyclohexane with 1-octanol as phase modifier and an O/A volume ratio of 1. For the aqueous phase, a 0.1 mol/dm^3 H_2SO_4 solution was used. The contact times were varied from 3 to 60 minutes as illustrated in Figure 3-5. Accordingly, both the V(IV) and Cr(VI) extraction reached a maximum after 15 minutes of 99 % and 57 % respectively remaining constant thereafter. These values confirm the repeatability of the study when considering the values attained in Figure 3-3. According to literature (Mane *et al.*, 2012) 5 minutes are sufficient for the extraction of Cr(VI) from a chloride solution using the amine extractant 2-octylaminopyridine. According to Mane *et al.* (2012) extraction decreases after 5 minutes, which can be ascribed to the dissociation of the metal ion complex due to mixing. A similar decline in extraction efficiency (80 % - 70 %) for V was observed after 30 minutes, when extracting V and Fe with D2EHPA (20 % v/v), which can again be ascribed to a degeneration of the metal-ligand complex over time (Chen *et al.*, 2015). It could thus be that the small decline observed for Cr after 10 minutes and V after 30 minutes (Figure 3-5) could have been caused by a similar dissociation. However, the changes for both metals is so small that it falls within the experimental error. According to Ning *et al.* (2014), the separation factor of V(V) over Cr(VI) increases with time when using the primary amine LK-N21. In this study the extraction of V(IV) decreased slightly after 30 minutes from 98.5 % to 97.2 % whereas the extraction of Cr(VI) increased slightly after 30 minutes suggesting a small decline in the separation factor of V(IV) over Cr(VI), but again the change is negligible. Since the separation factor of V(IV)/Cr(VI) did not significantly improve after 15 minutes a contact time of 15 minutes was deemed sufficient for equilibrium hence consecutive experiments were conducted under the same conditionS. To determine the experimental error, the above described time study experiment was repeated (data not shown), where it was found that the V(IV) and Cr(VI) extraction equilibrated after 30 minutes at 97 % and 51 % respectively showing an experimental error between the two experiments of 1.5 % for V(IV) and 9.5 % for Cr(VI) in terms of the amount extracted.

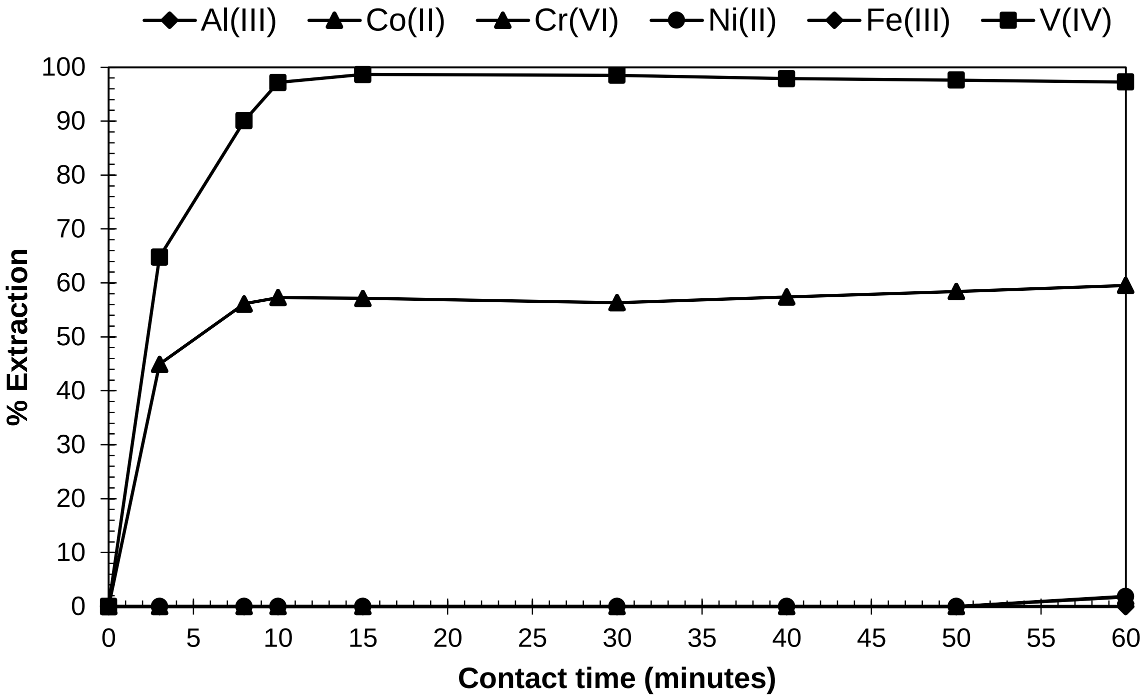

Figure 3-5: Extraction of V(IV) and other contaminants with 30 % (v/v) LIX-84-IC in 0.1 mol/dm^3 H_2SO_4 at different contact times

3.3.1.3 Influence of the diluent

According to literature, the extraction efficiency is influenced by the dielectric constant of the diluent, where it was shown that higher dielectric constants of the respective diluents result in lower extraction efficiencies due to a possible interaction of the diluents with high dielectric constants with the extractants (El-Nadi, 2010, Wu *et al.*, 2007). However, according to Mane *et al.* (2012), the extraction of Cr(VI) was not influenced by the type of diluent (aliphatic and aromatic), showing no correlation between the dielectric constant of the diluent and the extraction of Cr(VI) implying that this influence is system specific. Hence, the influence of various commercial diluents (cyclohexane, n-hexane, heptane, toluene and xylene) and 2 industrial diluents (ShellSol 2325 and ShellSol D70) on the extraction of the chosen metal salts was investigated. Again 30 % (v/v) LIX-84-IC was used in 0.1 mol/dm^3 H_2SO_4 with an O/A volume ratio of 1. In the absence of any significant extraction of the other metals (data not shown), only the extraction results for V(IV) and Cr(VI) are presented in Figure 3-6. As can be seen from the results there is a small difference in extraction efficiencies for V(IV) ranging between 95 % and 98 % when using different diluents. For Cr(VI), the effect was more significant showing extractions that varied between 46 % (heptane) and 56 % (toluene). Based on the observed extraction and selectivity, cyclohexane and ShellSol 2325 performed best with an extraction of V(IV) and Cr(VI) of 98 % and 49 % respectively.

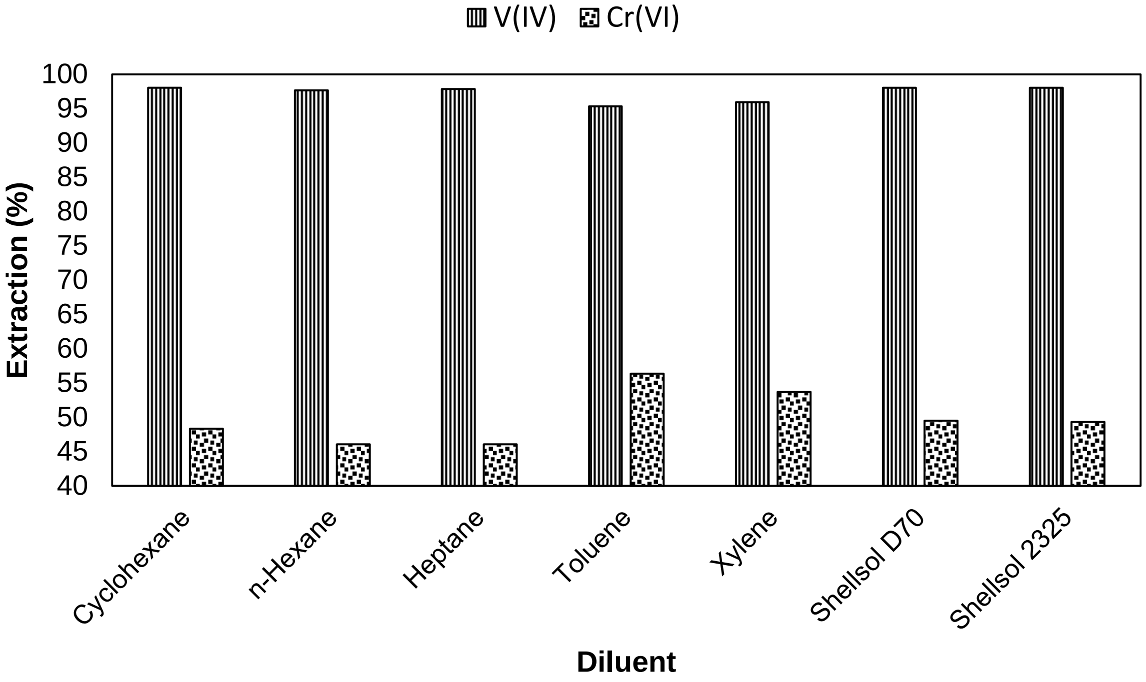

Figure 3-6: **Effect of the diluent on the extraction of V(IV) and Cr(VI) with 30 % (v/v) LIX-84-IC in 0.1 mol/dm^3 H_2SO_4**

Table 3-4: **Dielectric constants and the separation factors (β) of V(IV) and Cr(VI) of the diluents used in this study**

Diluent	Dielectric constant (ε)	Separation factor
n-Hexane	1.89	2.12
Heptane	1.92	2.12
Cyclohexane	2.02	2.09
ShellSol D70	2.15	1.99
Toluene	2.38	1.69
Xylene	2.54	1.78

ShellSol 2325	*	1.98

* ε is unknown

In Table 3-4 the diluents used are listed with their dielectric constants and the calculated separation factors (β) arranged with increasing dielectric constants. It is clear that the selectivity decreased with increasing dielectric constant except for xylene that had a slightly higher selectivity than toluene, which is similar to what had been observed in literature where toluene and xylene with higher dielectric constants (2.38 and 2.54) showed lower extraction efficiencies (Wu *et al.*, 2007). In view of the high selectivity attained and the fact that the initial studies presented in this paper were done using cyclohexane, cyclohexane was chosen as diluent for the further experimental work presented in this paper.

3.3.1.4 Effect of extractant concentration

In a previous study, where different concentrations of LIX-84-I (5 - 40 %) using kerosene as diluent were investigated, the optimal extractant concentration was determined as 40 % (v/v) (Barik *et al.*, 2014). This was confirmed when investigating the effect of LIX-84-I concentration on the extraction of Molybdenum(VI) (Mo(VI)) where again 40 % (v/v) LIX-84-I was optimal for extraction (Li *et al.*, 2012b, Park *et al.*, 2010). The behaviour of Mo in a SX system is significant since it has been reported that Mo and V display similar properties when dissolved in watery solutions (Guo and Shen, 2016).

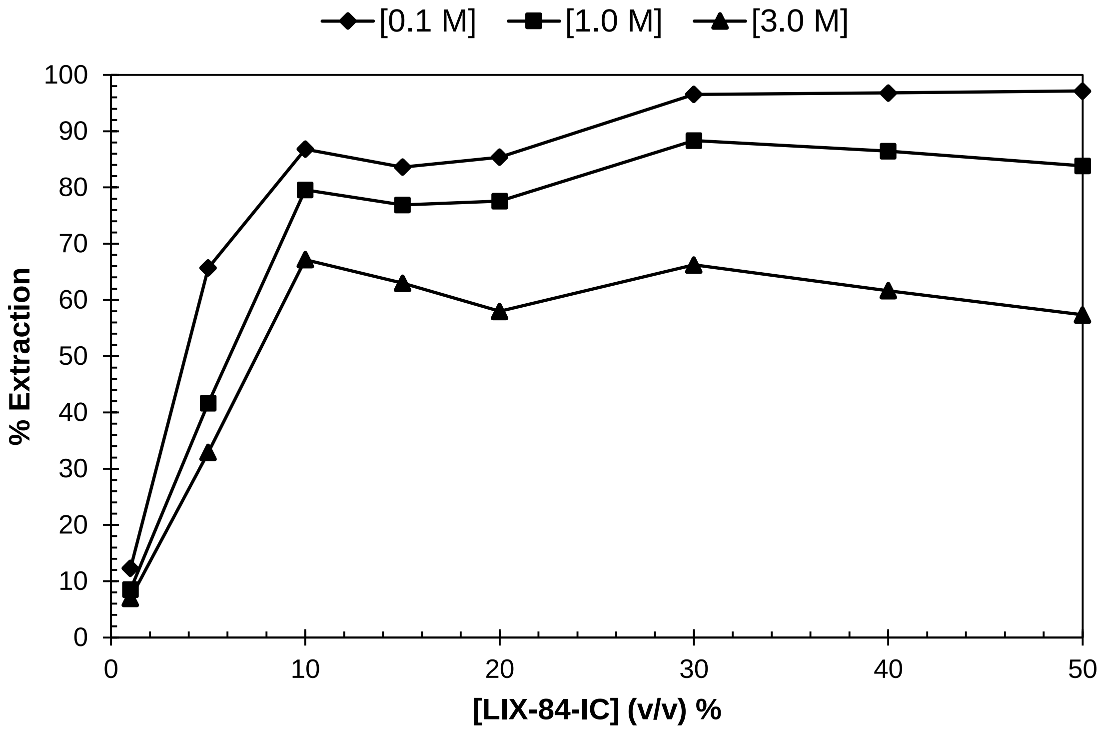

Figure 3-7: The extraction of V(IV) as a function of the LIX-84-IC concentration from 0.1, 1.0 and 3.0 mol/dm^3 H_2SO_4

According to Zhang *et al.* (1996), the extraction of V(IV) and Mo(VI) with LIX63 increased from 70 % to 96 % when increasing the concentration of the extractant from 20 % to 40 %, while observing little or no co-extraction of Co(II), Ni(II), Al(III) and Fe(III).

In this study, the influence of the extractant concentration on the extraction of V(IV) was studied in the range of 1 % - 50 % (v/v) at 0.1, 1.0 and 3.0 mol/dm^3 H_2SO_4 using an O/A volume ratio of 1 (Figure 3-7). Accordingly, the V(IV) extraction (from an 0.1 mol/dm^3 H_2SO_4 solution) increased from 12 % to 96 % when increasing the LIX-84-IC concentration from 1 % (v/v) to 30 % (v/v). However, a further increase of the LIX-84-IC concentration did not result in a further increase in extraction. Similar trends were observed at 1 mol/dm^3 and 3 mol/dm^3 H_2SO_4, with the only difference that the extraction decreased with increasing acid concentration with the highest extraction attained at 0.1 mol/dm^3 H_2SO_4 which correlates both with the results presented in Figure 3-3 and the literature discussion above. When investigating the extraction of all the salts as a function of the LIX-84-IC concentration at only 0.1 mol/dm^3 H_2SO_4 (Figure 3-8), a similar pattern as has been obtained previously was observed, i.e. the co-extraction of only Cr(VI). While the Cr(VI) extraction fluctuated significantly at lower extractant concentrations, a stable extraction of 40 % was attained above an extractant concentration of 30 %.

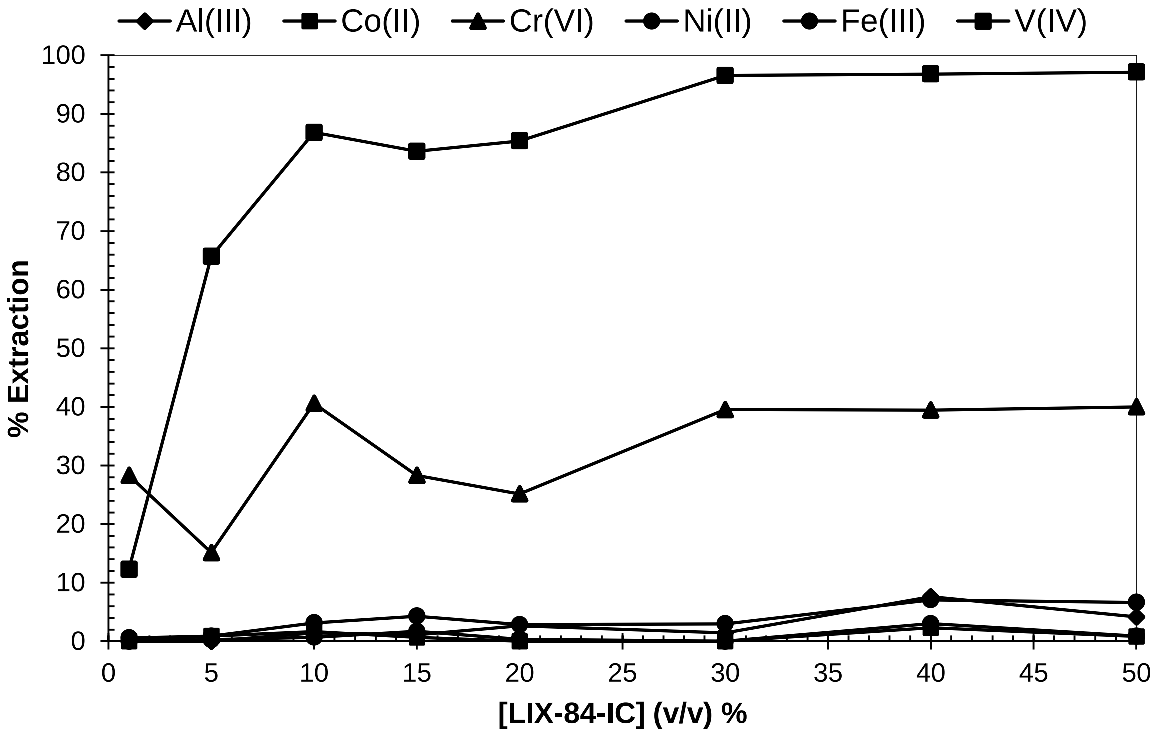

Figure 3-8: Effect of extractant concentration on the extraction of V(IV) and impurities in 0.1 mol/dm^3 H_2SO_4 with organic phase containing cyclohexane, 1-octanol and O/A volume phase ratio of 1

As shown previously, satisfactory extractions for both V(IV) and Cr(VI) were attained at high LIX-84-IC concentrations (30 % v/v). As discussed in Section 2.2.1.1, the polymerisation of the extractant to form macrocyclic structures could help explain the high concentration of LIX-84-IC required for optimal extraction. It should be mentioned that the LIX-84-IC used in this study was the concentrated version of the extractant, which differs from the LIX-84-I used by Barik *et al.* (2014) and Park *et al.* (2010).

To determine the extractant to metal (E:M) stoichiometric ratio of the V(IV) and LIX-84-IC, a Log D vs. Log [LIX-84-IC] graph was drawn (Figure 3-9) using the data from Figure 3-8. From the slope of the straight line fitted to the data the stoichiometric E:M ratio was 1.613 $\approx$ 2 (R^2 = 0.93). According to equations 1 and 2, the extraction mechanism depends on the pH of the solution. When comparing the pH of 0.7 (0.1 mol/dm^3) in this study to the pH $\approx$ 2 and pH $\approx$ 1 presented in literature (Li *et al.*, 2012a) this result confirms the cationic extraction mechanism with stoichiometric ratio of 2:1 (E:M) from lower pH solutions as reported by Li *et al.* (2012a). The slightly lower value could also be due to the co-extraction of the Cr(VI) reducing the availability of the extractant to V(IV).

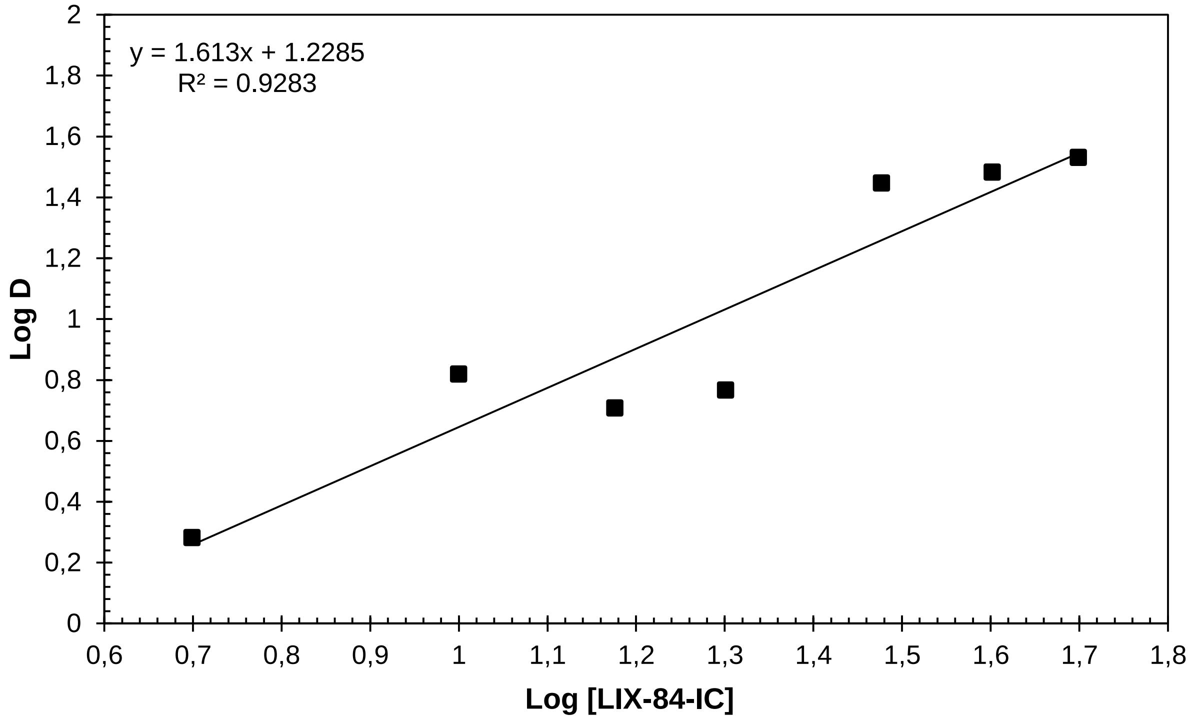

Figure 3-9: **Log D of V(IV) vs. Log [LIX-84-IC] to determine the E:M ratio of the V(IV) and the extractant from 0.1 mol/dm^3 H_2SO_4. The organic phase contained cyclohexane and 1-octanol and the O/A volume ratio was 1**

3.3.1.5 Effect of O/A volume ratio

To determine the effect of the O/A volume ratio, the extraction of V(IV) was carried out with O/A volume ratios varying from 0.1 - 10 using 0.1 mol/dm^3 H_2SO_4 and 10 %, 30 % and 50 % (v/v) LIX-84-IC. According to Figure 3-10, an increase in the volume ratio resulted in an initial increase in the extraction of V(IV). This is understandable considering the increased amount of extractant present with increasing extractant concentration. However already with an O/A volume ratio of 1, 98 % of V(IV) was extracted (along with 40 % Cr(VI) – results not shown), which confirms the repeatability when comparing the results to the extractant concentration experiments (Figure 3-8). It is thus clear that a volume ratio of 1 is optimal, confirming that the previous experiments were conducted under these optimal conditions.

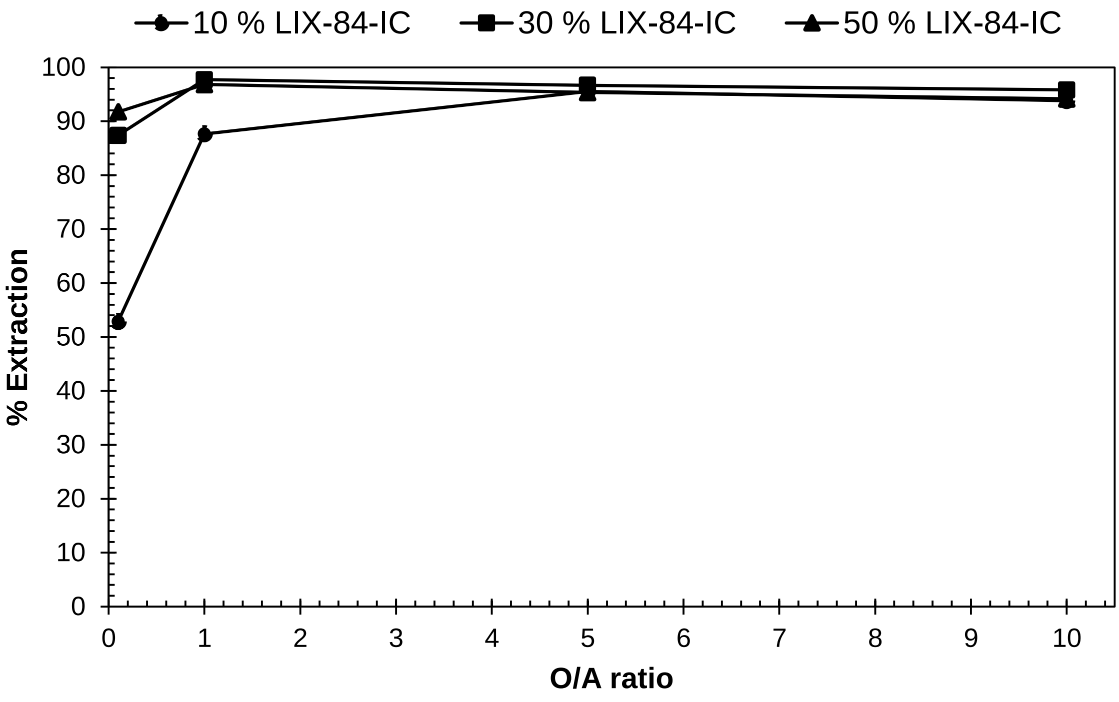

Figure 3-10: **Effect of the O/A volume ratio on the extraction of V(IV) with 10 – 50 % (v/v) LIX-84-IC**

3.3.2 Stripping

3.3.2.1 Effect of stripping agent and strippant concentration

According to literature, several stripping agents, including H_2SO_4, NH_4OH and NaOH, have been tested for the stripping or scrubbing of both V(V) and V(IV) (Li *et al.*, 2011b, Ma *et al.*, 2015, Biswas, 2013, Zhu *et al.*, 2015, Tavakoli and Dreisinger, 2014, Navarro *et al.*, 2007). Similarly, Cr(VI) was selectively stripped (81.4 %) from an 2-octylaminopyridine-metal complex using an 7 – 9 N NaOH solution (Mane *et al.*, 2012). In view of the co-extraction of Cr(VI) observed throughout this study, a stripping agent was sought that would selectively recover the V(IV) from the loaded organic phase thereby adding to the purification of V(IV). For this purpose, the stripping efficiency of H_2SO_4, HCl, and NaOH as a function of stripping agent concentration was investigated. Due to the difference in the concentration ranges used for the acid (0 - 10 mol/dm^3) and base (0 – 0.05 mol/dm^3) extractants, the stripping results obtained with the acid strippants and base strippants are presented separately in Figure 3-11 and Figure 3-12 respectively. For all acidic stripping agents (Figure 3-11), the stripping increased with increasing stripping agent concentration showing a higher stripping affinity for V(IV) than for Cr(VI). When increasing the H_2SO_4 concentration from 3 mol/dm^3 to 9 mol/dm^3, the stripping of V(IV) increased from 13 % to 87 % and that of Cr(VI) from 1.9 % to 36 %. When using HCl, a similar increased extraction of V(IV) with increasing HCl concentration was observed. For Cr(VI) there was initially (3 mol/dm^3 – 5 mol/dm^3 HCl) little to no stripping which increased between 5 mol/dm^3 and 9 mol/dm^3 HCl from 0.2 % to 10 %. The highest selectivity in HCl was observed at 7 mol/dm^3. Although LIX-84-IC is a phenolic oxime extractant, the results for both acidic stripping agents are in agreement with the extraction equation predicted in eq. 2 for organophosphorus extractants, where an increase in H^+ concentration will favour the reaction to the opposite of extraction, confirming the suitability of acids as stripping agents.

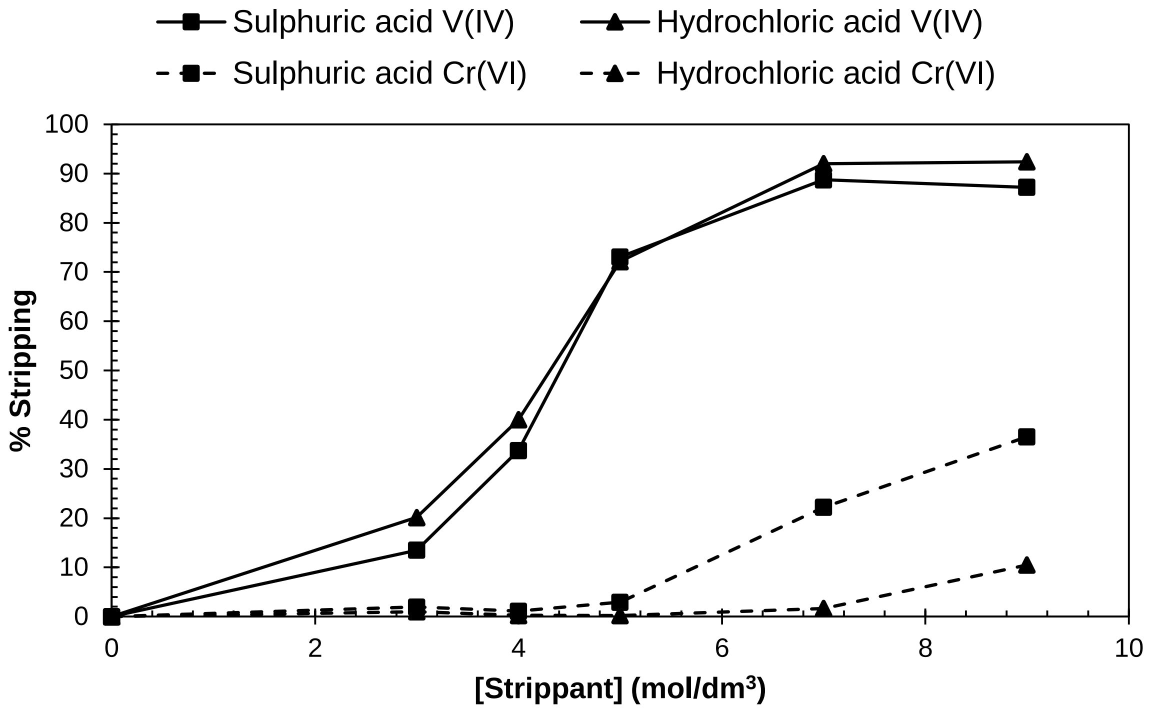

Figure 3-11: The effect of acidic stripping agents H_2SO_4 and HCl concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio of 1

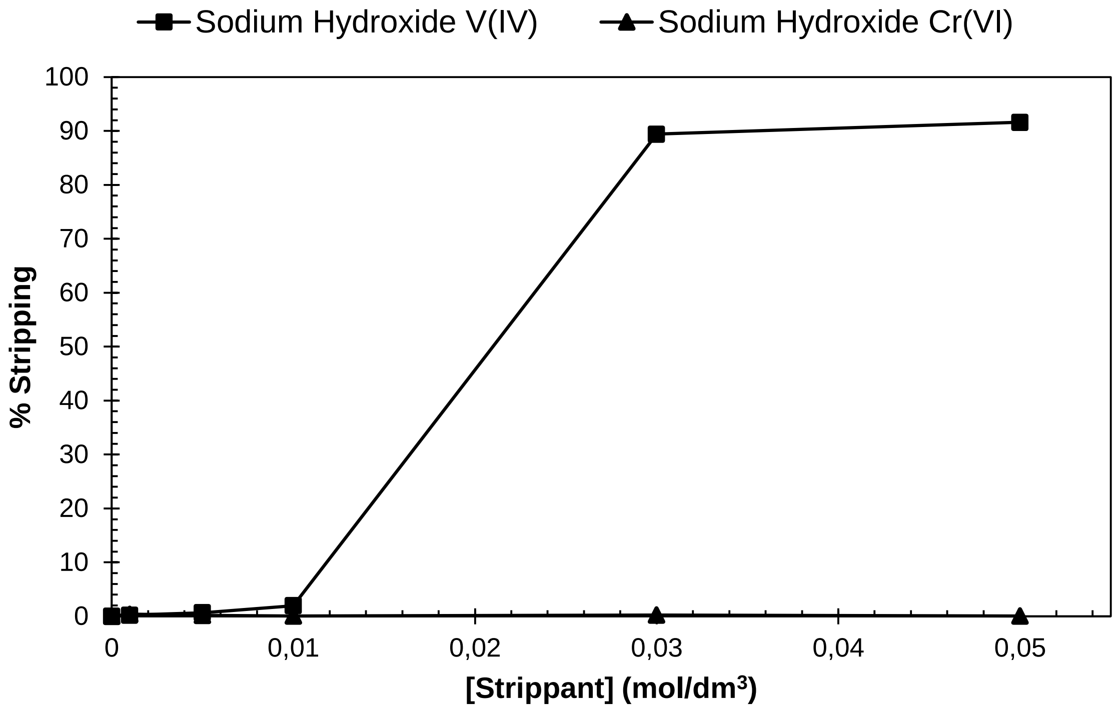

Figure 3-12: The effect of basic stripping agent, NaOH concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio of 1

It seems to contradict the aforementioned results that the stripping with NaOH (Figure 3-12) showed a significant increase in the stripping of V(IV) from 1.9 % to 91 % between 0.01 mol/dm^3 and 0.03 mol/dm^3 NaOH. In addition, the above 90 % recovery of V(IV) was obtained with little no co-stripping of Cr(VI) showing the suitability of NaOH for the selective stripping of V(IV) over Cr(VI) from a loaded LIX-84-IC organic phase. It is interesting to note that Mane *et al.* (2012) obtained no stripping of Cr(IV) when using 2-octylaminopyridine instead of the LIX-84-IC used in this study, confirming the influence of the extractant-metal complex during recovery. From the discussion above, both 0.05 mol/dm^3 NaOH and 7.0 mol/dm^3 HCl can be considered as suitable stripping agents. Accordingly, the yield and purities of V(IV) and Cr(VI) using both the stripping agents are listed in Table 3-5. The purities of V(IV) and Cr(VI) before extraction were 15.02 % and 16.60 % respectively. From the table it can be seen when using 7.0 mol/dm^3 HCl, a yield of 90.0 % for V(IV) and 49.0 % for Cr(VI) is obtained with purities of 99.00 % and 87.43 % for V(IV) and Cr(VI) respectively. With 0.05 mol/dm^3 NaOH, a yield of 90 % for V(IV) and 50 % for Cr(VI) is obtained with 99.96 % pure V(IV) and 87.03 % pure Cr(VI). Based on the results the purity of V(IV), when using optimum conditions in the extraction stage can be increased from 15.02 % to 96.96 % with a satisfactory yield of 90.0 % when using 0.05 mol.dm^{-3} NaOH in a single SX stage. For the purposes of this study, which is the purification of V(IV) from the chosen salts, higher purity values are favoured and according to the discussion and based on the results shown in Table 3-5 the highest purity for V(IV) is obtained with 0.05 mol/dm^3 NaOH. Hence, 0.05 mol/dm^3 NaOH was chosen as the optimal stripping agent for this study.

Table 3-5: The yield and purities of V(IV) and Cr(VI) using 7 mol/dm^3 HCl and 0.05 mol/dm^3 NaOH as stripping agents

Metal	Strip solution	Yield	Purity
V(IV)	7.0 mol/dm^3 HCl	90 %	99.00 %
	0.05 mol/dm^3 NaOH	90 %	99.96 %
Cr(VI)	7.0 mol/dm^3 HCl	49 %	87.43 %
	0.05 mol/dm^3 NaOH	50 %	87.03 %

3.3.3 The purification of V(IV)

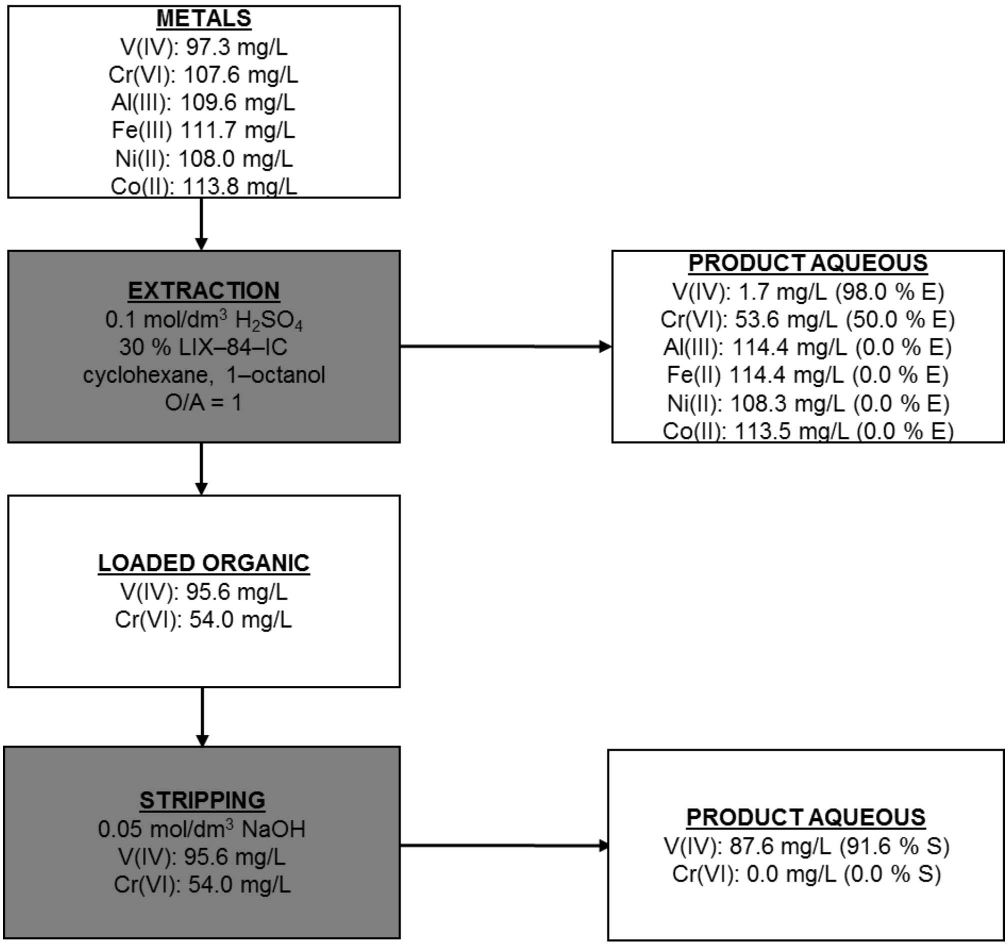

Figure 3-13: A proposed flow chart of the extraction and selective stripping for the recovery and purification of V(IV)

In Figure 3-13 a flowchart of the optimal extraction and stripping steps is provided, showing how the results obtained in this study could be combined to recover V(IV) from the chosen salts (Cr(VI), Fe(III), Al(III), Ni(II) and Co(II)). Since more than one component was extracted into the feed, it might be necessary to add an additional scrubbing step (Venkatachalam, 1998) in order to regenerate the diluent for a SX process. Accordingly, when using 30 % (v/v) LIX-84-IC as the extractant with cyclohexane and 1-octanol as the diluent and modifier respectively, 95.6 mg/L (98 %) and 54.0 mg/L (50 %) of the 97.3 mg/L V(IV) and 107.6 mg/L Cr(VI) from a 0.1 mol/dm^3 H_2SO_4 feed solution can be extracted with little to no co-extraction of the other impurities.

3.3.4 MBSX

3.3.4.1 Equilibrium study

Although 30 % (v/v) LIX-84-IC was the optimal extractant concentration according to the batch SX studies (Figure 3-7), a satisfactory V(IV) recovery was obtained when using 10 % (v/v) LIX-84-IC (86.1 %). Furthermore, from an economic perspective and for industrial application, lower extractant concentrations reduces overall process costs. Accordingly, to determine the suitability of the MBSX for this extraction, the separation of V(IV) from the chosen salts (Cr(VI), Fe(III), Al(III), Ni(II) and Co(II)) was investigated using 10 % (v/v) LIX-84-IC, cyclohexane and 1-octanol as the extractant, diluent and modifier respectively. The extraction was done for 42 hours of which the results are shown in Figure 3-14. While a direct comparison between the extraction kinetics of MBSX and batch SX cannot be drawn, some observations regarding the extraction kinetics can be given. While it was expected that the equilibrium time required for MBSX will be equal to, or even lower than the results obtained from the batch extraction studies in view of the expected high mass transfer capability when using HFMs (Tasker *et al.*, 2003, Moch, 1991), it is clear from Figure 3-14 that a significant longer time (36 hours) was required to reach equilibrium when using MBSX (90.7 %) compared to the 15 minutes required for a 99.0 % extraction when using batch SX (Figure 3-5). However, both the higher and faster extraction attained during batch SX is not only due to the use of the membrane but also to the use of only 10% extractant during MBSX compared to the 30 % used during SX.

During MBSX, the extraction of V(IV) reached a maximum (90.7 %) after 36 hours, with a not significant decrease (90.7 – 90.0 %) when the extraction time increased to 42 hours. When considering the Cr extraction, a similar tendency as was the case for V was observed. While the equilibrium time required for Cr(VI) batch extraction (57 %) was 15 minutes, an extraction time of 16 hours was required before equilibrium was attained (29.4 %) when using MBSX. The lower selectivity towards Cr(VI) can be attributed to the higher co-extraction of other impurities with maximum extraction values of 11.5 % for Fe(III), 13.5 % for Co(II) and 9.2 % for Al(III) after 16 hours and 11.1 % for Ni(II) after 2 hours. However, this co-extraction did not significantly influence the selectivity of the extractant for V(IV), possibly suggesting that the competition was only between Cr(VI) and the other impurities. As the extraction time increased from 16 hours to 30 hours the extraction of Cr(VI) decreased from 29.4 % to 22.8 %.

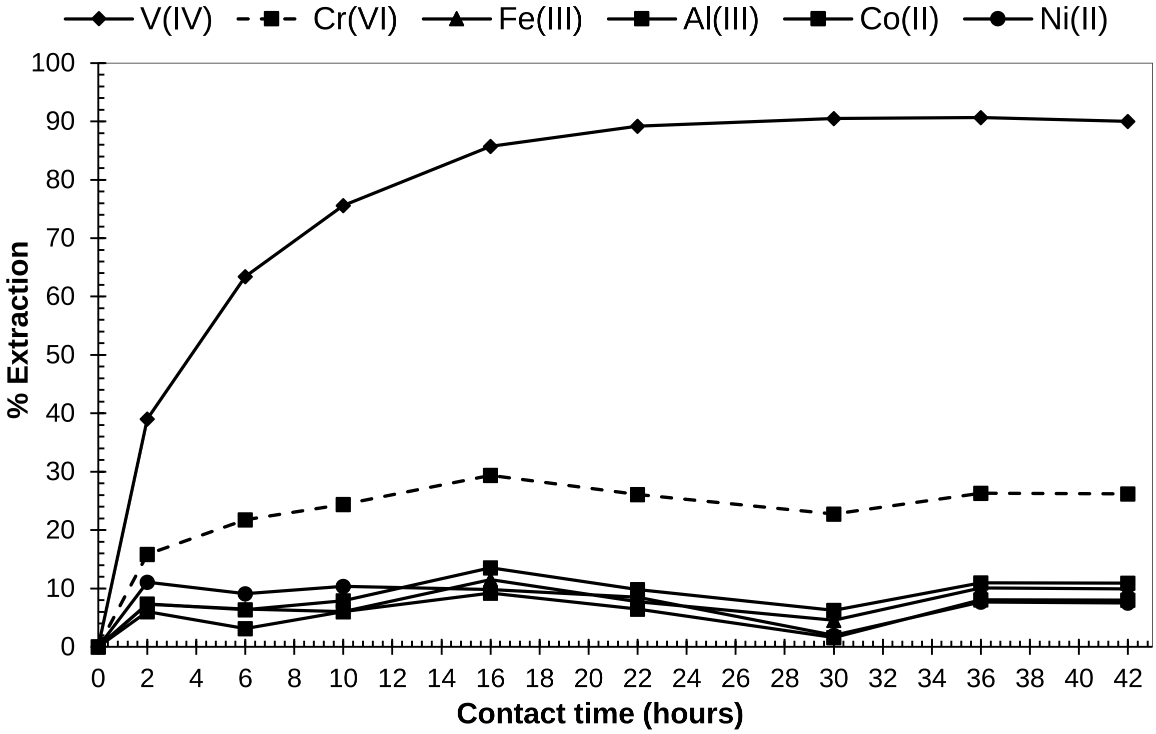

Figure 3-14: **The extraction of V(IV) and impurities with 10 % (v/v) LIX-84-IC in cyclohexane with 1-octanol as phase modifier and O/A volume ratio 1**

This decrease can again, similar to the trend observed in the batch extraction experiment, be ascribed to the dissociation of the metal-extractant complex due to mixing. A HFM based study conducted by Rout and Sarangi (2014) confirmed that V(V) could be selectively extracted from a mixture containing low concentrations of impurities (Cu, Ni, Co, Zn, Fe and Mn) using LIX-84-I as the carrier. The authors reported 100.0 % extraction of V(V) after only 1 hour. The reported extraction time is significantly lower than that observed in this study. A possible reason could be the difference in the specific density of the extractant used in this study and the extractant used in the study reported by Rout and Sarangi (2014). LIX-84-IC, which was the extractant used in this study, is the more concentrated version of the extractant. The differences in specific densities of the two versions of the extractant (LIX-84-I = 0.89 – 0.91 g/cm^3 and LIX-84-IC = 0.93 – 0.95 g/cm^3) could influence extraction efficiency. To determine this effect, the extractant concentration was varied in the next section to determine its influence on extraction time and efficiency. While the extraction of V(IV) was highest after 36 hours, 22 hours with a satisfactory V(IV) recovery percentage of 89.2 % was selected for the experiments conducted in Section 3.3.4.2.

3.3.4.2 Effect of extractant concentration

To determine the effect of the extractant concentration on the extraction when using MBSX, the effect of the LIX-84-IC concentration from 1 % (v/v) to 10 % (v/v) on the extraction of V(IV) and the chosen salts, (Cr(VI), Fe(III), Al(III), Co(II) and Ni(II)) was investigated of which only the V(IV) results are shown in Figure 3-15. The effect of LIX-84-IC concentrations higher than 10 % (v/v) was not included in this study hence 30 % (v/v) of the extractant produces an even more viscous solution which could result in higher extraction, however could also result in a further increase in the required extraction time. High extraction is already obtained with 10 % v/v LIX-84-IC, hence in this particular case, conditions where lower equilibrium time is possible is preferable. In view of the results in Figure 3-15, the extraction of V(IV) increased with an increase in extractant concentration, which is similar to the trend observed from the batch extraction experiments (Figure 3-7) and in accordance with the results reported in literature (Rout and Sarangi, 2014).

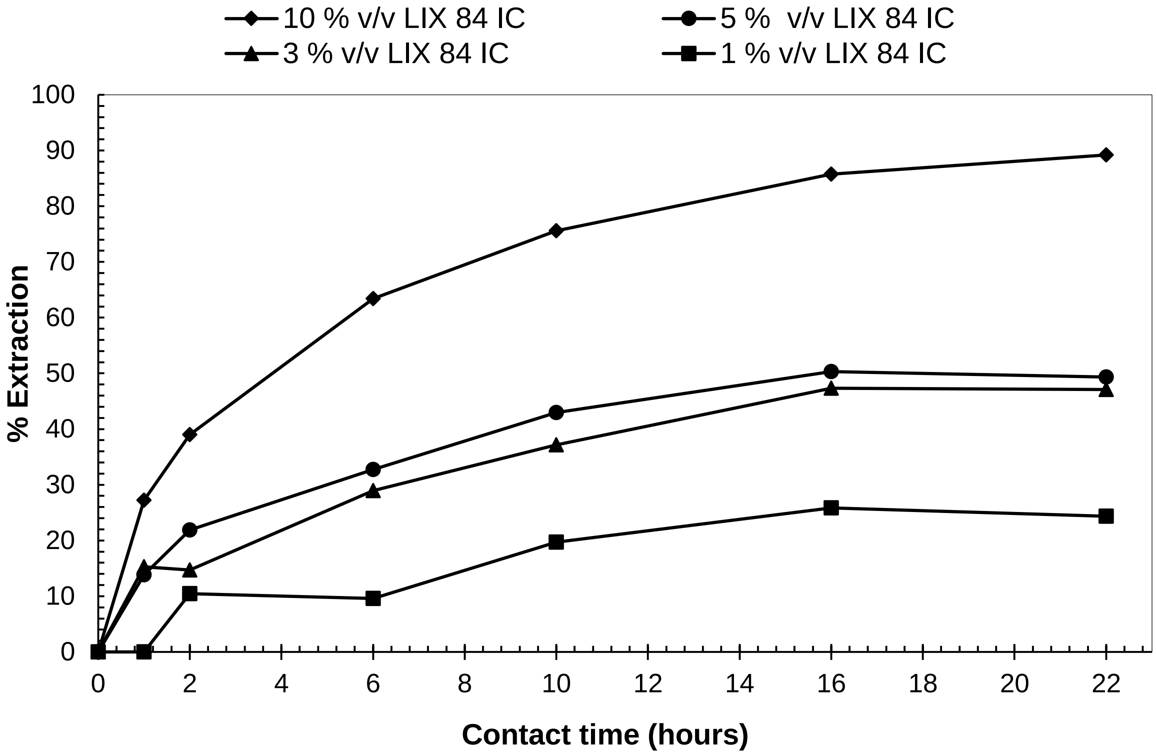

Figure 3-15: **The extraction of V(IV) form 0.1 mol/dm^3 H_2SO_4 with LIX-84-IC at different concentrations using cyclohexane and 1-octanol as phase modifier and O/A volume ratio of 1**

While the increase in LIX-84-IC concentrations resulted in an increase in V extraction (24.5 % V(IV) extraction using 1 % (v/v) LIX-84-IC, 47.1 % V(IV) extraction using 3 % (v/v) LIX-84-IC and 49.4 % V(IV) extraction using 5 % (v/v) LIX-84-IC), the decreasing extractant concentration did not result in a significant decrease in equilibrium time required, which implies that neither the viscosity nor the density change had contributed to the significant increase in equilibrium time required when using MBSX. This does then point to possible mass transfer limitations present when using MBSX.

3.4 Conclusion

The extraction and purification of V(IV) using SX from a mixture of salts was investigated as a function of different extractants, diluents, H_2SO_4 concentrations, molar ratios and extraction times. Subsequently, extraction studies were conducted using MBSX, which included an equilibrium study as well as the effect of the extractant concentration. The SX results showed that phenolic oxime extractant LIX-84-IC at 30 % (v/v) was most suitable for the selective extraction of V(IV) and Cr(VI) in 0.1 mol/dm^3 H_2SO_4. Optimal conditions were determined to be 30 % (v/v) LIX-84-IC in cyclohexane, 5 % (v/v) 1-octanol, O/A volume ratio of 1 with a contact time of 15 minutes. Although co-extraction of Cr(VI) was observed (53 %), over 98 % V(IV) was extracted in a single contact. Subsequently, the V(IV) in the loaded organic phase was stripped efficiently with a 0.05 mol/dm^3 NaOH yielding a recovery of 91 % with no co-stripping of Cr(VI). To remove the Cr(VI) and perhaps negligible amounts of contaminating metals that may have co-extracted from the organic phase, additional steps including a scrubbing step would be required. When using MBSX, the equilibrium time for optimal V(IV) extraction (89.2 %) was significantly higher (22 hours) compared to the batch experiments while the amount of co-extracted Cr(VI) had decreased (29.4 %) at the cost of slightly higher co-extraction of the other impurities.

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CHAPTER 4 – THE PURIFICATION OF $VOSO_4.5H_2O$ WITH ALAMINE 336 USING SX AND MBSX

4.1 Introduction

According to Moskalyk and Alfantazi (2003), V can be found in 50 minerals, including, among many others that are listed in Chapter 2 (Section 2.1.1), magnetite ore. South Africa produces 40 % (Polyak, 2016a) of the global V_2O_5, of which most is consumed by the steel industry due to unique chemical properties, such as a high melting point (1915 °C), making V a suitable constituent for the production of alloys with good resistance against elevated temperatures. Although the majority of V is consumed by the steel industry, various other new and existing applications of V, listed in Chapter 2, created the opportunity for the development or improvement of recovery and purification methods of this transition metal. From the literature chapter of this dissertation, it was determined that solvent extraction via a hydrometallurgical route would be most suitable for the purification of V, and the use of ion exchange extractants, such as amines, has several advantages over other commonly used extractants (Kislik (2012e)). Two examples of these advantages include fast reaction kinetics and a wide range of amine extractants to choose from. The wide range of amine-based extractants can be categorised into primary-, secondary-, tertiary- and quaternary amines of which the selectivity of the extractants is as follows: tertiary/quaternary > primary/secondary (Kim *et al*., 2015). Examples of the different amine-based extractants are listed in Table 2-2. Sun *et al.* (2016) studied the effect of the degree of acidification of the primary amine N1923 and found that the amine extractant N1923 had no extraction efficiency without acidification, increasing linearly with increasing acidification (Sun *et al*., 2016). As expected, the extraction of both V(V) and V(IV) with a variation of amine extractants, including primary (Sun *et al*., 2016, Ning *et al*., 2014), tertiary (He *et al*., 2007, Sahu *et al*., 2013, Chagnes *et al*., 2010, Kim *et al*., 2015, Kurbatova *et al*., 2015, Yang *et al*., 2015) and quaternary (El-Nadi *et al.*, 2009) amines has been investigated, but the commercialisation of amine-based purification of V is limited, which, according to Ning *et al*. (2014), is partly due to equipment corrosion and extractant oxidation by Cr(VI) (Ning *et al.*, 2014). Furthermore, the appearance of a third phase remains a challenge during the separation process; however, as discussed in Chapter 2, third phases can be avoided using MBSX. According to literature, tertiary amine extractants and quaternary amine extractants have shown to be more selective than primary and secondary extractants (Kislik, 2012e) and, according to a study conducted by Kim *et al*. (2015), it has been shown that tertiary amines show better extraction efficiency than that of quaternary amines in low pH environments (Kim *et al.*, 2015, Chagnes *et al.*, 2012). According to Kim *et al*. (2015) it is, however, expected that the extraction efficiency of the tertiary amines will be similar.

Of these, Alamine 336 holds the industrial advantage due to its ease of stripping off the loaded metals and the high purity yield of the final product after solvent extraction (Kim *et al.*, 2015). Chagnes *et al*. (2012) studied the stability of the extraction solvent (Alamine 336, 1 – tri-decanol and dodecanol) when extracting V(V) and H_2SO_4 from an aqueous phase. They found that the presence of V(V) in the solvent could result in the chemical degradation of either the extractant directly, or the modifier that consequently resulted in the degradation of the extractant indirectly (Chagnes *et al*., 2012). Accordingly, the use of V(IV) could be preferable (Chagnes *et al*., 2012), which can be attained due to the easy reduction of pentavalent vanadium to tetravalent vanadium in acidic solutions using suitable reducing agents (Bobtelsky and Glasner, 1942).

In this study, the extraction, separation and recovery of V(IV) with Alamine 336 as extractant from sulphate electrolyte solutions containing the typical impurities (Ni(II), Cr(VI), Al(III), Co(II) and Fe(III)), of which some are commonly found in magnetite ore, are studied. Several experimental parameters such as the concentration of the extractant, the concentration of H_2SO_4, the type of diluent, contact time and O/A volume ratio were investigated. The extractant used in this study was the tertiary amine (Alamine 336), with cyclohexane and 1-octanol as diluent and phase modifier, respectively. Subsequently, suitable stripping agents (HCl, H_2SO_4, NaOH and NH_4OH) were investigated to recover the extracted metal from the loaded organic phase. The extraction of V(IV) in the presence of the abovementioned impurities was also investigated using MBSX. Finally, an equilibrium study was conducted and the effect of carrier concentration on the V(IV) extraction was investigated.

4.2 Experimental

4.2.1 Materials, reagents and solutions

The commercial extractant Alamine 336 was supplied by Sigma-Aldrich. 1-Octanol (Labchem) was used as phase modifier to prevent emulsion or third-phase formation (Al-Siddique *et al*., 1980). The purities and suppliers of the diluents (used without further purification) and the metal salts in the synthetic solution used are listed in Table 3-1 and Table 3-2, respectively. Aqueous solutions for both the extraction and stripping experiments were prepared with deionised water and H_2SO_4 (98 %) or HCl (32 %) supplied by Labchem. The NaOH (25 wt. %) and NH_4OH used in the stripping experiment were both supplied by Labchem. The membrane used in this study was the same as the membrane used in the study from Chapter 3 (Liqui-cel® 2.8 x 8 membrane). The features and specifications of this membrane are listed in Table 3-3.

4.2.2 Extraction

Similar to the procedure described in Chapter 3, the extraction experiments were conducted by mechanically shaking (360 rpm) the organic solvent (diluent, extractant and modifier) and aqueous (deionised H_2O, H_2SO_4 and metal salts) phase in a shaking incubator at 25 °C unless indicated otherwise. All extractions (except when investigating the effect of contact time) were done for 60 minutes. The O/A volume ratio was kept at 1, unless stated otherwise, while 5 % (v/v) 1-octanol was used as phase modifier. After phase separation, the samples were diluted before measuring the concentrations of the V(IV) and impurities in the aqueous phase before and after extraction using ICP-OES. The metal concentrations in the loaded organic phases were calculated from the difference between the metal concentration in the feed phase before and after extraction using a mass balance *(Zhang et al.*, 1996) and the D was calculated as described in section 2.2.5 of Chapter 2.

4.2.3 Stripping

For the stripping studies, two acidic-, and two basic stripping liquors, namely HCl, H_2SO_4, NaOH and NH_4OH, were investigated. The loaded organic and stripping phases were shaken at 360 rpm, again with the shaking incubator, for 60 minutes at 25 °C. The concentrations of V(IV) and other impurities in the aqueous phase before and after extraction were again determined using ICP-OES, as mentioned before.

4.2.4 MBSX

For the MBSX experiments, the same experimental procedure was followed and the same experimental setup was used as described in section 3.2.4 in Chapter 3 (See Figure 3-1 and Figure 3-2).

4.3 Results and discussion

4.3.1 Extraction

4.3.1.1 Effect of acid concentration in feed

According to a study conducted by Kim *et al*. (2015), the effect of pH on the extraction of V(IV) and Mo(VI) with Alamine 336 from an oxalic acid-leached solution showed that extraction increased (5-99 %) when the pH increased from 0.6 to 3.8. Similarly, Sahu *et al.* (2013) investigated the extraction of V(V) with Alamine 308 from an H_2SO_4 feed solution; however, contradictory to Kim et al. (2015), they found that extraction decreased (99.7-85.5 %) when pH increased from 1.28 to 2.35. Furthermore, Sahu *et al*. (2013) confirmed that, since extraction was obtained from low pH solutions, the extraction followed an anionic exchange extraction mechanism. In the first set of experiments, the influence of Alamine 336 and the effect of the H_2SO_4 concentration (0.0002 mol/dm^3 to 9 mol/dm^3) on the extraction of V(IV) was investigated. The organic phase consisted of 10 % (v/v) extractant with cyclohexane as diluent and 5 % (v/v) 1-octanol as phase modifier. The O/A volume ratio was maintained at 1. In Figure 4-1, the results obtained for the extraction of the V(IV) and other metal salts (Fe(III), Al(III), Co(II), Ni(II) and Cr(VI)) with Alamine 336 are shown.

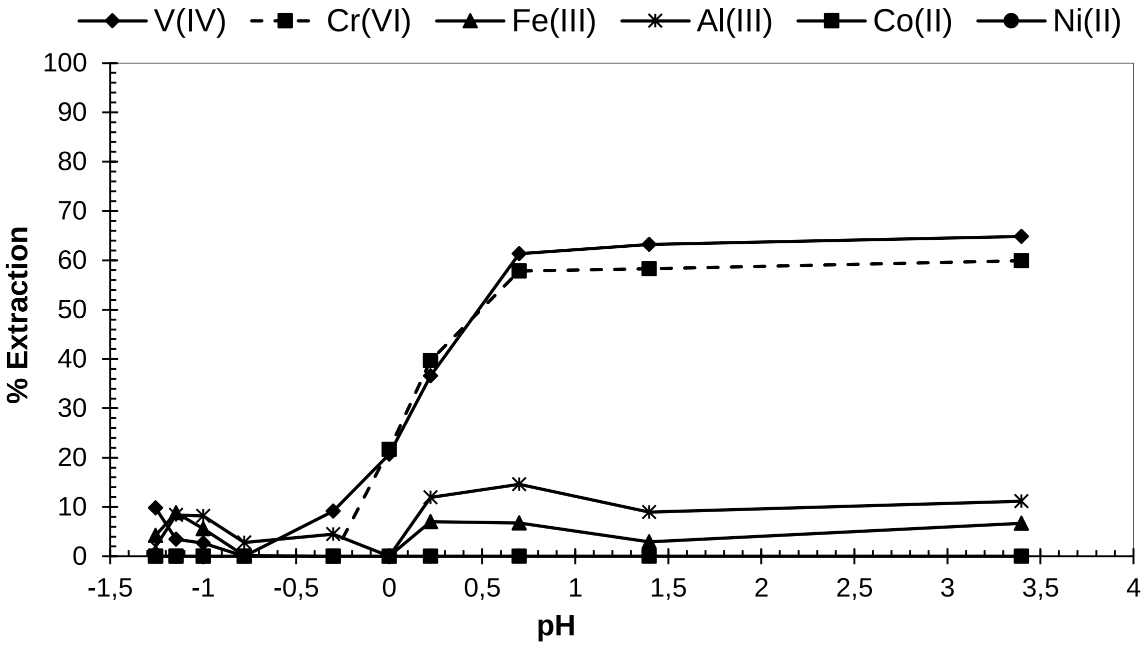

Figure 4-1: **Extraction of V(IV), Cr(VI), Ni(II) Co(II), Al(III) and Fe(III) as a function of pH with 10 % (v/v) Alamine 336 in cyclohexane and 1-octanol with an O/A volume ratio of 1**

Based on the results, the extraction of V(IV) and Cr(VI) with Alamine 336 increased with increasing pH, reaching a near plateau at a pH = 0.7, and thereafter increasing slightly reaching a maximum of 64.8 % V(IV) when extracting from 0.0002 mol/dm^3 H_2SO_4 (pH ≈ 3.4). Below a pH of 0.7, the extraction of V(IV) decreased (61-0.0 %) when the H_2SO_4 concentration increased to 3 mol/dm^3 (pH ≈ 0.78), while increasing again to 9.8 % when H_2SO_4 increased from 3 mol/dm^3 to 9 mol/dm^3 (pH ≈ - 0.78 to -1.26). It is clear that the extraction of V(IV) with Alamine 336 is pH dependent, which suggests the likelihood of a speciation effect, comparable to what both Kim *et al*. (2015) and Sahu *et al*. (2013) have found. Furthermore, it is clear that the extraction of V(IV) is higher in the higher pH range (as previously mentioned, where V(IV) exists in anionic form), confirming that extraction follows an anionic exchange extraction mechanism as suggested by Sahu *et al*. (2013). Since the extractant was used without pre-conditioning, and loading was attained by increasing the pH, acidic stripping agents were considered accordingly in order to comply with the ‘pH-swing’ method (Section 2.2.2). Based on the results for the other metals, Alamine 336 does not only show affinity for V(IV), but also for Cr(VI), with no significant extraction of Ni(II) and Co(II) and only slight co-extraction of Al(III) (14.6 % and 11.1 % in 0.1 mol/dm^3 and 0.0002 mol/dm^3 H_2SO_4, respectively) and Fe(III) (7.0 % and 6.7 % in 0.3 mol/dm^3 H_2SO_4 and 0.0002 mol/dm^3, respectively). The Cr(VI) extraction showed a similar trend to that of V(IV), where extraction decreased (59.9-0 %) when H_2SO_4 concentration increased from 0.0002 mol/dm^3 to 9 mol/dm^3. Based on these results and the similarity with the V(IV) extraction, it is possible that Cr(VI) may also have followed an anionic exchange extraction mechanism, confirming the chemical similarities between V and Cr. This is, in fact, confirmed by Sun *et al*. (2016) who reported that Cr(VI) exists as CrO_4^{2-}, $Cr_2O_7^{2-}$ and $HCrO_4^-$ in acidic solutions and CrO_4^{2-} in basic solutions (metalate anions), respectively. Based on the results, the extraction of V(IV) with Alamine 336 from a 0.0002 mol/dm^3 feed solution was selected as a suitable H_2SO_4 concentration for the consecutive experiments.

4.3.1.2 Effect of extractant concentration

Several authors have investigated the effect of amine extractant concentration on the extraction of V (Mishra *et al*., 2011, El-Nadi *et al*., 2009, Sahu *et al*., 2013, Yang *et al*., 2015, Yang *et al*., 2016) and Cr (Mane *et al*., 2012, Ning *et al*., 2014). As expected, the extraction efficiency increased linearly as the amine extractant concentration increased (Mishra *et al*., 2011, El-Nadi *et al*., 2009, Sahu *et al*., 2013, Yang *et al*., 2016). In this study, the effect of extractant concentration on the extraction of the chosen synthetic solution was investigated in the range of 1 to 30 % (v/v) at 0.0002 mol/dm^3 H_2SO_4 using an O/A volume ratio of 1 (Figure 4-2).

Accordingly, the V(IV) extraction showed a gradual increase (6.1-97.2 %) when the extractant concentration increased from 1 to 30 % (v/v). This result was expected due to the presence of more extractant available for extraction. However, this would have been expected for all of the metals present in the synthetic solution. However, for Fe(III), the extraction percentage remained constant, perhaps with a small decline when the extractant concentration was increased (1-15 %). However, when increasing the extractant concentration from 15 to 30 % (v/v), a significant increase in the extraction efficiency was observed (0.2-23.9 %). This result was similar to what Yang *et al*. (2016) found during the V extraction using N_{235} from an H_2SO_4 feed solution, where extraction increased (51.5-95.2 %) when the extractant concentration increased from 5 to 40 % (v/v). They also observed the co-extraction of Fe, P and Si with increasing extractant concentration.

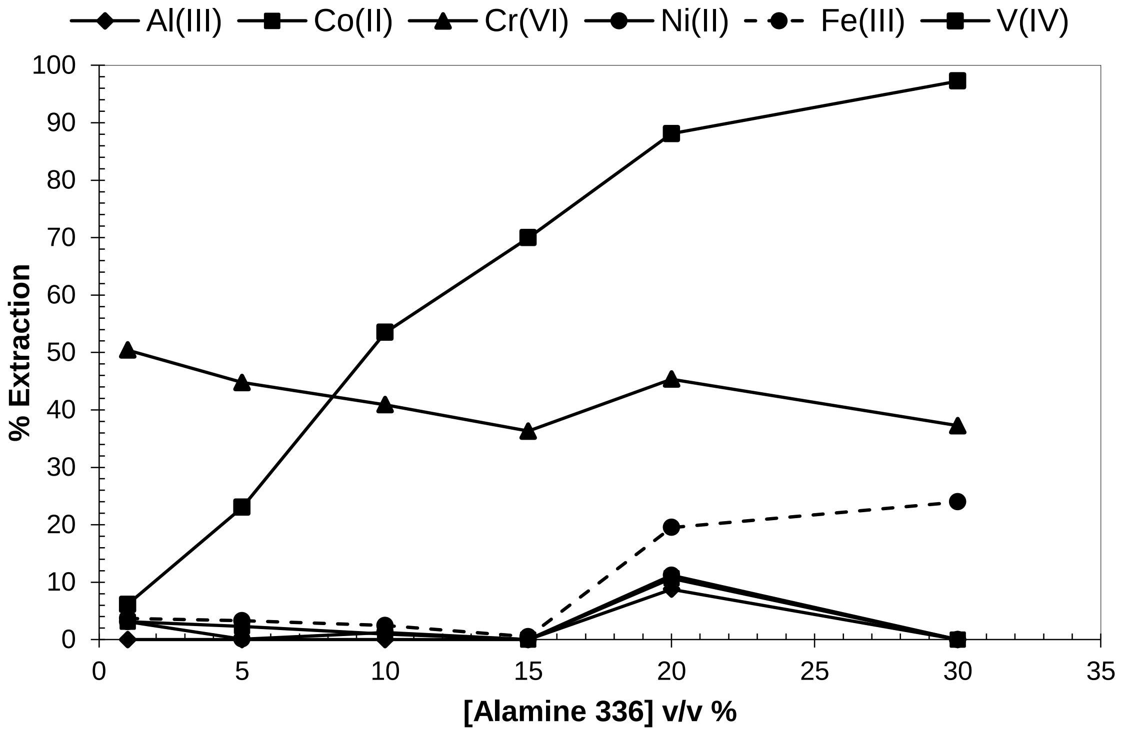

Figure 4-2: **The effect of Alamine 336 concentration in the range of 1-30 % (v/v) on the extraction of V(IV) and impurities in 0.0002 mol/dm^3 H_2SO_4 with organic phase containing cyclohexane, 1-octanol and O/A volume phase ratio of 1**

For Cr(VI), an initial increase in the extractant concentration from 1 to 15 % (v/v) resulted in a decrease in extraction from 50.4 to 36.3 %. Thereafter, a slight increase in extraction (36.3-45.4 %) was observed when the Alamine 336 concentration increased from 15 to 20 % (v/v) and finally Cr(VI) extraction decreased again to an extraction percentage of 37.3 % at 30 % (v/v) Alamine 336. Similar results were reported by Mane *et al*. (2012), where an initial increase in extractant (2 to 2-octylaminopyridine (OAP) concentration from an HCl aqueous solution resulted in higher Cr(VI) extraction; however, with higher extractant concentrations (0.073 mol/dm^3 to 0.4850 mol/dm^3), the Cr(VI) extraction decreased. The authors ascribed the lower extraction efficiency with high extractant concentrations to the formation of a stable ion pair between the extractant and the acid. Similarly, Ning *et al*. (2014) found a decrease in extraction efficiency for Cr(VI), with an increase in extractant (LK – N21) concentration, attributing it to the association of the extractant with itself by H-bonding, thereby lowering the concentration of available extractant for metal-extraction complexation and thereby not only influencing extraction efficiency, but also phase separation, resulting in crud formation. Finally, a study conducted by Yang *et al.* (2015) investigated the effect of tertiary amine (TEHA) concentration (20-80 % (v/v)) on the extraction of H_2SO_4 and V(IV). The authors found that both H_2SO_4 and V(IV) extraction increased with an increase in extractant concentration. Interestingly, more than 70 % of H_2SO_4 was co-extracted with 60 % v/v TEHA. This could be a possible explanation why such a high concentration of extractant was required in this study, if not only metal anions, but also H_2SO_4 was extracted into the organic phase. To determine the stoichiometric ratio between V(IV) and Alamine 336, a LogD vs. Log[Alamine 336] graph was constructed (Figure 4-3) using the data obtained from Figure 4-2. Based on the results, the slope of the straight line observed was 1.74 (presumed to be 2) with $R^2 = 0.90$, suggesting an E:M ratio of 2:1. In view of the results, 20 % (v/v) Alamine 336 was chosen as a suitable extractant concentration due to the satisfactory extraction of V(IV) and separation obtained ($\beta_{V(IV)/Fe(III)} = 4.51$ and $\beta_{V(IV)/Cr(VI)} = 1.94$). Therefore, the consecutive experiments were conducted with 20 % (v/v) Alamine 336.

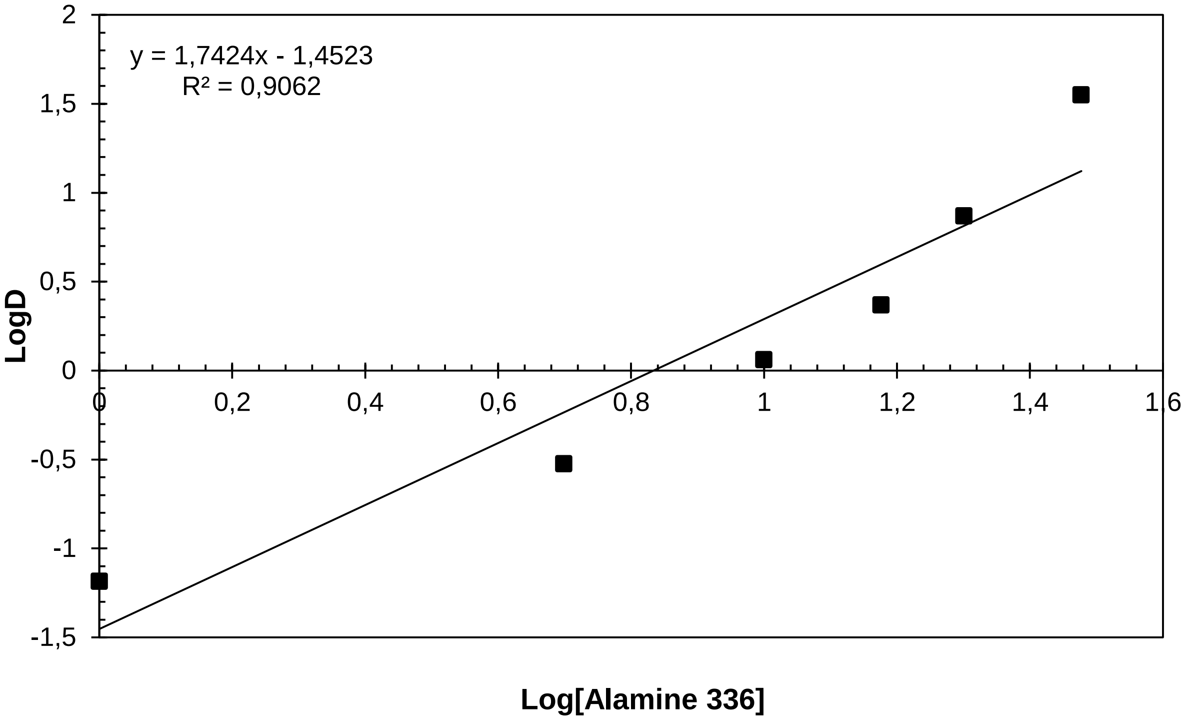

Figure 4-3: **LogD of V(IV) vs. Log[Alamine 336] to determine the E:M ratio of the V(IV) and the extractant from a 0.0002 mol/dm^3 H_2SO_4 solution. The organic phase contained cyclohexane and 1-octanol and the O/A volume ratio was 1**

4.3.1.3 Effect of contact time

To determine the effect of contact time on extraction, a 0.0002 mol/dm^3 H_2SO_4 solution was contacted with 10 %, 20 % and 30 % (v/v) Alamine 336, cyclohexane and 1-octanol as phase modifier and an O/A volume ratio of 1. The contact times were varied from 1 to 120 minutes, as illustrated in Figure 4-4, Figure 4-5, and Table 4-1.

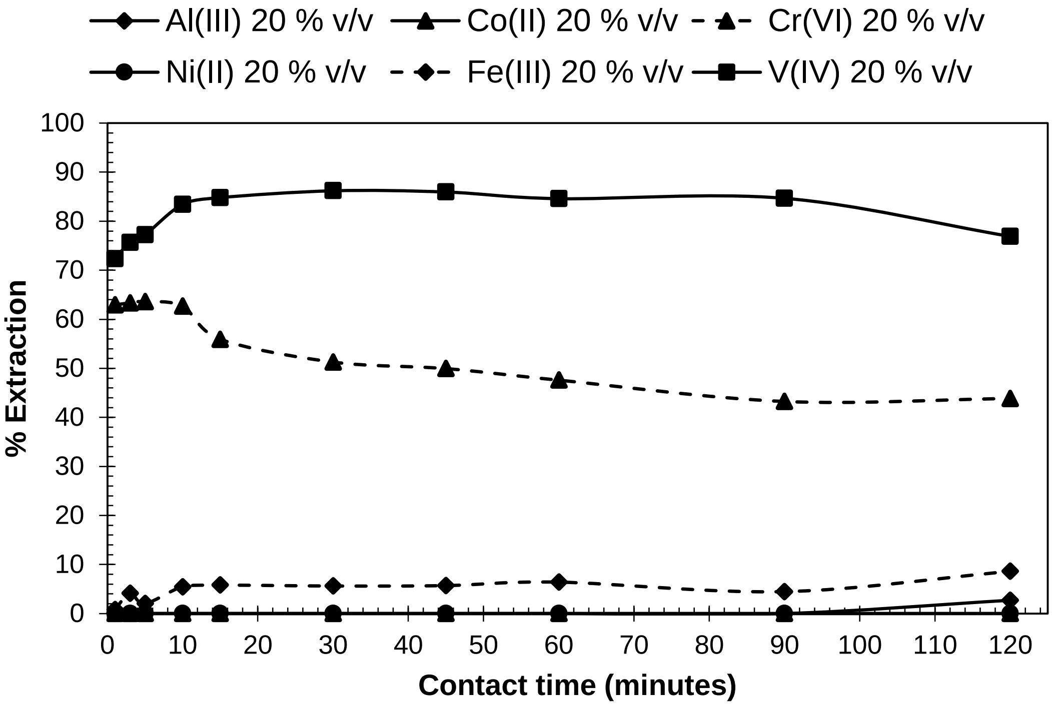

Figure 4-4: **Extraction of V(IV) and other contaminants with 20 % (v/v) Alamine 336 in 0.0002 mol/dm^3 H_2SO_4 at different contact times**

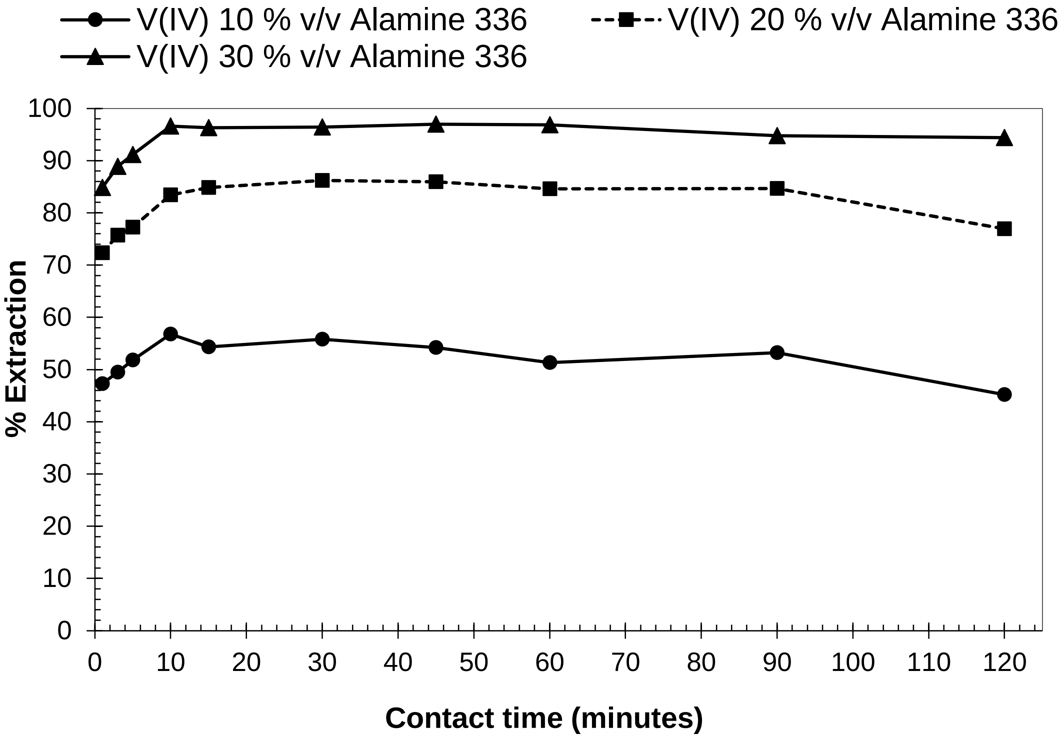

Figure 4-5: **Extraction of V(IV) with 10 %, 20 % and 30 % (v/v) Alamine 336 in 0.0002 mol/dm^3 H_2SO_4 at different contact times**

Since the trends obtained with 10 and 30 % (v/v) Alamine 336 were similar, albeit with different extraction values, to the extraction obtained with 20 % (v/v) Alamine 336, the results obtained with 20 % (v/v) Alamine 336 will be discussed in more detail. Accordingly, V(IV) extraction reached a maximum (86.2 %) after 30 minutes, with a slight decrease (86.2-84.7 %) when the extraction time was prolonged to 90 minutes. However, the decline in extraction is so small that it falls within experimental error. However, after 90 minutes, the extraction of V(IV) considerably decreased from 84.7 to 76.9 %. For Cr(VI), an extraction time of 5 minutes was sufficient to reach equilibrium (63.6 %). Similar to V(IV), a gradual decline in the extraction of Cr(VI) (63.6-43.85 %) was observed when the contact time increased from 5 minutes to 120 minutes. For Fe(III), the extraction remained constant, with a small variation in extraction values (4.1-4.5 %) between a contact time of 3 and 90 minutes. After 90 minutes, Fe(III) extraction increased from 4.5 to 8.6 %, reaching a maximum after 120 minutes. When only considering the V(IV) extraction as a function of time and extractant concentration, it confirms that the extraction rates were similar for 10, 20 and 30 % (v/v) Alamine 336 reaching maxima after 10 to 20 minutes of 57, 86 and 97 %, respectively.

Table 4-1: **Separation factors (β) of V(IV)/Cr(VI) and V(IV)/Fe(III) at different contact times with 20 % v/v Alamine 336**

Contact time (minutes)	Separation factor $\beta_{V(IV)/Cr(VI)}$	Separation factor $\beta_{V(IV)/Fe(III)}$
1	1.54	328.60
3	1.80	72.39
5	1.94	164.53
10	3.00	87.61
15	4.40	90.85
30	5.93	105.01
45	6.13	101.20
60	6.05	80.26
90	7.25	117.90
120	4.26	35.40

Based on the results from Table 4-1, a steady increase in the separation between V(IV) and Cr(VI) was observed, where the $\beta_{V(IV)/Cr(VI)}$ reached a maximum value of 7.25 after 90 minutes. However, after 120 minutes, the $\beta_{V(IV)/Cr(VI)}$ decreased from 7.25 to 4.26. In view of the $\beta_{V(IV)/Fe(III)}$ results, no correlation was apparent between the β and contact times. However, for V(IV) and Fe(III), the highest separation was observed after only 1 minute with a notable $\beta_{V(IV)/Fe(III)}$ of 328.60. A less notable, yet high separation of 72.39 was observed after 90 minutes as opposed to optimal separation observed between V(IV) and Cr(VI). In view of the chemical composition of typical V-containing ore, the majority of the ore would consist of Fe. Therefore, a higher β between V(IV) and Fe(III) might be preferential. However, there have been many reports of the successful separation of V(IV) from Fe(III), but fewer for V(IV) from Cr(VI), due to the intrinsic similarities in chemical properties. Consequently, an optimal contact time of 90 minutes for this study was determined.

4.3.1.4 Effect of O/A volume ratio

According to Sahu *et al*. (2013), an increase in the O/A volume phase ratio from 0.2 to 3, when using Alamine 308 as the extractant, increased the V(V) extraction from 89.9 to 99.8 %. However, a coloured precipitate was observed at lower O/A phase ratios. Similarly, Kim *et al.* (2015) reported that an increase in O/A volume ratio with Alamine 336 as the extractant from 0.2 to 3 resulted in increased V(IV) extraction. Interestingly, Yang *et al*. (2016) investigated the effect of O/A volume phase ratio and found that a ratio higher than 1 resulted in the appearance of a precipitate in the raffinate. Therefore, the effects of the O/A volume ratio on the extraction of V(IV) and the chosen salts (Cr(VI), Fe(III), Al(III), Co(II) and Ni(II)) were investigated with O/A volume ratios varying from 0.1 to 10 using 20 % (v/v) Alamine 336 from 0.0002 mol/dm^3, 0.02 mol/dm^3 and 0.1 mol/dm^3 H_2SO_4. Based on the results, an increase in O/A volume ratio from 0.1 to 1 resulted in an increase in the extraction of V(IV) from 0.0002 mol/dm^3 (27.26 % to 91.17 %), 0.02 mol/dm^3 (23.32 % to 80.93 %) and 0.1 mol/dm^3 (7.03 % to 48 %) H_2SO_4. This is expected, due to more extractant accessible for the respective metal salts, which also confirmed the results obtained by Sahu *et al*. (2013) and Kim *et al*. (2015). However, in this study, the lower O/A volume ratio did not result in a precipitate (Sahu *et al*., 2013).

Interestingly, for Cr(VI), the increased O/A volume ratio resulted in a slight decrease in extraction values from 0.0002 mol/dm^3 (63.60 to 52.80 %), 0.02 mol/dm^3 (61.52 to 58.66 %) and 0.1 mol/dm^3 (56.67 to 51.95 %) H_2SO_4. This result confirmed the trend observed for Cr(VI) extraction shown in section 4.3.1.2. Finally, the results for Fe(III) showed little to no extraction with an increase in O/A volume ratio from 0.1 to 1 from 0.0002 mol/dm^3 to 0.1 mol/dm^3. However, from 0.02 mol/dm^3 H_2SO_4, the extraction increased from 0.44 to 13.12 %. When the O/A volume phase ratio increased to a volume ratio between 5 and 10, a yellow precipitate was formed (aqueous phase), similar to what Yang *et al.* (2016) had reported. The optimal extraction (91.17 %) of V(IV) was obtained with an O/A volume ratio of 1 when extracting from 0.0002 mol/dm^3 H_2SO_4, which also confirms the repeatability of these results (Figure 4-5).

4.3.1.5 Influence of the diluent

Mishra *et al*. (2011) investigated the effect of the diluent on the extraction of Fe(III) from a specific leach solution using Aliquat 336 and the authors found that the extraction efficiencies for aliphatic diluents was higher than that of aromatic diluents. Furthermore, Mane *et al*. (2012) found a correlation between the extraction of Cr(VI) with 2-OAP and the dielectric constants (ε) of the respective diluents. In this study, the influence of suitable diluents, both commercial (cyclohexane, hexane and heptane) and industrial (Kerosene, ShellSol 2325 and ShellSol D70) on the extraction of V(IV), Cr(VI), Fe(III), Al(III), Co(II) and Ni(II) was studied. The extraction efficiency of the chosen salts is shown (extraction %) in Table 4-2, whereas in Table 4-3, the extraction efficiency of V(IV), Cr(VI) and Fe(III) (salts that showed significant extraction) was displayed in terms of $\beta_{V(IV)/Cr(VI)}$ and $\beta_{V(IV)/Fe(III)}$. Again, 20 % (v/v) Alamine 336 was used to extract from a 0.0002 mol/dm^3 H_2SO_4 solution with an O/A volume ratio of 1. Based on the results (Table 4-2), there was a slight variation in the extraction of V(IV) and Cr(VI) (< 6 % and < 4 %) when using different diluents. However, for Fe(III), the effect was more significant, showing extractions that varied between 8.1 % (cyclohexane) and 19.9 % (ShellSol D70) (< 12 %) with no correlation observed between extraction and ε of the respective diluents for either of the extracted salts (V(IV), Cr(VI) and Fe(III)), contrary to what Mane *et al*. (2012) had found. This may suggest that the structural differences between various amine extractants influence the behaviour of the extractant in different diluents. According to the results obtained for Fe(III), the extraction was higher for the aliphatic commercial diluents (hexane and heptane) than for the aromatic commercial diluent (cyclohexane). As for the industrial diluents, which consist of a combination of aromatic and aliphatic constituents, the highest extraction was obtained with ShellSol D70 (14.9 % with ShellSol 2325, 15.8 % with Kerosene and 19.9 % with ShellSol D70), which in fact has a lower aromatic content (< 0.5 %) and higher aliphatic content than that of ShellSol 2325 (19 %) and Kerosene (< 25 %), confirming the results that Mishra *et al.* (2011) reported. As can be seen from the results, industrial solvents, ShellSol 2325 and ShellSol D70 yielded the highest extraction (95.7 % and 95.1 %) for V(IV), whereas ShellSol D70 and hexane gave the highest extraction for Cr(VI) (60.6 % and 58.1 %). In Table 4-3, the chosen diluents are listed in terms of increasing ε and by the $\beta_{V(IV)/Cr(VI)}$ and $\beta_{V(IV)/Fe(III)}$ obtained during extraction. It is clear that there is no correlation between either the ε of the diluent or the $\beta_{V(IV)/Cr(VI)}$ and $\beta_{V(IV)/Fe(III)}$. However, ShellSol 2325 showed the highest selectivity for V(IV) ($\beta_{V(IV)/Cr(VI)} = 16.37$ and $\beta_{V(IV)/Fe(III)} = 125.95$). In view of these results, industrial solvent ShellSol 2325 seems optimal for this system, and is recommended as the diluent for future experimental work.

Table 4-2: **The extraction of V(IV), Cr(VI), Fe(III), Al(III), Co(II) and Ni(II) with several diluents from 0.0002 mol/dm^3 H_2SO_4 and 20 % (v/v) Alamine 336**

Diluent	Extr. (%)					
	V(IV)	Cr(VI)	Fe(III)	Al(III)	Co(II)	Ni(II)
Kerosene	94.9	57.5	15.8	0.87	0.00	0.00
Hexane	93.8	58.1	12.3	0.00	0.00	0.00
Heptane	93.9	56.8	11.9	3.85	0.00	0.00
Cyclohexane	90.1	54.1	8.1	3.85	0.00	0.00
ShellSol D70	95.1	60.6	19.9	4.72	4.40	2.64
ShellSol 2325	95.7	57.4	14.9	0.00	0.00	0.00

* ε is unknown

Table 4-3: **Dielectric constants (ε) and the separation factors (β) (V(IV)/Cr(VI) and V(IV)/Fe(III)) of the diluents used in this study**

Diluent	Dielectric constant	Separation factor	Separation factor
	(ε)	(β) V(IV)/Cr(VI)	(β) V(IV)/Fe(III)
Kerosene	1.80	13.82	99.88
Hexane	1.89	10.96	108.27
Heptane	1.92	11.74	114.33
Cyclohexane	2.02	7.73	103.39
ShellSol D70	2.15	12.59	78.06
ShellSol 2325	*	16.37	125.95

* ε is unknown

4.3.2 Stripping

4.3.2.1 Effect of stripping agent and strippant concentration

A study conducted by Zhao *et al*. (2015) reported the stripping of V(V) with NaOH (0.05 mol/dm^3 to 2.0 mol/dm^3) and HCl (1.0 mol/dm^3) from a loaded organic phase containing a mixture of a primary amine (N1923) and a tertiary amine (Alamine 336) (synergistic extraction). The results showed that the stripping efficiency increased with an increase in NaOH concentration (100.0 % V(V) recovery with 2 mol/dm^3 NaOH). Furthermore, the low stripping efficiency obtained (≈ 37 %) with 1 mol/dm^3 HCl was attributed to the strippant concentration being excessively acidic, which would favour extraction instead of stripping. Similarly, results reported by El-Nadi *et al*. (2009) and He *et al*. (2007) showed 1.0 mol/dm^3 and 1.5 mol/dm^3 NaOH removed 99 % and 96 % V(V) from loaded Aliquat 336 and N_{235} respectively, when using either acid (HCl) or alkali (NaOH) as the aqueous feed solution. Additionally, NH_4OH recovered 81.4 % of the loaded V(V) using HCl as aqueous feed component. Accordingly, stripping studies conducted by Sahu *et al.* (2013) reported increased NH_4OH concentrations, which resulted in higher recovery of V(V) (96.2-100 %) (Sahu *et al.*, 2013). However, Kim *et al*. (2015) considered NH_4OH for selectively stripping V(IV) from Alamine 336-loaded V(IV) and Mo(VI), where V(IV) again precipitated at higher pH values, and consequently, Kim *et al.* (2015) investigated the stripping efficiency of H_2SO_4 from 0.2 mol/dm^3 to 2.5 mol/dm^3. Accordingly, a 99.5 % V(IV) stripping was obtained between 1.5 and 2.5 mol/dm^3 H_2SO_4. One has to keep in mind, however, that stripping at a lower pH is preferable since high acidity environments will require more neutralising agents to precipitate the metal (Kim *et al*., 2015). In this study, the stripping efficiency of H_2SO_4 and HCl, NaOH and NH_4OH as a function of stripping agent concentration was investigated. The stripping results obtained with the acid and base strippants for both V(IV) and Cr(VI) are presented in Figure 4-6 (H_2SO_4), Figure 4-7 (HCl), Figure 4-8 (NaOH) and Figure 4-9 (NH_4OH), respectively. Due to limited amounts of the extractant available, the stripping studies were conducted using 10 % (v/v) Alamine 336 concentration and not 20 % v/v Alamine 336, which was determined to be the optimal extractant concentration (Figure 4-2). When increasing the concentration from 0.1 mol/dm^3 to 9 mol/dm^3 H_2SO_4 (Figure 4-6), the stripping of Cr(VI) increased from 40.6 % to 79 % (reaching a maximum of 84.4 % with 3 mol/dm^3 H_2SO_4), and that of V(IV) from 48.6 % to 77.3 %, with insignificant variations between these extractants that could be attributed to experimental error. This increased stripping with increasing H_2SO_4 concentration is similar to the trend reported by Kim *et al.* (2015). However, based on this result, H_2SO_4 did not show selectivity for either V(IV) or Cr(VI), confirming the unsuitability of H_2SO_4 as a stripping agent, yet again confirming the chemical similarities between V(IV) and Cr(VI) (Sun *et al*., 2016).

Similar to H_2SO_4, when using HCl (Figure 4-7), an increased stripping efficiency for Cr(VI) (10.6-82.4 %) with increasing HCl concentration (0.1 mol/dm^3 to 9 mol/dm^3) was observed. However, for V(IV), an initial decrease in stripping efficiency (66-12.6 %) was observed (0.3 mol/dm^3 to 5 mol/dm^3), in accordance with Zhao *et al*. (2015), which then increased from 12.6 % to 59.9 % when the HCl concentration was increased from 5 mol/dm^3 to 9 mol/dm^3. In terms of selectivity, there are two possible stages where separation between V(IV) and Cr(VI) is possible.

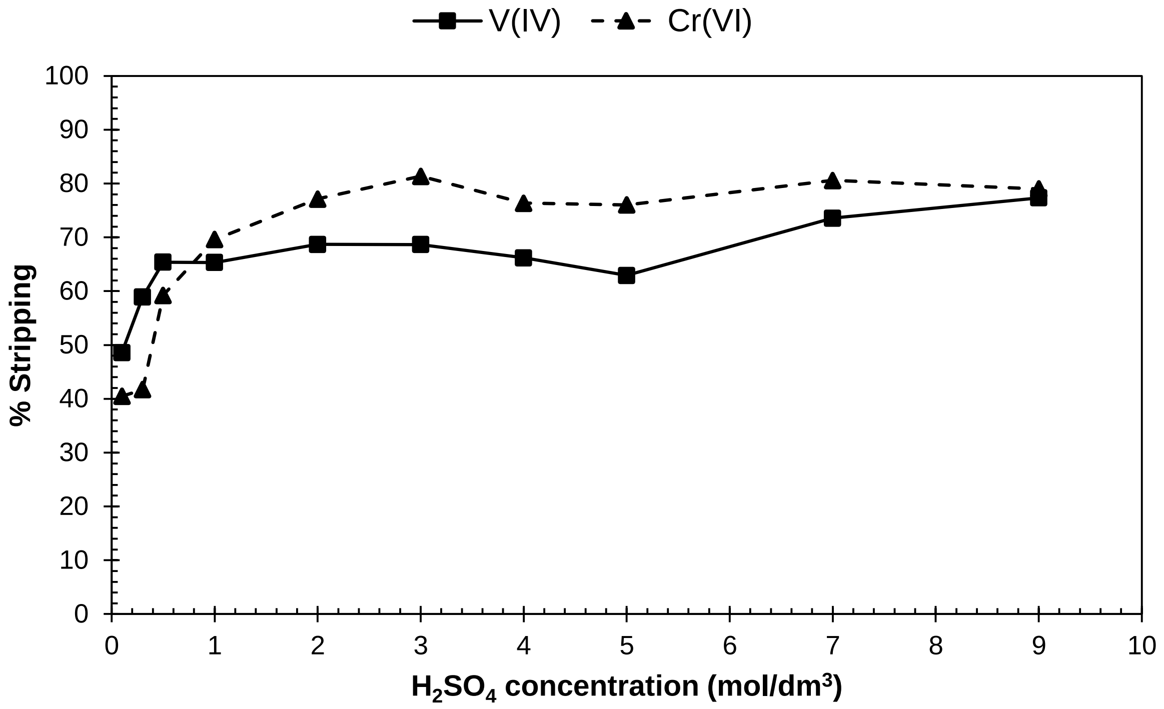

Figure 4-6: **The effect of H_2SO_4 concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio 1**

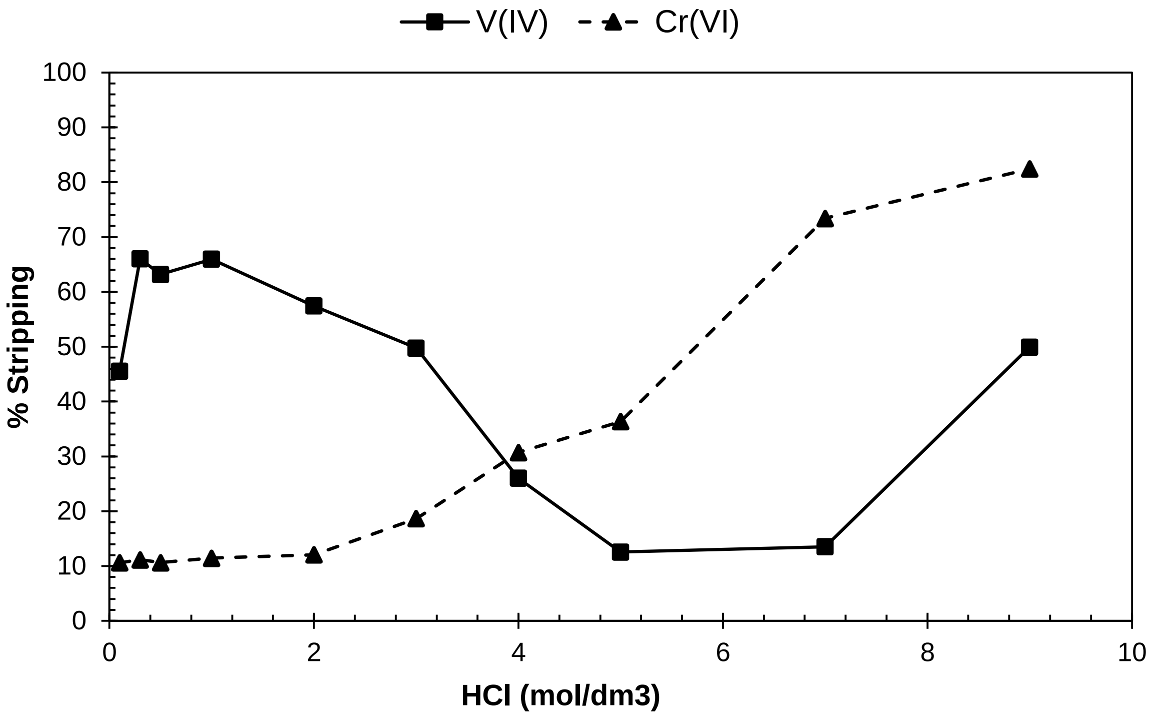

Figure 4-7: **The effect of HCl concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio 1**

The highest selectivity was obtained with 0.3 mol/dm^3 HCl resulting in a $\beta_{V(IV)/Cr(VI)}$ of 5.92, while at 7 mol/dm^3 HCl, the separation for $\beta_{Cr(VI))/V(IV)}$ was 5.43. In view of the co-extraction of Cr(VI) observed throughout this study, a stripping agent was sought that would selectively recover the V(IV) from the loaded organic phase, thereby adding to the purification of V(IV). Moreover, since the aim of the study is to purify V(IV), the requirements for a suitable stripping agent would be the selective stripping of V(IV), and not Cr(VI). Additionally, as mentioned earlier, the high acid concentration required could be disadvantageous for industrial application, since more neutralising agent would be required for precipitation of the purified product (Kim *et al*., 2015). Therefore, based on these results, 0.3 mol/dm^3 HCl would be a preferable strippant for the purification of V(IV). The preferential selectivity towards Cr(VI) at 7 mol/dm^3 HCl could be used as a scrubbing step to remove the Cr(VI) impurities from the loaded organic phase prior to the stripping of the V(IV). In this way, it could be possible to regenerate the extractant (Alamine 336) for continuous use.

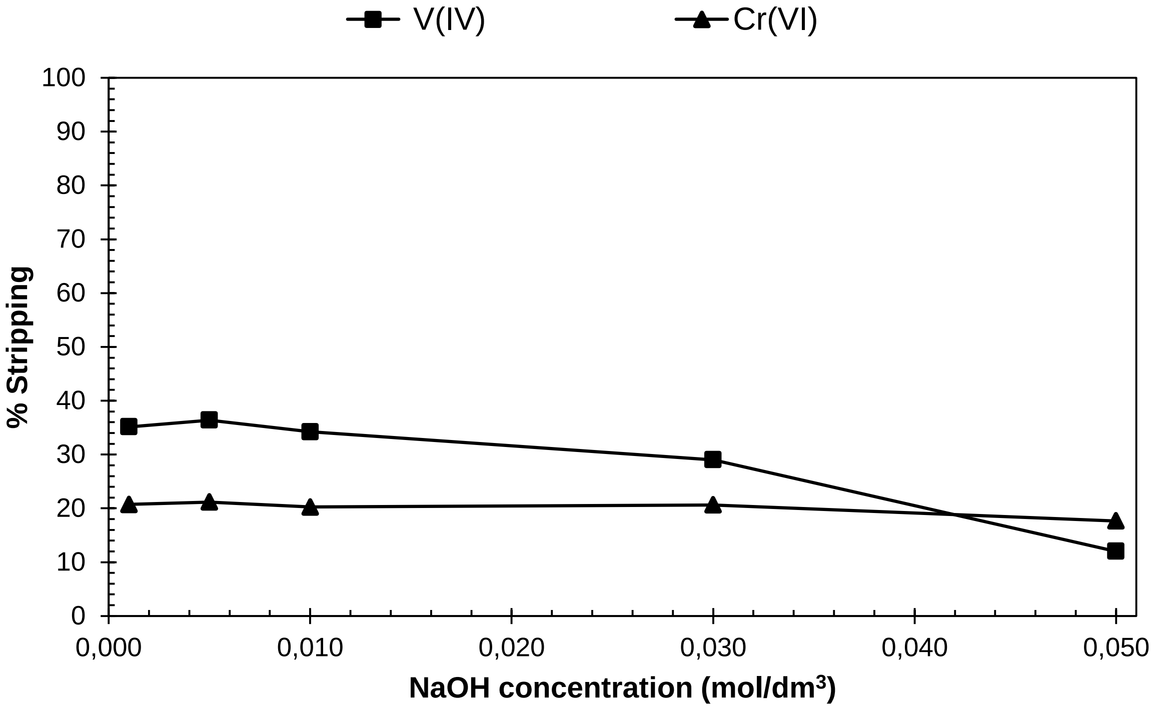

Figure 4-8: **The effect of NaOH concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio 1**

Stripping with NaOH (Figure 4-8) showed little to no selectivity for V(IV) or Cr(VI) in the range of 0.001 mol/dm^3 to 0.05 mol/dm^3 NaOH, where the stripping of Cr(VI) decreased slightly (27.2-23 %), while that of V(IV) decreased from 39.3 to 13.5 %. Aside from the difference in the concentration range of the NaOH investigated, this result contradicts that of Zhao *et al*. (2015), where an increase in NaOH concentration led to an increased stripping of V(V), suggesting that the metal-extractant complex influences metal recovery, while the presence of Cr(VI) may also affect stripping. High recoveries of V(V) obtained by El-Nadi *et al.* (2009) and He *et al.* (2007) also confirmed that the V(V)-extractant complex may be different than that of the V(IV)-extractant complex used in this study and that the former is recovered more easily with NaOH. It furthermore seems that the selectivity of the strippant changes from being V(IV) selective to Cr(VI) selective when the strippant concentration increased above 0.03 mol/dm^3, while the low recovery of V(IV) (< 41 %) confirms the unsuitability of NaOH as stripping agent.

When using NH_4OH (Figure 4-9), a slight selectivity for V(IV) was observed with a small decrease in stripping efficiency (39.7-37.8 %) when the strippant concentration changed from 0.001 mol/dm^3 to 0.01 mol/dm^3, whereas for Cr(VI), a small increase in stripping efficiency (27.1-29.6 %) was observed over the same range. When the strippant concentration increased from 0.01 mol/dm^3 to 0.05 mol/dm^3, a significant decrease in V(IV) stripping was observed (37.8-6.5 %), confirming the trend observed with the other basic strippant NaOH (Figure 4-8), which again contradicts the results obtained by Sahu *et al*. (2013), whereas the Cr(VI) stripping slightly decreased with 6.8 %. For Cr(VI), an optimal stripping percentage of 42.9 % was observed when using 0.1 mol/dm^3 NH_4OH with a 12.24 % co-stripping of V(IV) ($\beta_{Cr(VI)/V(IV)}$ = 3.5).

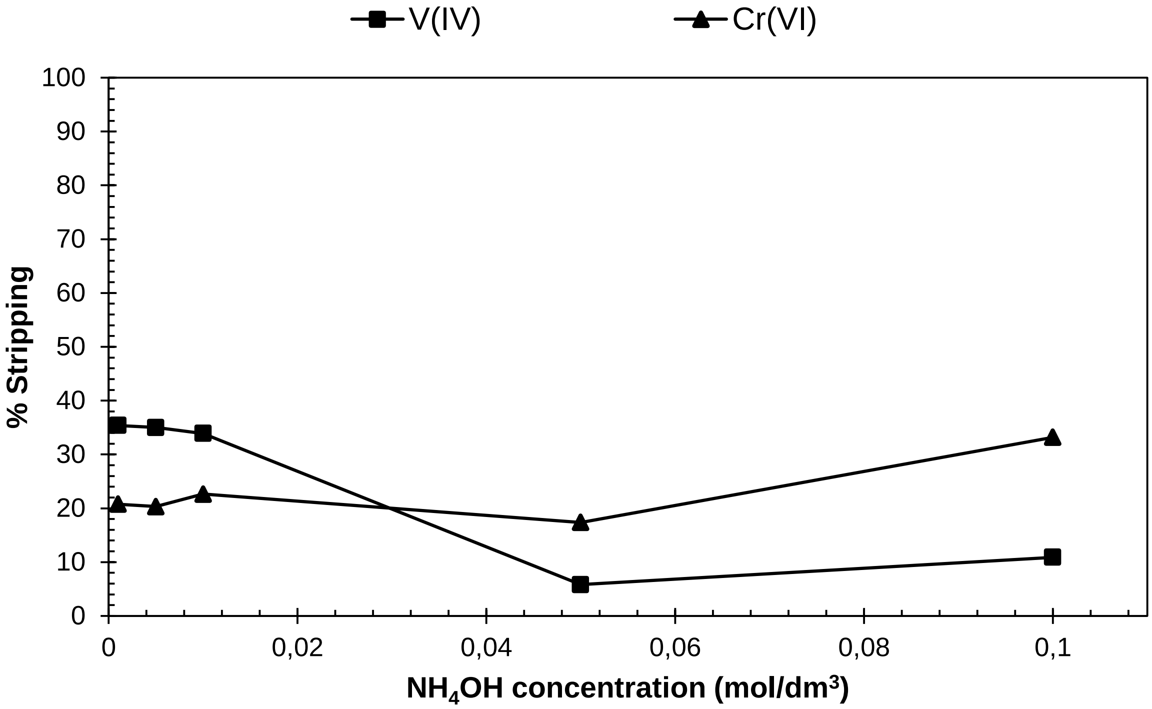

Figure 4-9: **The effect of NH_4OH concentration on the stripping efficiency of V(IV) and Cr(VI) with O/A volume phase ratio 1**

Based on this result, NH_4OH would be considered a suitable strippant for the purification of Cr(VI); however, as previously discussed, V(IV) selectivity is preferable. In view of the superior stripping results obtained when using HCl ($\beta_{V(IV)/Cr(VI)}$ of 5.92), 0.3 mol/dm^3 HCl was chosen as the optimal strippant and concentration for this SX system.

4.3.3 The purification of V(IV) using SX

In Figure 4-10, a flowchart of the optimal extraction and stripping steps is provided, showing how the results obtained in this study could be combined to recover V(IV) from the specific mixture of salts.

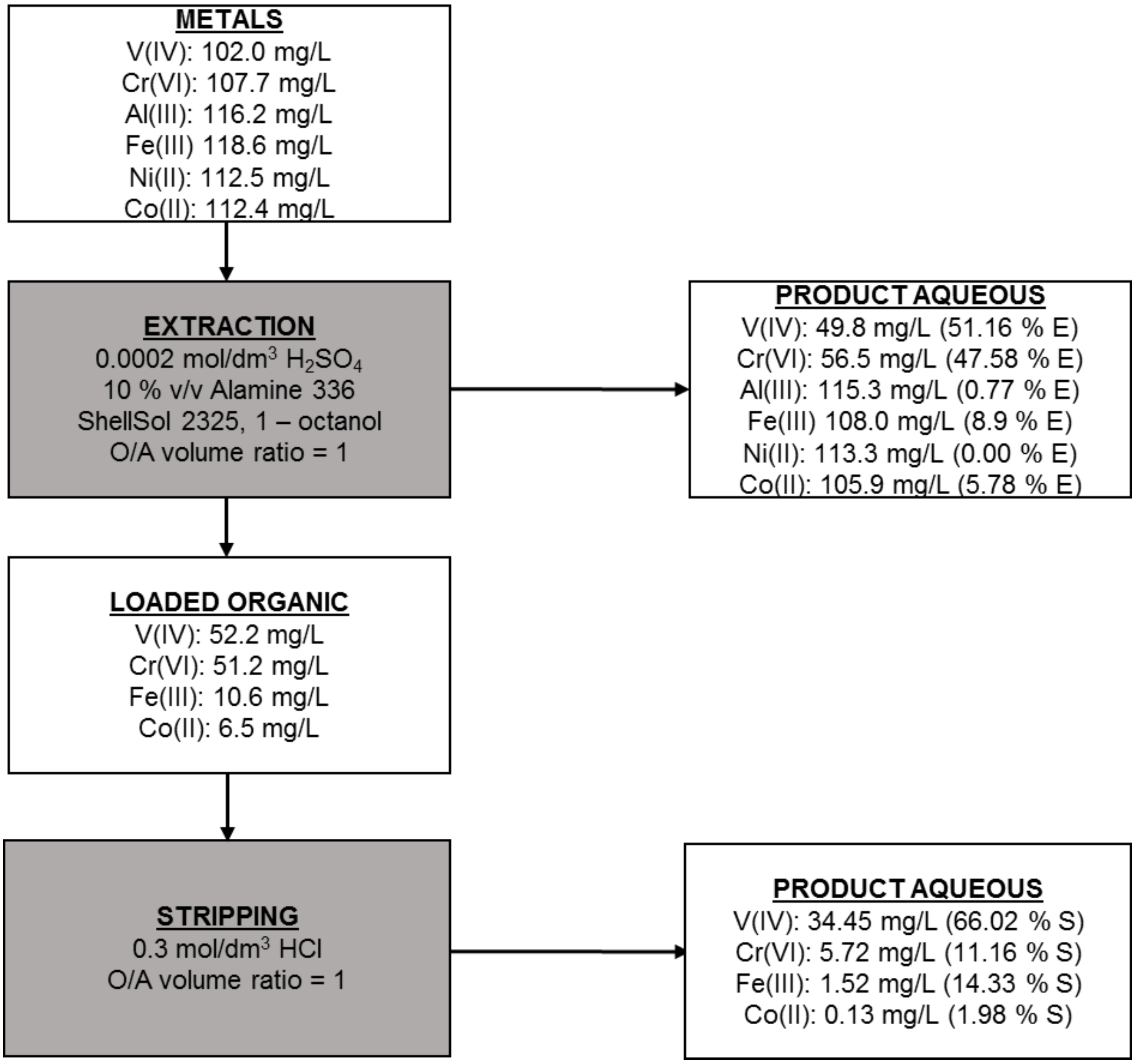

Figure 4-10: A proposed flow chart of the extraction and selective stripping for the recovery and purification of V(IV)

Since more than one component was extracted into the feed, it might be necessary to add an additional scrubbing step (section 2.2.3) (Venkatachalam, 1998) in order to regenerate the extractant for an SX process. As previously mentioned in the stripping studies (section 4.3.2), 10 % v/v of the extractant was used due to limited amounts of the extractant available. Consequently, when using 10 % tertiary amine, Alamine 336 (v/v) as the extractant and ShellSol 2325 and 1-octanol as the diluent and modifier, respectively, with an O/A ratio of 1, 52.2 mg/L V(IV), which is 51.16 % extraction, 51.2 mg/L Cr(VI), which is 47.58 % extraction, 10.6 mg/L Fe(III), which is 8.9 % extraction and 6.5 mg/L Co(II), which is 5.78 % extraction can be loaded from a 0.0002 mol/dm^3 feed solution. When using a 0.3 mol/dm^3 HCl strip solution with an O/A volume ratio of 1, 34.45 mg/L V(IV) of the original 102.00 mg/L V(IV), 5.72 mg/L Cr(VI) of the original 107.7 mg/L, 1.52 mg/L Fe(II) of the original 118.6 mg/L and 0.13 mg/L Co of the original 112.4 mg/L can be recovered.

4.3.4 MBSX

4.3.4.1 Equilibrium study

The extraction of V(IV) and Cr(VI) using a supported ionic liquid membrane with tri-n-octyl methyl ammonium chloride (TOMAC) was investigated by Nosrati *et al*. (2013). The authors found that the extraction kinetics increased from an acidic aqueous feed solution without adjusting the pH. Furthermore, the authors reported that selective stripping was obtained from a V(IV) and Cr(VI) loaded organic. According to a study conducted by Palet *et al.* (1995), the selectivity of V(V) extraction from a synthetic solution differs between normal SX and supported liquid membrane (SLM) extraction. The co-extraction of Mo with Aliquat 336 was obtained from SX experiments; however, the transport of Mo through the SLM was not observed. Therefore, the selectivity may increase depending on the purification method. The authors, however, did observe the co-extraction of Cr(VI) with V(V) when using either SX or SLM with Aliquat 336 as the extractant. In this study, the separation of V(IV) from Cr(VI), Fe(III), Al(III), Ni(II) and Co(II), using the optimised operating variables from the extraction experiments (20 % v/v Alamine 336 as extractant, ShellSol 2325 as the diluent and 1-octanol as phase modifier, from a 0.0002 mol/dm^3 H_2SO_4 aqueous feed solution), was investigated as a function of time (1 minute to 120 minutes) from an HFM (Figure 4-11). Using MBSX V(IV), Cr(VI) and Fe(III) were extracted, confirming the general trend observed from the batch extractions. However, the co-extraction of Al(III) and Co(II) was not observed, as seen from the SX experiment in section 4.3.1.1, confirming that selectivity may change based on the purification process, as reported by Palet *et al*. (1995). For V(IV), extraction equilibrium was observed after only 15 minutes (100 %) with 65 % and 5.58 % co-extraction of Cr(VI) and Fe(III), respectively.

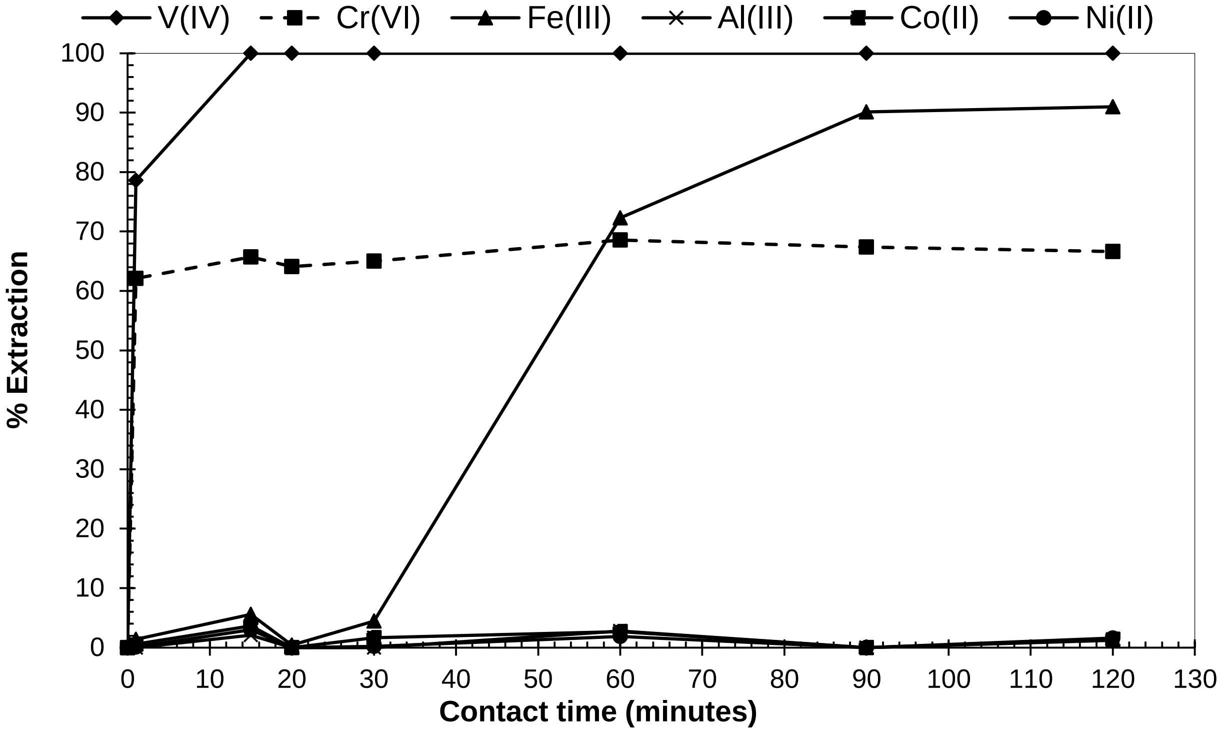

Figure 4-11: **The MBSX of V(IV) and impurities with 20 % v/v Alamine 336 in ShellSol 2325 with 1-octanol as phase modifier and O/A volume ratio of 1**

The extraction efficiency for Fe(III) after 15 minutes was similar to that found using SX (5.8 %, seeFigure 4-4); however, for V(IV) and Cr(VI), the extraction increased from 84.81 % and 55.9 % (Figure 4-11) to 100 % and 65 %, respectively, when using MBSX. This suggests that the speed of extraction for V(IV) and Cr(VI) improved when using MBSX as separation method. This is confirmed by the extraction efficiency of Fe(III), which remained close to 0 for the first 30 minutes, which is comparable to the 8.6 % obtained using SX, but then increased significantly from 4.5 % (30 minutes) reaching 91 % after 120 minutes. For Cr(VI), the extraction remained near constant (62.1-66.64 %) when the extraction time increased from 1 minute to 120 minutes. Since V(IV) extraction attained a maximum after 15 minutes (100 %), with no co-extraction of Fe(III), 15 minutes was chosen for optimal V(IV) selectivity.

4.3.4.2 Effect of extractant concentration

The effect of the extractant (Alamine 336) concentration (1 % - 20 % v/v) on the extraction of V(IV) and the chosen salts was investigated. The conditions were identical to those presented in section 4.3.1. The extraction results for V(IV) only are shown in Figure 4-12, showing that the extraction efficiency increased with an increase in extractant concentration.

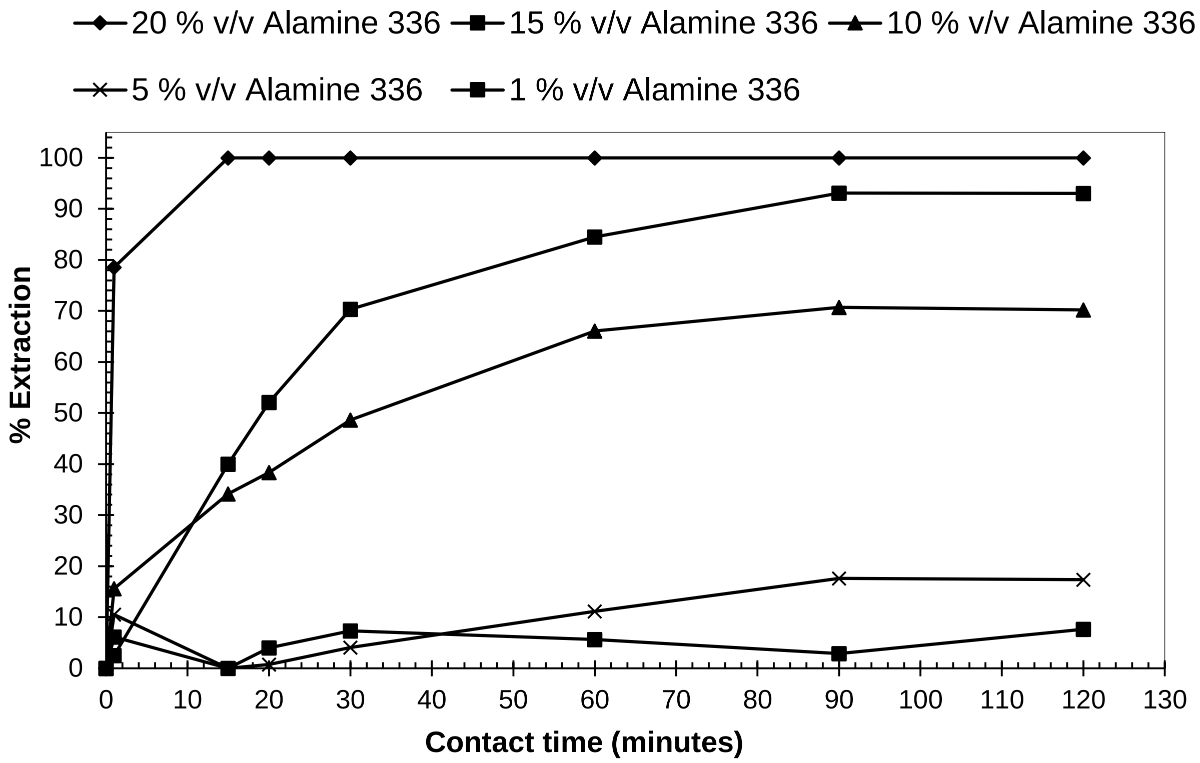

Figure 4-12: The extraction of V(IV) from 0.0002 mol/dm^3 H_2SO_4 with Alamine 336 at different concentrations using ShellSol and 1-octanol as phase modifier and O/A volume ratio 1

Again, this result was expected due to the presence of more extractant available for metal-extractant coordination. After 90 minutes, where equilibrium had been reached irrespective of the Alamine 336 concentration, extraction increased from 2.9 to 93 % when the extractant concentration increased from 1 to 15 % v/v. Interestingly, the equilibria for all concentrations of Alamine 336 (1 % – 15 % v/v) were reached only after 90 minutes, while the extraction with 20 % v/v Alamine 336 reached its equilibrium after only 15 minutes. Similar results were discussed in section 4.3.1.4, where the excess of extractant, Alamine 336, resulted in precipitation. For this reason, it was decided that the most suitable results were attained when using 15 % v/v Alamine 336 and extracting for 60 minutes, thereby avoiding precipitation while still obtaining high recoveries of V(IV) (84 %) and Cr(VI) (62 %), with no co-extraction of Fe(III).

4.4 Conclusion

The extraction and purification of V(IV) from a mixture of salts was investigated as a function of Alamine 336 concentration, diluents, H_2SO_4 concentrations, O/A volume molar ratios and extraction times. In view of the results for the SX experiments, amine extractant (Alamine 336) at a concentration of 20 % (v/v) was most suitable for the selective extraction of V(IV) from a mixture containing Cr(VI), Fe(III), Al(III), Ni(II) and Co(II) from 0.0002 mol/dm^3 H_2SO_4. Optimal conditions were determined to be 20 % (v/v) Alamine 336 in ShellSol 2325, 5 % (v/v) 1-octanol, and O/A volume ratio of 1 with a contact time of 90 minutes. Although co-extraction of Cr(VI) was observed (48 %), 51 % V(IV) was extracted in a single contact. Subsequently, the V(IV) in the loaded organic phase was stripped efficiently with a 0.3 mol/dm^3 HCl stripping solution, yielding a recovery of 66 % with slight co-stripping of Cr(VI) (11 %). To remove the Cr(VI) and perhaps negligible amounts of contaminating metals that may have co-extracted from the organic phase, additional steps including a scrubbing step would be required. Ultimately, the results for the purification of V(IV) using MBSX appear to be promising with higher selectivity and extraction kinetics obtained compared to the SX results, suggesting that MBSX could be considered as a purification method for V(IV) from multicomponent electrolyte solutions.

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CHAPTER 5 – EVALUATION AND RECOMMENDATIONS

5.1 Introduction

The growing demand for V in existing as well as new applications has created the opportunity for the development of new or improved V purification methods. This demand is of such magnitude that primary sources have become insufficient and that secondary sources have to be used. While various methods are already used for V recovery, pure V remains expensive. The aim of this study was therefore to develop or improve upon existing SX-based purification methods for the recovery of specifically $VOSO_4.5H_2O$ from a mixed electrolyte solution containing Fe(III), Al(III), Co(II), Ni(II) and Cr(VI) using SX. In this regard, a preliminary experiment was conducted to determine which of the eight extractants investigated was most suitable for V(IV) extraction. This study was followed by a single salts extraction experiment, which provided valuable information concerning V(IV) speciation in aqueous solutions. To further optimise the SX process, operating variables such as i) the extractant concentration, ii) the effect of contact time, iii) the effect of diluent, iv) the effect of organic and aqueous volume phase ratios, v) the effect of acid concentrations, vi) the effect of the stripping agents, and vii) stripping agent concentrations for both the extractants were investigated and optimised. The feasibility of the process was investigated using MBSX with a hollow fibre membrane (HFM), using the optimised SX conditions. In this chapter, the successes and shortcomings of this research will be evaluated based on the aims presented in Chapter 1.

In Chapter 3, it was shown that oxime (LIX-84-IC)-based and amine (Alamine 336)-based extraction is suitable for V(IV) purification from low H_2SO_4 concentrations. Additionally, the single salts study confirmed the complexity of V speciation when in $V – H_2O – H_2SO_4$ solutions, while confirming the possibility of an impurity effect on extraction. It became clear that the V was probably present as various V species. It was further shown that the results from this chapter correlated with results presented in literature. Subsequently, the optimisation of V(IV) purification using oxime extractant, LIX-84-IC, from a 0.1 mol/dm^3 H_2SO_4 feed solution, is presented in Chapter 3. Optimal conditions were determined as 30 % (v/v) LIX-84-IC with a contact time of 15 minutes using cyclohexane and 1-octanol as the diluent and modifier, respectively, and an O/A volume ratio of 1:1. V(IV) stripping was achieved using a 0.05 mol/dm^3 NaOH solution with a yield of 90 %, while the purity was increased from 15.02 % to a satisfying 99.96 %. The chapter concludes with MBSX data that showed that mass transfer limitations are probably present when using MBSX, and the increased equilibrium time and lower selectivity obtained indicated that purification under the optimised conditions determined in SX is not suitable for MBSX.

In Chapter 4, the SX process was optimised using the amine-based extractant Alamine 336. Lower H_2SO_4 concentrations confirmed that amine extractants are most efficient in less acidic solutions, and since amine extractants follow an anion exchange extraction mechanism, it is clear that metal complex anions were present in the specific pH range. Optimal conditions using SX with this amine-based extractant were determined as 20 % (v/v) Alamine 336 from a 0.0002 mol/dm^3 H_2SO_4 feed solution with a contact time of 90 minutes using ShellSol 2325 and 1-octanol as the diluent and modifier, respectively, and an O/A-volume ratio of 1:1. Selective V(IV) stripping was achieved using a 0.03 mol/dm^3 HCl solution with a yield of 29 %, while the purity of V(IV) increased from 15.26 % to 90.42 %. For the extraction studies conducted using MBSX, higher selectivity and recovery were obtained with no significant change in extraction kinetics, confirming the feasibility of V(IV) extraction using MBSX.

5.2 Evaluation

5.2.1 SX

5.2.1.1 LIX-84-IC vs. Alamine 336

To evaluate the extractants used in this research, the efficiency of each was calculated in terms of the distribution factor (D), the % purity and the % yield of V(IV) for both LIX-84-IC and Alamine 336. These particular values were calculated for each stage (extraction and stripping using LIX-84-IC and extraction, scrubbing and stripping using Alamine 336) of which the results are presented in Table 5-1.

Based on the calculated values shown in Table 5-1 when comparing the two extractants, the D factor for V(IV) during the extraction stage was highest (49.0) when using LIX-84-IC with a significantly lower D factor obtained (1.05) when using Alamine 336. For the stripping stage, the D ratio of V(IV) using Alamine 336 was relatively low (0.47) with good V(IV) recovery; however, higher recovery of V(IV) was obtained using LIX-84-IC with a D factor of 0.12. The initial purity of V(IV) in the respective synthetic solutions before extraction was 15.02 % (LIX-84-IC) and 15.26 % (Alamine 336), respectively. When using LIX-84-IC, after a single extraction stage, the purity increased from 15.02 % to 98 % with a yield of 64 %. After a single stripping stage, the yield increased to 88 % with a satisfactory V(IV) purity of 99.98 %. When using Alamine 336, after a single extraction/scrubbing step, the purity of V(IV) increased from 15.2 % to 77 % with a yield of 39.7 %. A single stripping stage resulted in a further loss of V(IV), which resulted in an aqueous strip raffinate of 27.1 % V yield and an increase in purity from 77 % to 95.3 %.

Table 5-1: The D ratio, the purity and the yield of V(IV) calculated from the results obtained when using LIX-84-IC and Alamine 336 in the extraction, scrubbing and stripping steps

Extractant	LIX-84-IC		Alamine 336	
V(IV)	Extraction	Stripping	Extraction	Stripping
D	49	0.12	1.05	0.47
∝	98.00%	99.98%	77.00%	95.30%
φ	64 %	88 %	39.7 %	27.10%

In conclusion, to meet the aim set for this MSc project, a feasible purification process by separating V(IV) from a multi-component electrolyte solution containing Fe(III), Al(III), Co(II), Ni(II) and Cr(VI) needs be developed in order to meet the expected growing demand for this transition metal. From the SX studies conducted using two unique extractants, and from the evaluation thereof discussed in the above paragraph, both the extractants generated positive results with a significant increase in the purity of V(IV) from the respective synthetic solutions. The hypothesis that both the extractants would be suitable for the purification of V(IV) as predicted in the literature chapter, was therefore confirmed. From the two possible purification routes to follow, based on the discussion above, the most suitable method for the purification of V(IV) from the chosen salts was when using the oxime extractant, LIX-84-IC, under the optimised conditions determined in Chapter 3.

5.2.2 SX equilibrium vs. MBSX equilibrium

In this section, the results obtained from the SX studies and the MBSX studies are compared to discuss the feasibility of the purification of V(IV) via an MBSX process. A significant change in the equilibrium time was required comparing SX and MBSX, whereas Figure 3-2 illustrates the change in the selectivity of the extractant obtained with SX compared to the selectivity attained when using MBSX (refer to the discussion in section 3.4.1 in Chapter 3). When using Alamine 336, as discussed in section 3.4.1 of Chapter 3, a difference in the equilibrium time as well as selectivity was observed, as seen in section 3.4.1 of Chapter 3.

In conclusion, when using LIX-84-IC, rapid extraction kinetics (Figure 3-3) as well as higher selectivity (Figure 3-5) from the SX experiments were observed, whereas when using Alamine 336, MBSX was more suitable where no significant change in the equilibrium times was observed, while higher selectivities for V(IV) were obtained. These results suggest the suitability of an SX purification route when using the oxime-based extractant LIX-84-IC, whereas purification via MBSX would be feasible when using the amine-based extractant Alamine 336.

5.3 Recommendations

The authors have the following recommendations for future work for the batch SX studies:

- This purification method could be optimised in a multi-stage pilot plant to obtain higher yields and improved purification of the desired metal.
- Although high purity V(IV) is already achievable, it is recommended that a study be conducted where various scrubbing agents are investigated, which could possibly further increase the purity of V(IV) and also generate the opportunity for the regeneration of the extractant, which could be advantageous for industrial application.
- Since the speciation of V in aqueous solutions can be highly complex, the authors recommend accurately determining the respective V species present in the synthetic solution using suitable analytical techniques, such as a UV detector, from which a complete extraction reaction mechanism can be deduced.
- Positive results have been obtained using the cationic exchange, oxime-based extractant LIX-84-IC and anionic exchange, amine-based extractant, Alamine 336. Future studies using other extractants, not investigated in this study, similar to LIX-84-IC and Alamine 336, could produce higher yields and increased purities.

The authors have the following recommendations for future work for the MBSX studies:

- To possibly increase the slow mass transfer observed, the authors recommend that further experimental work should be conducted where specific operating variables could be investigated and experimental conditions could be adjusted to possibly increase the mass transfer rate. Furthermore, a HFM was used throughout this study; however, investigating other membrane types (examples thereof mentioned in section 2.2.4 of the literature chapter) could generate more extraction data, which could determine whether the slow extraction kinetics can be attributed to a chemical or physical resistance.

APPENDIX A

A: Screening experiment

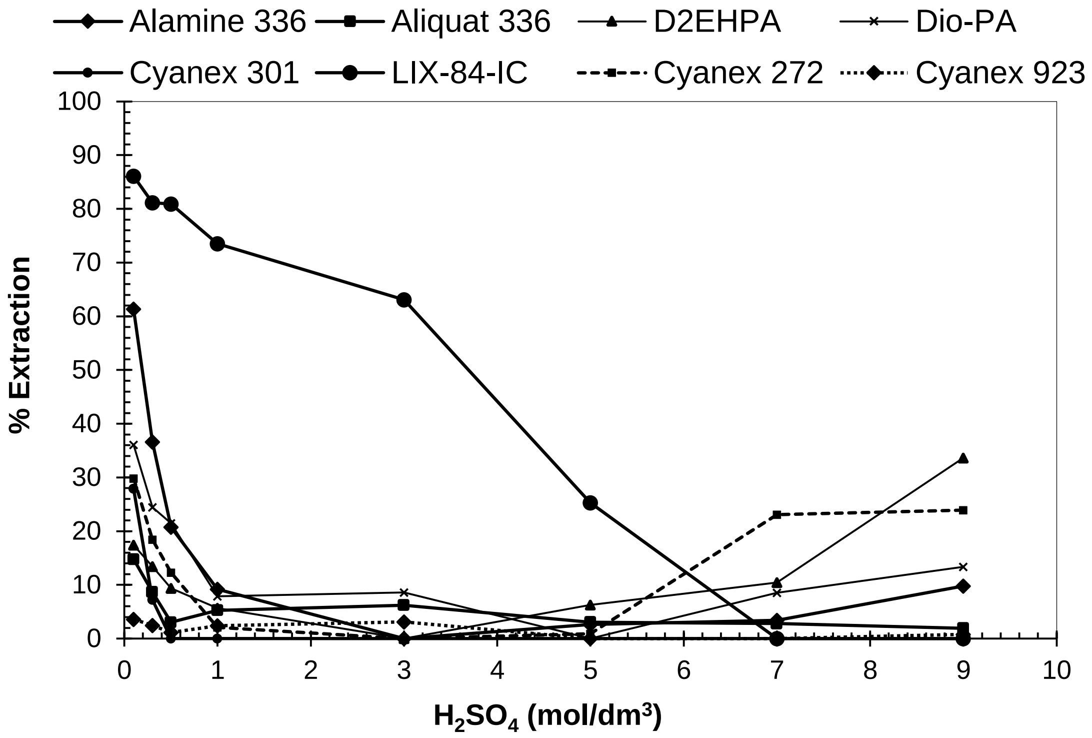

Figure A1: **The extraction of V(IV) from 0.0002 mol/dm^3 H_2SO_4 with various extractants at different concentrations using cyclochexane and 1-octanol as phase modifier and O/A volume ratio 1**