RECOVERY OF VANADIUM AND NICKEL FROM OIL FLY ASH

by

© Jiabin Liu

A Thesis submitted to the

School of Graduate Studies

in partial fulfillment of the requirements for the degree of

Master of Engineering

Civil Engineering Department

Faculty of Engineering and Applied Science

Memorial University of Newfoundland

May 2017

St. John's Newfoundland

ABSTRACT

Oil fly ash (OFA) is a by-product originated from burning of crude and residual oil for energy. OFA is defined as hazardous waste in many countries because it is acidic and contains harmful heavy metals, which raises the risk of its contamination to the surrounding environment. However, OFA contains up to 90% carbon and numerous studies have been conducted on developing adsorbents derived from OFA. The group in the Faculty of Engineering and Applied Science at Memorial University has been focusing on the research that utilizes modified OFA in water and wastewater treatment for the last seven years. However, the cleaning of the OFA prior to use has not been systemically investigated yet. In addition, studies showed that OFA can be a potential source for vanadium and nickel and it is possible to recover these metals from the OFA cleaning process, so that the economic value of the OFA can be further maximized.

The selection of OFA cleaning and metal (mainly vanadium and nickel) recovery processes is heavily dependent on the properties of the OFA such as ash content, metal composition & oxidization state, sulfur content, pH, and particle size. Although various methods with high recovery rates had been proposed in literatures, they may not obtain the same result with different OFAs. Therefore, the purpose of this study is to develop a practical integrated cleaning and metal (vanadium and nickel) recovery process specifically for the OFA that the group has been dealing with. In this work, the leachability of five major metals (vanadium, nickel, iron, magnesium, and aluminum) by sulfuric acid, sodium hydroxide and ammonia at different concentrations were tested.

After identifying the preferred leaching conditions, three metal recovery methods (i.e., chemical precipitation, ion exchange resin and solvent extraction) were evaluated. Based on the results, three complete metal leaching and recovery processes were proposed and their performances were assessed by mass balance calculation.

Briefly, the study showed that both strong acid and strong base can effectively extract vanadium from the OFA, however, base leaching may require additional leaching processes to recover nickel and carbon. Therefore, strong acid, sulfuric acid in this case with concentration ranging from 0.5N to 1N, solid/liquid ratio of 1:10 and mild heating, was selected for the sequential selective metal recovery tests. Among those three metal recovery processes, solvent extraction showed better extraction rate and selectivity. Between the selected solvents, Trioctylamine (TOA) is preferred over Di-(2-ethylhexyl) phosphoric acid (D2EHPA) for high iron OFA (SPP) as it only extracts vanadium (V), while D2EHPA co-extracts both vanadium and iron. The complete integrated process showed that 89.7% nickel and 59.2% of vanadium was recovered by acid (sulfuric acid) leaching and TOA solvent extraction. The study also found that the metal content in OFA has great impact on the recovery rate as higher metal concentration in the leachate leads to higher extraction and precipitation rates. Since the vanadium and nickel content in OFA varies greatly, a segregation process is recommended to treat high carbon OFA and high metal OFA separately.

ACKNOWLEDGEMENTS

I would first like to express my sincere gratitude to my supervisor and my mentor, Dr. Tahir Husain. I really appreciate his guidance, motivation, patience, and trust.

I would also like to thank all the group members and other graduate students who are working in the Environmental Lab (NRPOP Lab). Working with these knowledgeable, dedicated and friendly individuals is very enjoyable. Thanks to all the great staffs and technicians from the Faculty of Engineering and Applied Science and CREAIT Lab Network for their valuable assistance.

Lastly, I would like to thank my parents, my sister and my brother-in-law for their continuous encouragement and support throughout my life. This accomplishment would not have been possible without them.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

BV	Bed volume
CFA	Coal fly ash
D2EHPA	Di-(2-ethylhexyl)phosphoric acid
EHEHPA	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
ESP	Electrical static precipitators
OFA	Oil fly ash
RCE	Rotating cylinder electrode
TBP	Tri-n-butyl phosphate
TOA	Trioctylamine

1 Introduction

1.1 Background

Oil fly ash (OFA) is a type of carbon enriched solid waste generated from burning of crude and residual oil. Transition metals are naturally presented in the fuel oil and during combustion they react with oxygen and condense in the oxidized form with unburned carbon as particles when temperature drops (Di Pietro et al., 2009). These particles are then collected by electrostatic precipitators (ESP) as OFA.

OFA is extensively produced in those countries which consume crude and residual oil for relative inexpensive energy. It is estimated that 3 kg of OFA will be generated when burning one kiloliter of fuel oil (Hsieh & Tsai, 2003). In Taiwan, the annual production of OFA is 43,000 tons and in Italy the annual production rate is about 40,000 ton (M. Seggiani et al., 2002). In Saudi Arabia, more than one hundred tons of OFA are produced daily from the Shoaibah Power Plant and the Rabigh Power Plants in the western region. In Canada, 90,000 tons of OFA is generated annually by burning petroleum coke for heating in the oil sand industry (Gosselin et al., 2010).

Currently, most of the OFA is disposed of through landfilling. In some cases, cement or lime are added to limit the migration of the heavy metals in OFA to adjacent groundwater. However, landfilling can be problematic due to the presence of the polycyclic compounds and the soluble heavy metals in OFA. Therefore, OFA is considered as hazardous waste in many countries, and as a result, the cost of its disposal increases dramatically (Caramuscio et al., 2003). Beside its threat to groundwater resources, higher risk of chronic impairment of respiratory system is also expected for those who work or live in the vicinity of the OFA-generating power plants (Tatár et al., 2005).

1.2 Utilization of OFA

The utilization of the fly ash derived from coal combustion has been studied widely, including construction material, adsorbents, agriculture, geopolymers etc., which are summarized in the literature reviews published by Blissett and Rowson (2012) and Ahmaruzzaman (2010). Comparing to coal fly ash (CFA), the composition of OFA varies greatly. For example, OFA contains much less silica (Si) and aluminum (Al), which makes it less favorable to be used as construction material. On the other hand, OFA comprises fine porous particles and has high carbon content, thus, it can be an potential precursor of activated carbon and numerous studies have already been conducted on this application (Azhar Uddin et al., 2007; Caramuscio et al., 2003; Davini, 2003; Maurizia Seggiani et al., 2005; Maurizia Seggiani et al., 2007).

It is known that the porous characteristics of activated carbon are greatly affected by the nature of its raw precursor. Studies showed that the micro-pores of OFA is limited, even after activation (Caramuscio et al., 2003; Maurizia Seggiani et al., 2005). Therefore, it is more suitable for removing large molecular pollutants such as dyes and hydrocarbons

(Andini et al., 2008; Mofarrah, 2014). In addition, OFA has good thermal stability, its applications in flue gas treatment could also be feasible (Davini, 2002).

1.3 Impurities in OFA

The impurities in OFA comprise metal oxides and sulfates which are mainly derived from ash bearing fuel. The level of impurity ranges from 1% to 60 % depending on the fuel type as well as the combustion conditions. Major metals in OFA include vanadium (V), nickel (Ni), iron (Fe), magnesium (Mg) and aluminum (Al). Usually, Mg is not significantly found in fuel oil but it is added as a fuel additive to prevent system corrosion (Rasoulnia & Mousavi, 2016). Fe in OFA is possibly originated from the system corrosion. Prior to utilization, these impurities must be removed to obtain clean carbonaceous material.

Among the metal impurities, V and Ni are the major ones and they are also the most valuable ones. For instance, vanadium pentoxide (V_2O_5) is commonly used as the catalyst for producing sulfuric acid from sulfur dioxide. OFA may contain up to 13% V (Ni up to 7%), which is comparable to the conventional V enriched sources such as stone coals and black shale (<5%)(Cai et al., 2013; C.-x. Li et al., 2010; M. T. Li et al., 2012; Nazari et al., 2014). Therefore, recovery of V and Ni from OFA can be economically feasible.

1.4 Objective of this Study

The research group in the Faculty of Engineering and Applied Science at Memorial University has been studying the application of OFA in water and wastewater treatment extensively for the past seven years. However, in our previous researches, the purification of OFA has not been investigated in detail yet and excessive acid and water were consumed, which would generate significant amount of unnecessary wastewater if implemented in real applications. In addition, studies showed that OFA can be a potential source for V and Ni, therefore, the beneficial reuse of OFA would be maximized if V and Ni can be recovered from the wastewater generated from OFA cleaning.

Although V and Ni recovery techniques had been proposed by various literatures, they may not be suitable for all OFAs which have distinctive physical and chemical properties. In addition, only one technique was proposed in most literatures and there is no horizontal comparison among different ones, which indeed is an essential component in determining the most suitable process in real applications.

The purpose of this study is to develop an integrated OFA cleaning (leaching) and metal (V and Ni) recovery process specially for the OFA which the group has been dealing with. In this work, various leaching and recovery methods had been tested and their mechanisms were discussed.

1.5 Overviews of this Thesis

Chapter 1 of this thesis describes the background of OFA and its current management. It also outlines the justifications and objectives of this research. Chapter 2 summarizes the literature reviews on the current research regarding metal extraction from OFA as well as V and Ni recovery. Chapter 3 details the experimental work conducted in this research.

The whole research consists of two major components: metal leaching and selective recovery. For metal leaching, different hydrometallurgy methods were evaluated with sensitivity analyses. After identifying the most suitable leaching method with its conditions optimized, various metal recovery methods, such as chemical precipitation, ion exchange resin and solvent extraction, had been tested. Chapter 4 discusses the results of the experiment. Chapter 5 concludes the findings of the study and summarizes the recommendations for future work.

2 Literature Review

2.1 Metal Extraction

Roasting followed by leaching is one of the most common approach for V and Ni recovery from OFA, as it significantly removes the carbonaceous fraction and concentrates the metals in the roasting residual, leading to higher precipitation rate and lower water consumption. With the presence of sodium carbonate (Na_2CO_3), V forms water soluble sodium metavanadate ($NaVO_3$) (Tsai & Tsai, 1998b). After that ammonia or ammonium salt is added to form ammonium metavanadate (NH_4VO_3) precipitate and it is finally pyrolyzed to V_2O_5 at the temperature in between 500°C and 600°C.

Vitolo et al. (2001) proposed a direct roasting approach with acid leaching. The results showed that the leaching and precipitation yield of V reaches 99% and 89% respectively, when the roasting temperature is at 850°C. Further increasing the roasting temperature, however, decreases the yield due to evaporation losses as well as formation of refractory alloy. Holloway and Etsell (2004) modified the salt roasting technique that the OFA was first pre-ignited to remove carbon and sulfur, then roasted at elevated temperature to form water soluble $NaVO_3$ by mixing with alkali salt, such as sodium carbonate (Na_2CO_3), sodium chloride (NaCl) and sodium sulfate (Na_2SO_4). Finally, the hot roasted ash liquor was poured into water directly and V was precipitated after cooling. The authors found that roasting efficiency is highest (in between 75% and 85%) when NaCl is used with the dose ranging from 20% to 30% at temperature from 850°C to 900°C for 2 to 3 hours.

Despite the advantages of roasting, it is worth noting that the roasting technique generates considerable emissions and carbon cannot be reused. In addition, the OFAs with less impurities may have higher ignition temperature or low reactivity, which may require more energy input (Maurizia Seggiani et al., 2007).

Alternatively, hydrometallurgical extraction and recovery of V and Ni from OFA have brought great research attention. Tsai and Tsai (1998a) evaluated the correlation between metal extraction rate and different leaching medias such as sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and ammonia (NH_3). The authors found that H_2SO_4 extracts V, Ni and Fe altogether and the extraction rate increases as the acid concentration increases. However, this trend is not linear, once the pH of the leaching solution is lower than 1, the increasing trend of the leaching rate diminishes gradually and the V extraction rate stabilizes at around 86% when acid concentration is at 2N. When leached by NaOH, all three metals (V, Ni and Fe) are partially extracted at pH lower than 13. Once the pH of the solution is higher than 13, only V can be extracted, while the other two metals are hardly leachable, which indicates good V selectivity of NaOH. The leachability of V is lower by NH_4OH than by NaOH, which is about 60%, and about 60% for Ni. Comparing with acid leaching, alkaline leaching (e.g. NaOH) has its advantage that only V can be extracted (Parvizi et al., 2012). However, additional acid leaching will be required if Ni needs to be recovered as well. Tokuyama et al. (2003) compared the leaching efficiency of hydrochloric acid (HCl) and H_2SO_4. The study showed that HCl and H_2SO_4 give insignificant difference in terms of extraction percentage. The authors also suggested a solid liquid (S:L) ratio higher than 1:5. Although lower ratio can extract most of the metals, significant percentage of solution will be retained with OFA, therefore, the extraction rate will be much lower.

Table 1 tabulates the recommended leaching conditions that were reported in various literatures, which shows that relative low concentration of acid, ranging from 0.5M to 1M (1N to 2N), was recommended by most of the literatures. Elevating leaching temperature was adopted to improve the metal dissolution efficiency. The contact time, however, varies greatly, perhaps because some of the authors would like to lengthen the contact time to ensure the complete equilibrium.

In addition to roasting and hydrometallurgical methods, other unconventional techniques have also been reported. Rasoulnia and Mousavi (2016) tested bioleaching V and Ni using fungi and the maximum recovery rate of V and Ni was 97% and 50% respectively. However, this process requires a minimum duration of 7 days. Murase et al. (1998) recovered V and Ni using chlorination and vaporization by N_2-Cl_2 gas, achieving a purity of V more than 99%.

2.2 Vanadium Recovery

2.2.1 Chemical Precipitation

Chemical precipitation, ion exchange resin, and solvent extraction are three most common methods for V recovery. After acid leaching, V can be precipitated by addition of oxidant and followed by pH adjustment. Vitolo et al. (2000) used H_2SO_4 to leach out the metals from OFA, oxidized the leachate by $NaClO_3$ and then precipitated V and Fe red cake maintaining the pH at about 2 to 3 under boiling temperature. However, relative high Na content was found in the precipitate due to addition of Na_2CO_3 for pH adjustment. To solve this problem, the authors introduced repeat washing using acidic solution to eliminate sodium. For chemical precipitation, oxidation is necessary because V^{4+} is more soluble than V^{5+}. Common oxidants include $NaClO_3$, H_2O_2 and $Na_2S_2O_8$, and among them, Tsygankova et al. (2011) suggested H_2O_2 to minimize the contamination of alkali cations.

Table 1 Summary of Recommended Leaching Conditions Reported by Literatures

Reference	Leaching Agent	Concentration	S:L Ratio	Temperature	Time	Maximum Extraction Rate	
						V	Ni
(Tsygankova et al., 2011)	H_2SO_4	5%, 9%	1:4	60°C, 80°C	30-60min	90.0	100.0
(Vitolo et al., 2000)	H_2SO_4	1M	1:3	Boiling	-	80-90	-
(Navarro et al., 2007)	H_2SO_4	0.5M	1:4	n/a	24h	98%	12%
	NaOH	2M	1:4	40°C	24h	85%	Not extractable
	Na_2CO_3	0.66M	1:4	n/a		80%	Not extractable
(Tokuyama et al., 2003)	H_2SO_4	1M	1:5	n/a	6h	95.5	80.1%
	HCl	1M	1:5	n/a	6h	94.2	79.5%
(Nazari et al., 2014)	H_2SO_4	19.47v/v%	9.15wt%	80°C	2h	94.28	81.01%

Vanadium pentoxide (V_2O_5) is usually the final product form. Prior to that, V^{5+} is precipitated as NH_4VO_3 by addition of ammonium salt at pH 8 to 9. Ammonium chloride (NH_4Cl) is commonly used because of its low cost. F. Liu et al. (2013) reported that increasing the addition of NH_4Cl more than theoretical amount prompts NH_4VO_3 precipitation as it decreases the solubility of NH_4VO_3.

2.2.2 Ion Exchange Resin

Ion exchange resin is widely applied for heavy metal removals in water and wastewater treatment and some researchers utilized ion exchange resin to selectively separate Ni and V. Tokuyama et al. (2003) developed a process that recovers Ni and V from OFA based on different selectivity of different ion exchange resins including Diaion CR20, Duolite C467, and Diaion SK1B. Firstly, Ni and other metals were leached by water and then Ni was selectively recovered by Diaion CR20. V and Fe in water washed fly ash was extracted by H_2SO_4 and V was separated from Fe by Duolite C467. It was reported that more 80% of Ni and V can be recovered.

2.2.3 Solvent Extraction

Solvent extraction has been a conventional metal recovery technique since 1956. Common solvents for V extractions are organophosphorus acids, amines, and hydroxyoximes (Zhang et al., 2014). The extraction efficiency of the solvent is dependent on the valance of V and polymeric degree of the V complexes. In OFA leaching solution, V(IV) and V(V) are the main V oxidization states, and generally organophosphorus acids, such as Di(2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-

2-ethyl hexyl ester (EHEHPA) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), are used for extracting V(IV), while amines, such as trialkylamine (Alamine 336), trioctylamine (TOA) and 5-dodecylsalicylaldoxime (LIX 860-I), are applied for V(V).

The interaction between the solvent and V is affected by the form of the V complexes, which is dependent on the solution pH and the concentration of V ions. For example, the interaction between D2EHPA and V(IV) is described by Equation 1 (Hu et al., 2014). It indicates that the solution should be acidic to form VO^{2+}, as shown in Figure 1, which prompts cationic ion exchange with H^+ from D2EHPA. However, if the pH of the solution is too low, the extraction rate will decrease as the reaction moves towards the left side of Equitation 1.

Equitations 2 to 4 describe the extraction mechanism of TOA with V(V), which shows that TOA interacts with $H_2V_{10}O_{28}{}^{4-}$ (Ludmilla D. Kurbatova et al., 2015). As indicated in Figure 1, $H_2V_{10}O_{28}{}^{4-}$ presents in solution at the pH in between 1 and 4, while $VO_2{}^+$ is predominant at low pH, so theoretically the extraction rate of TOA decreases as the solution pH decreases. Other influencing factors include O:A ratio, extraction stages, temperature, contact time, solvent composition, stripping agent & ratio, presence of other metals and etc. Numerous studies have been conducted on optimizing these factors for each specific application.

$$\boldsymbol{VO^{2+} + H_2A_{2(O)} \leftrightarrow VOA_2 \cdot 2HA_{(O)} + 2H^+}$$ **Equitation 1**

$$\boldsymbol{2R_3N + 2H^+ + SO_4{}^{2-} \rightarrow (R_3NH)_2SO_4}$$ **Equitation 2**

$$\boldsymbol{2R_3N + 4H^+ + SO_4{}^{2-} \rightarrow 2(R_3NH)HSO_4}$$ **Equitation 3**

$$\boldsymbol{2(R_3NH)_2SO_4 + H_2V_{10}O_{28}{}^{4-} \rightarrow (R_3NH)_4H_2V_{10}O_{28} + 2SO_4{}^{2-}}$$ **Equitation 4**

For V(IV) extraction, Zeng and Cheng (2009) reported that solvent containing 5%-20% D2EHPA in kerosene is able to rapidly extract VO^{2+} at the pH ranging from 1.5 to 2.5 and stripped with weak H_2SO_4. Similarly, Y.-h. Liu et al. (2010) extracted V(IV) from stone coal using D2EHPA and suggested that the pH of the solution should be in between 2.5 and 2.8 as further increases the pH could lead to hydrolysis of Fe and Al. In addition, longer contact time increases the extraction rate of V(IV) but Fe(III) is also dramatically extracted, if it exceeds 10min. H_2SO_4 was selected as the strippant and the authors reported that higher acid concentration improves stripping but also leads to excess residual acid, leading to more consumption of ammonia (NH_4OH). Therefore, 1.5M of H_2SO_4 was selected. The optimal conditions, as listed in Table 2, were determined considering all factors, which obtained an overall V recovery rate of 70%.

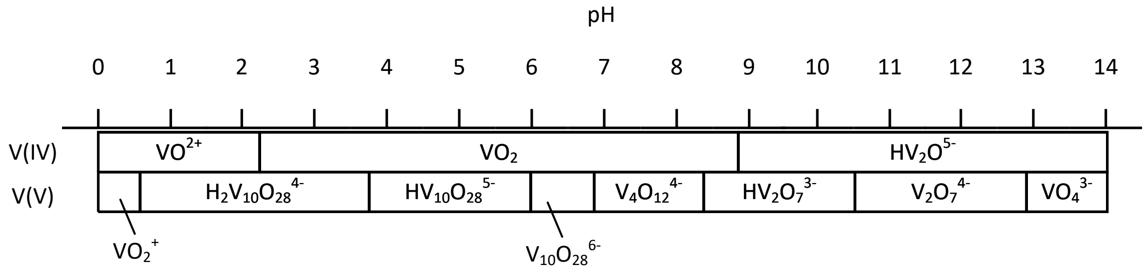

Figure 1 Vanadium (IV) and (V) Speciation Table at 5,000ppm [Retrieved from the speciation diagrams reported by Cai et al. (2013) and W. Li et al. (2013)]

Noori et al. (2014) tested the mixture of D2EHPA and Cyanex 272 to separate V and Ni at different pH ranges. The authors' preliminary experiments found that the extraction of V(IV) by both D2EHPA and Cyanex 272 is predominant at pH lower than 3, while Ni(II) can be extracted at high rate by both solvents as well at pH 5 to7. However, the more expensive Cyanex 272 showed more distinguished optimal pH range for V(IV) and Ni(II), while co-extraction of both metals was found for D2EHPA. To balance the cost of the solvents and performance, the authors proposed to add Cyanex 272 to D2EHPA at the ratio of 0.35M to 0.25M, and the optimal pH for V(IV) extraction is 2.5 and it is 5.5 for Ni(II).

Impurities presented in the leaching solution play an important role in D2EHPA extraction. W. Li et al. (2013) revealed considerable co-extraction of Fe(III) by D2EHPA when the Fe(III) concentration ranges from 5g/L to20 g/L. However, extraction of Fe(II) is limited when the Fe concentration is in the same range. Therefore, D2EHPA extraction usually involves a reduction process of V(V) to V(IV) and multiple stages are also needed due to relatively low partition coefficient.

TOA shows good selectivity on rear metals which form anions in acidic condition as illustrated by Equitation 4. L. D. Kurbatova et al. (2014) tested TOA for extracting V(V), identified that the optimal pH ranges from 2 to 3.5 and further increases pH leads to destruction of decavanadate anion $H_2V_{10}O_{28}^{4-}$. It was also found that increasing the temperature prompts the extraction, thus, the reaction is endothermic. However, higher temperature than 60°C decreases the extraction due to lower stability of V(V)

Table 2 summarizes the recommended conditions of some typical solvents for V extraction. The table shows that the suggested pH range of V extraction is 1 to 3 mostly. The O:A ratio of 1:1 is usually used and the recovery rate of V is very high, up to 99%. H_2SO_4 is the most common strippant for D2EHPA and its concentration is roughly from 10% to 20% (w/w). On the other hand, basic solution is commonly used for TOA stripping

Table 2 Summary of Recommended Solvent Extraction Conditions for Vanadium Recovery Report by Literatures

Solvent Type	Target Vanadium Valance	Solvent Composition	pH	A:O Ratio	Efficiency	Strippant	Stripping A:O Ratio	Stripping efficiency	Reference
D2EHPA [di-(2-ethylhexyl)phosphoric acid]	V(IV)	15% (v/v) D2EHPA, 5% (v/v) TBP in sulfonated Kerosene	1.5	5:1	99%	1.5M H_2SO_4	n/a	n/a	(W. Li et al., 2013)
		10%(v/v) D2EHPA in n-heptane	0.56 (approximated)	1:1	99%	20% H_2SO_4	1:10	98%	(Hu et al., 2014)
		10wt% D2EHPA,	2.5-2.8	2:1, 5 stages	99%	1.5M H_2SO_4	1:5, 4 stages	99%	(Y.-h. Liu et al., 2010)

		5wt% TBP in sulfonated Kerosene							
EHEHPA (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester)	V(IV)	5%(v/v) in sulfonated Kerosene	2	1:1	95%	1M H_2SO_4	1:1, 3 stages	100%	(Cai et al., 2013)
LIX 84-I (2-hydroxy-5-nonylacetophenone oxime)	V(V)	40% in Kerosene	0.35-0.1	1:1	99%	15% NH_4OH	1:3, 2 stages	>99.9%	(Barik et al., 2014)
TOA(Trioctyl amine)	V(V)	0.1mol/L	2-3.5	1:1	n/a	n/a	n/a	n/a	(Ludmilla D.

									Kurbatova et al., 2015)
Aliquat 336(quaternary ammonium Salt)	V(V)	60mM in kerosene	3	1:1	99%	NH_4Cl/NH_4OH (1.5M each)	1:1	48%	(Navarro et al., 2007)

2.3 Nickel Recovery

Nickel is usually recovered from the raffinate after V extraction. Chemical precipitation, solvent extraction and electrolysis are common approaches for Ni(II) recovery. Coman et al. (2013) conducted a literature review that summarizes the Ni recovery methods from various waste streams. The review reported that Ni can be precipitated out in basic condition, typically, at pH from 9 to10. The recovery efficiency increases with increasing Ni concentration.

Barik et al. (2014) used ammonium oxalate ($(NH_4)_2C_2O_4$) to precipitate Ni(II) in acidic solution. It was found that 4 times of stoichiometric amount of ammonium oxalate would be sufficient to complete precipitate the Ni in the raffinate that contains Al(III), Fe(II) and Mg(II). At the solution pH of 2, the Ni concentration dropped from 18.871g/L to 0.025g/L, giving a precipitation efficiency of 99.9%. After that, NiO was obtained by thermal decomposition of nickel oxalate (NiC_2O_4) at 450°C for 2 hours.

Electrolysis method is also commonly applied for recovering Ni from waste effluents. For example, Almazán-Ruiz et al. (2015) proposed the rotating cylinder electrode (RCE) technique to recover Ni(II) from the electroplating rinsing effluent. Since the formation of hydrogen gas becomes more predominant than Ni(II) reduction at pH lower than 4, the pH of the liquid close to the cathode is critical to Ni recovery. To maintain the pH, boric acid is commonly added. The authors reported that the Ni recovery reaches 97% with the pH control at 3.9 to 4.0 and the energy consumption is also reduced.

For ion exchange resin method, Maurizia Seggiani et al. (2006) compared three chelating resins: Lewatit TP-207, Purolite S-930 and Amberlite IRC-748, on Ni adsorption from orimulsion fly ash leachate at pH 4. The results showed that increasing temperature improves the adsorption capacity of all three resins and TP207 exhibited better extraction of Ni(II), which was 1.32mmol of Ni per gram of dry resin. Ni then was stripped from the resin by 4 bed volume (BV) of 10% H_2SO_4.

3 Experimental and Methodology

3.1 OFA Samples

The OFA samples used for this research were collected from two thermal power plants consuming crude oil and heavy fuel oil. Among all the OFA samples that our group has been investigating, two typical samples, SPP and RPP, were selected. SPP is the main sample used for most of the experiments as its V and Ni contents are more representative to the average value of all the OFA samples. On the other hand, RPP sample contains very high level of V and Ni, and it was used for the experiment which requires variable V and Ni concentrations (through dilution).

3.2 Sample Characterization

The sample characterization procedures are briefed in the following sections:

3.2.1 pH

The pH of the samples was measured by a pre-calibrated pH meter after mixing 4 g of OFA with 50ml of boiling water for 3 min, and then the mixture was cooled down to room temperature.

3.2.2 Moisture Content

Roughly 2 g of sample was transferred in a crucible pre-ignited at 650°C and dried in a conventional oven at 105 ± 5°C for sufficient time, typically around 24 hours. After that the sample was cooled down in a dissector to room temperature and the moisture content was calculated by the weight difference.

3.2.3 Ash Content

The ash content of the OFA was determined by igniting approximate 1 g of dried sample in a muffle furnace at 650°C until the weight of the sample remained constant, typically less than 16 hours. After cooling down to room temperature in a desiccator and the ash content was calculated by the weight difference.

3.2.4 Particle Size Distribution

The particle size distribution of the sample was measured by the Horiba Laser Particle Size Analyzer LA-950. A small amount of sample was added into the analyzing pool containing 2% of trisodium phosphate (Na_3PO_4). Dispersant and ultrasound were used to ensure that the sample was homogenously dispersed in the solution prior to measurement.

3.2.5 Morphology

The surface morphology of the OFA was imaged by the scanning electron microscopy and energy dispersive spectroscopy (JEOL JSM 7100F Field Emission SEM). A small amount of sample was adhered on the sample holder by carbon tape. Compress air was used to remove any lose particles, and then the sample was inserted into the SEM for imaging and elemental analysis.

3.2.6 Elemental Analysis

The elemental composition of the OFA was analyzed by the Perkin Elmer 5300 DV ICP-OES. Before analysis, the sample was digested by concentrated HNO_3, H_2O_2, HF, Aqua Regia and HCl separately in a Teflon container at 120°C. Before adding each reagent, the sample was completely dried to eliminate the reagent. After digestion, the sample was diluted by weak HNO_3 and then centrifuged to remove undissolved solids prior to analysis.

3.3 Leaching Tests

The leaching tests were conducted to evaluate the leachability of the major metals in basic and acidic solutions. For acid leaching, H_2SO_4 was selected because HCl, H_2SO_4 and HNO_3 showed marginal difference based on our preliminary study. In addition, H_2SO_4 is the most common acid used in hydrometallurgy comparing with HCl and HNO_3 which are also more volatile.

Various concentrations of the acid were mixed with the OFA at different ratios in conical flasks and shaked in a shaking water bath at different temperatures for 4 hours, ensuring the equilibrium condition. The leachates then were filtered and the metal concentration were analyzed by ICP-OES. For base leaching, NaOH and NH_4OH were tested and the procedure was same as the acid leaching process. After the leaching tests, one optimal leaching condition was selected for all the sequential metal recovery experiment.

3.4 Ion Exchange Resin

Two types of sodium based ion exchange resins, Lewatit TP 207 and Diaion CR11, were tested in this study and their general descriptions are tabulated in Table 3. Since the initial pH of the ion exchange resins is around 8 to 9 and direct mixing of the resin with the metal solution will cause significant precipitation, thus, they were pretreated by water and weak acid to decrease their pH close to the level of the metal solutions.

To compare the performance of the selected resins, a preliminary batch test was conducted that the metal solution was mixed with the resins at the solid: liquid ratio (S:L)=1:1 (v/v) for 10 hours. The pH of the leachate solutions was maintained below 3 to prevent metal precipitation.

After batch test, one resin (Lewatit TP 207 in this study) was selected for column test to develop the adsorption isotherms of the resin. The metal solution leached from RPP OFA was used for this test. It was diluted due to high metal concentration, otherwise the resin may be quickly saturated and its selectivity will be hard to distinguish. Therefore, 50ml of sample RPP solution was diluted to 500ml and passed through the column. The loading rate of the solution was 4-7ml/min, which gives a specific velocity of 5.8 to 10.2 BV/h. The filtrate after passing through the ion exchange resin was collected every five minutes. After saturation (the color of outflow became close to that of inflow), the resin column was flushed by approximate 200ml of deionized water to remove the metals that were not adsorbed, and then it was desorbed by 10% (1.1M) H_2SO_4 at the same specific velocity. The metal concentrations in the sample solutions were analyzed by ICP-OES.

Table 3 Characteristics of Lewatit TP 207 and Diaion CR11*

Properties	Lewatit TP 207	Diaion CR11
Ionic form	Na+	Na+
Functional group	iminodiacetic acid	Iminodiacetate
Matrix	crosslinked polystyrene	Styrene-DVB
Structure	macroporous	Highly Porous
Selectivity	Cu > V (VO^{2+}) > U (UO_2^{2+}) > Pb > Ni > Zn > Cd > Fe(II) > Be > Mn > Ca > Mg > Sr > Ba >>> Na	$Cr^{3+} > In^{3+} > Fe^{3+} > Ce^{3+} > Al^{3+} > La^{3+} > Hg^{2+} > UO^{2+} > Cu^{2+} > VO^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Be^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+}$

* note: the technical data were retrieved from www.lenntech.com

3.5 Solvent Extraction

Two commonly used solvents for V recovery, D2EHPA and TOA, were selected and the compositions of the solvents are listed in Table 4. The metal solution was prepared by leaching RPP sample because it contains the high level of V and Ni, which is more suitable for optimizing the extraction and stripping conditions.

3.5.1 Impact of Oxidation State on Selectivity

D2EHPA and TOA have different selectivity of V(VI) and V(V) as well as Fe(II) and Fe(III). This was firstly confirmed by using synthetic V and Fe solutions. The final concentrations of the synthetic solutions were determined by ICP-OES. The extraction process was conducted in a 60ml glass vial and the solvent and metal solution was mixed at different O:A ratios, then vigorously shaked for 8min. After sufficient settling, the solvent and aqueous layers were separated.

After the preliminary test, the impact of metal oxidization state on the extraction of RPP metal solution by D2EHPA and TOA was tested. Prior to extraction, sodium sulfite (Na_2SO_3) was applied to reduce V(V) and Fe(III) to Fe(II) and V(IV), while hydrogen peroxide (H_2O_2) was used to oxidize V(IV) and Fe(II) to V(V) and Fe(III).

Table 4 Compositions of D2EHPA and TOA Solvent

D2EPH Solvent	TOA Solvent
15% v/v di-2-ethylhexyl phosphoric acid – D2EPH	10% v/v trioctylamine - TOA
5% v/v tri-n-butyl phosphate - TBP	5% v/v tri-n-butyl phosphate - TBP
80% v/v kerosene	85% v/v kerosene

3.5.2 Impact of pH Level

The solution pH is one of the most important factors that affect the extraction efficiency as well as the selectivity of a solvent. Since the initial pH of the RPP metal solution was lower than 1, it was adjusted by addition of Na_2CO_3 or NaOH.

3.5.3 Stripping

For stripping V enriched D2EHPA solvent, only 1.5M H_2SO_4 was tested as the strippant at O:A ratio of 5:1. For V enriched TOA solvent, basic solutions, such as, Na_2CO_3, NaOH and NH_4OH/NH_4Cl can be used(Zhang et al., 2014). Thus, their stripping efficiencies were tested at the O:A ratio of 2:1.

3.5.4 Fe Removal

A preliminary experiment showed that D2EPHA extracts Fe from the metal solution but cannot be stripped by H_2SO_4. Therefore, additional stripping process is required for Fe. Singh et al. (2013) reported the following order of Fe stripping: oxalic acid>phosphoric acid>hydrochloric acid>sulfuric acid>mixture of sulfuric and hydrofluoric acids> ascorbic acid>citric acid. Oxalic acid, therefore, was selected at the concentration of 7% as suggested by Hu et al. (2014).

3.6 Quality Assurance and Quality Control (QA/QC)

To obtain reliable data and findings, the following QA/QC measures were adopted: 1) once received, OFA samples were properly recorded and stored in chemical resistant containers specially for solid samples; 2) all chemicals used in this study are reagent grades; 3) none recyclable vials and containers are metal free type; 4) acid treatment (10% nitric acid) was applied for reusable items to prevent metal contamination; 4) analyses and testes were confirmed by duplicates, and samples were retested if great discrepancy was observed; 5) the rationality of the results were justified by comparison with historical data and other results.

4 Results and Discussion

4.1 Sample Characterization

4.1.1 Physical Properties

The properties of the SPP and RPP sample are listed in Table 5. As shown in the table, the pH of SPP and RPP is 1.49 and 1.22 respectively, indicating that the samples are acidic due to the presence of sulfates and bisulfates. The sulfur content of SPP is 6.31% and 37.60% for RPP, so higher sulfur content of RPP leads to its lower pH. The ash content of RPP is 33.47%, much higher than that of SPP sample (14.35%).

4.1.2 Elemental Analysis

Comparing with SPP sample, V and Ni content in RPP is much higher, which is 10.57% and 3.6%, indicating that it could be a good alternative source for V and Ni. On the other hand, V and Ni level in SPP sample is only 0.88% and 0.34% respectively. Actually, all metals in RPP, except Fe, are about 10 times higher than SPP sample, possibly because RPP OFA is generated from burning of residual oil, which is the heavy fraction of crude oil. Relatively high Fe in SPP could be a result of system corrosion.

4.1.3 Particle Size and Morphology

Figure 2 displays the SEM images of the SPP OFA, which shows that the SPP OFA comprises hollow particles with pores. Table 6 lists the EDS results of three selected points marked on Figure 2. The first point is selected on the external surface of a OFA particle and the analysis indicates that it is mainly carbon and sulfur. The rest points were selected on the mineral aggregates attached to the OFA particle, showing much less carbon but more metal oxidizes. Figure 3 displays the SEM images of the RPP sample, indicating that the sample mainly contains amorphous aggregates. The EDS results, as listed in Table 7, confirms low carbon level but high mineral content.

Figure 4 and Figure 5 are the particle size distributions of the RPP and SPP sample, the mean particle size of the SPP sample is 81.6μm, while the RPP sample is much finer and its mean particle size is 25.6μm.

Table 5 Characteristics of OFA Samples

Properties	SPP	RPP
pH Value	1.49	1.22
Moisture Content (%)	2.43	0.23
Ash Content, %	14.35	33.47
Fe, %	1.26	1.59
V, %	0.89	10.57
Ni, %	0.34	3.6
Mg, %	0.31	3.69
Al, %	0.14	1.11
S, %	6.31	37.60

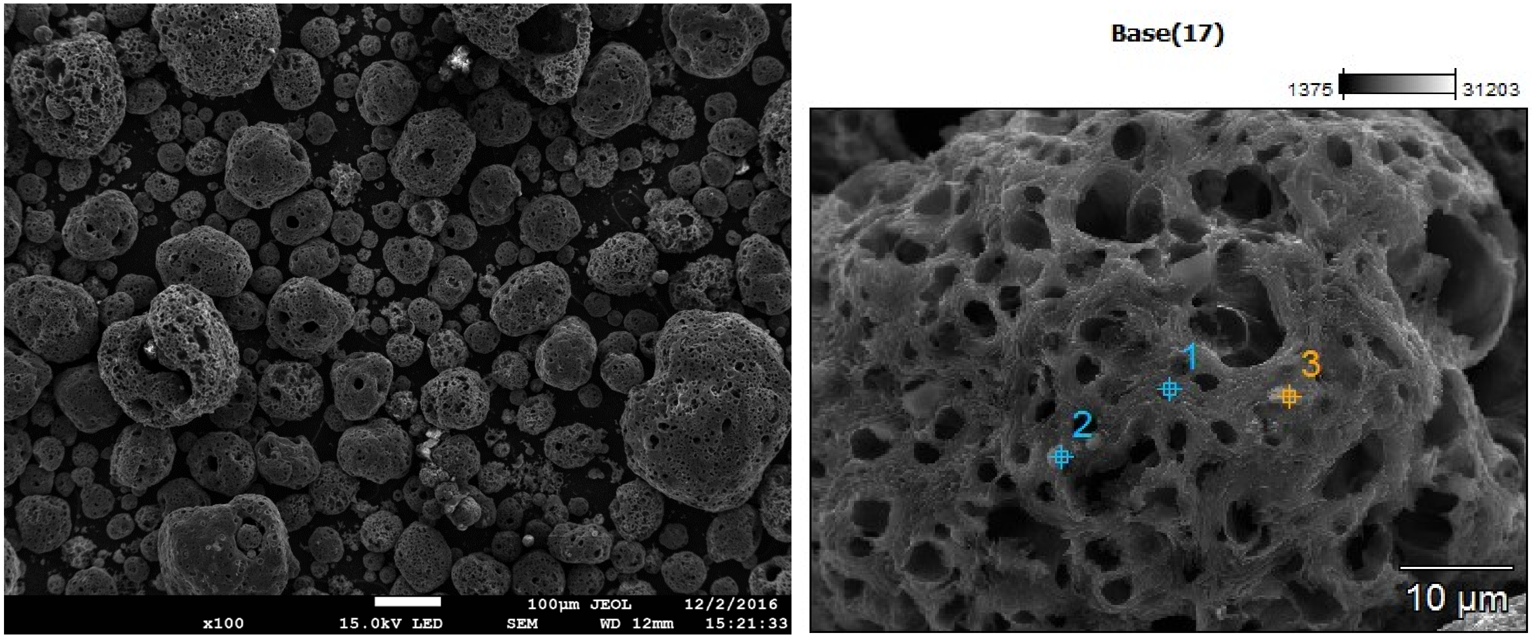

Figure 2 SEM Images of the SPP Sample

Table 6 Elemental Composition of the SPP Sample at the Selected Points by EDS

	C, %	O, %	Na, %	Mg, %	Al, %	S, %	V, %	Fe, %
pt1	88.49	-	-	-	-	11.51	-	-
pt2	47.64	35.15	-	0.64	0.33	10.85	1.48	3.92
pt3	49.23	28.05	1.98	-	-	11.78	-	8.96

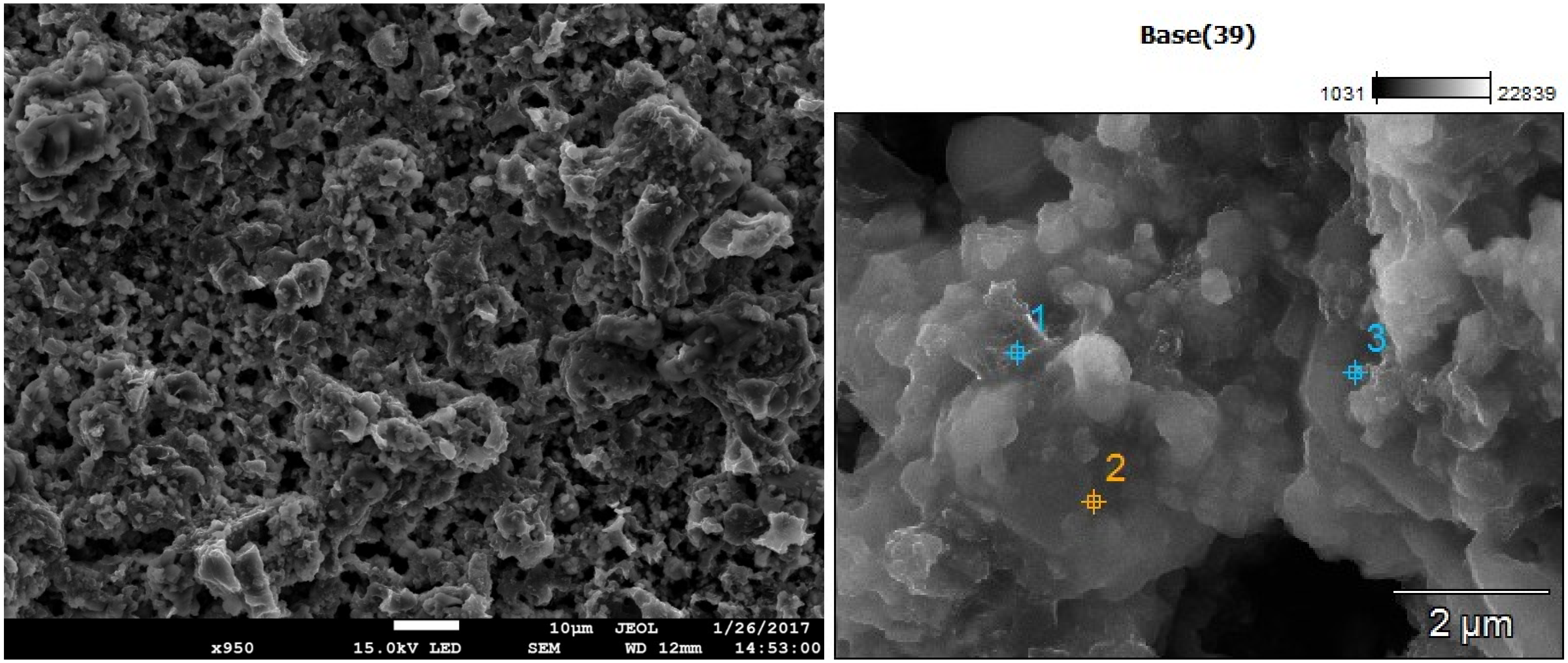

Figure 3 SEM Images of the RPP Sample

Table 7 Elemental Composition of the RPP Sample at the Selected Points by EDS

	C, %	Na, %	Mg, %	Al, %	S, %	Ca, %	V, %	Fe, %	Ni, %
pt1	53.86	1.67	3.87	0.63	24.84	0.22	7.38	3.23	3.14
pt2	26.56	3.68	6.67	0.94	37.12	-	8.66	10.22	6.15
pt3	35.65	1.30	1.94	1.05	27.11	-	22.36	2.92	4.70

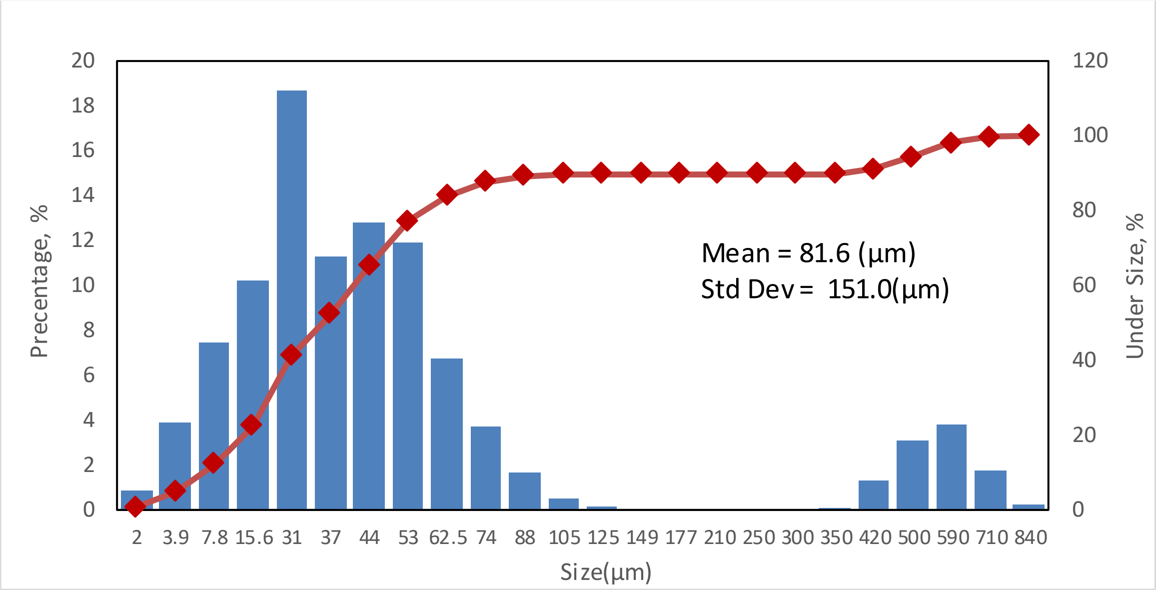

Figure 4 Particle Size Distribution of the SPP Sample

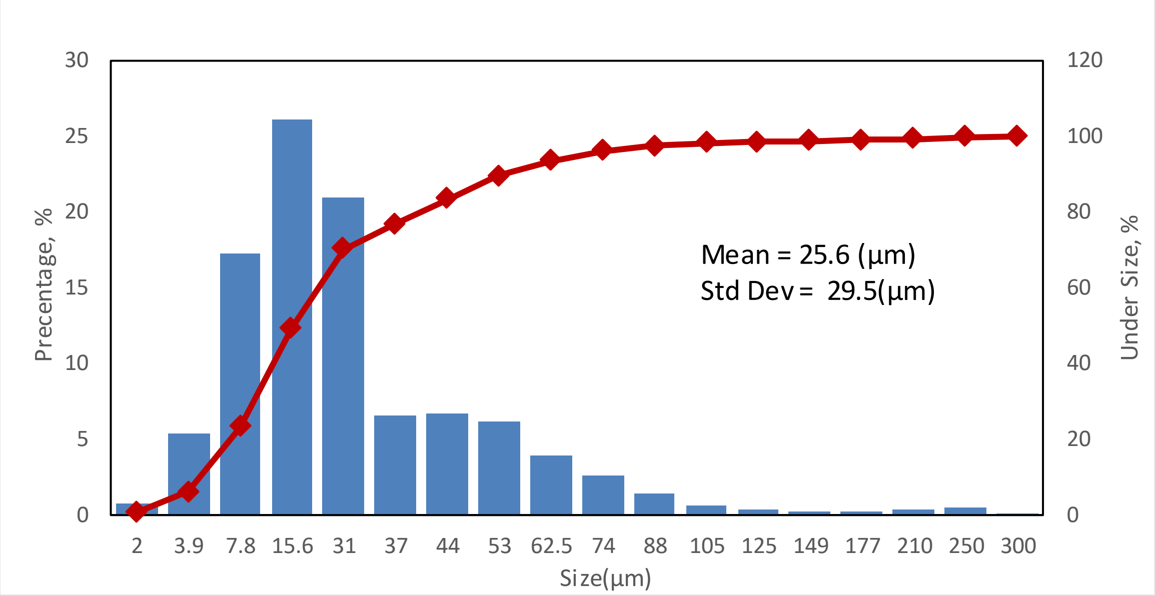

Figure 5 Particle Size Distribution of the RPP Sample

4.2 Acid Leaching

Firstly, acid Leaching experiment was conducted using H_2SO_4 at the concentrations ranging from 0 to 4N. The experiment (Figure 6) indicated that the leaching rate of V and Fe increased with increasing acid concentration in the range between 0 and 1N and then remained constant until 2N. Further increasing the acid concentration beyond 2N decreased the V and Fe extraction, which is not consistent with the findings reported by some of the authors such as and Tokuyama et al. (2003). Leaching of other metals showed little variation throughout the pH range. The result also indicates that the pH of the solution should be lower than 1 to maximize the extraction.

During the acid leaching process, the following reactions occur (F. Rahman & Skyllas-Kazacos, 1998):

$$H_2SO_4 \leftrightarrow H^+ + HSO_4{}^-$$

Equation 7

$$HSO_4{}^- \leftrightarrow H^+ + SO_4{}^{2-}$$

Equation 8

$$VOSO_4 \leftrightarrow VO^{2+} + SO_4{}^{2-}$$

Equation 9

$$V_2O_5 + H_2SO_4 \leftrightarrow 2VO_2{}^+ + H_2O + SO_4{}^{2-}$$

Equation 10

$$M_n(SO_4)_m \leftrightarrow nM^{\frac{2m}{n}+} + mSO_4{}^{2-}, where, M = metals$$

Equation 11

Interestingly, V(IV) and V(V) exhibited opposite interaction with H_2SO_4. F. Rahman and Skyllas-Kazacos (1998) reported that $VOSO_4$ is most soluble in water and higher H_2SO_4

concentration inhibits the dissolution of V(IV). On the other side, the stability of V(V) ion is better in higher H_2SO_4 concentration as described by Equitation 10.

It is believed that V(IV) and Fe (II) are the predominant oxidization states in the OFA samples rather than V(V) and Fe (III) because OFA is formed in an environment with high temperature but lack of oxygen, so V and Fe will most likely to be reduced due to the presence of carbon. Furthermore, the leachate solution showed blue color and it turned to red after the addition of H_2O_2, implying that V(IV) and Fe(II) are the major oxidization states. This also could be the reason that the leaching of V slightly decreases at higher H_2SO_4 concentration as the reaction equilibrium moves towards the left side of Equation 9. Since the fuel type and combustion system vary (e.g fuel type, air flow, burning temperature, fuel additives, OFA collection efficiency), the properties of OFA (e.g. particle size, ash content, sulfur content, pH, metal composition and valance state) may differ greatly, as a result, the leaching behavior observed in this study may show different trend.

Based on the results, the optimal H_2SO_4 concentration should be in between 0.5N and 1N, which is constant with the conclusion reported by Navarro et al. (2007). Considering the variation of the OFA composition, higher acid concentration, 1N, was selected for the sequential experiments to ensure maximum leaching rate.

Figure 7 shows the impact of S:L ratio at the same acid concentration, which is 1N in this case. The trend indicates that the solution volume plays an important role in the metal leaching process. With excess volume of acid, S:L=1g:40ml, all metals reaches their highest extraction rate. Increasing OFA quantity gradually decreases the unit leaching rate, despite that the metal concentrations in the leachate increase greatly. However, changing S:L ratio has little impact on the solution pH, it only showed minor flocculation ranging from 0.5 to 0.7.

Note that although the metal extraction is higher at lower S:L, it may not be practical because it consumes more water and acid to leach unit amount of OFA. In addition, the metal concentration may not be sufficient for the following metal recovery process. Therefore, S:L=1:10 was selected to balance the leaching rate, water/acid consumption and metal concentration.

Temperature (Figure 8) moderately affects the metal leaching, higher temperature generally improves the leaching performance. This agrees with the finding reported by Nazari et al. (2014) that the leaching process is endothermic but the trend is non-linear, possibly because higher temperature slightly decreases the solubility of V(V) (Faizur Rahman & Skyllas-Kazacos, 2009). The leaching of Ni showed little changes, only marginal increase at higher temperature.

The impact of salting effect had also been studied by adding Na_2SO_4 and NaCl. Generally, common salt effect inhibits the dissolution of metals, while increasing uncommon salt concentration will prompt the dissolution of metals (Boyd, 2015). However, the experiment (see Figure 9) exhibited different trend that adding anions improves the leaching rate, no matter same or different salt. H^+, indeed, followed the salting effect based on the pH variation. When SO_4^{2-} increases, pH increases because the reaction tends to move toward the left side of Equation 7 and Equation 8. On the other side, increasing Cl^- prompts the release of H^+, therefore, the pH drops sharply. It is worth mentioning that the real concentration of 4M Na_2SO_4 and NaCl would be lower because not all the salt can be full dissolved.

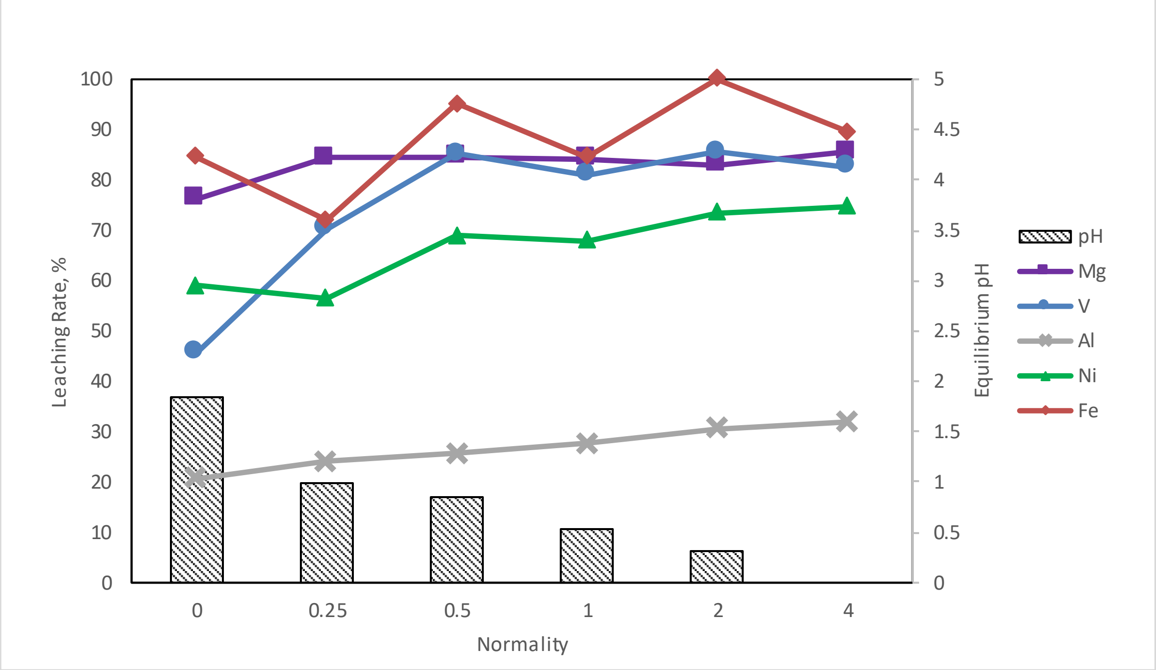

Figure 6 Metal Leaching by Different Concentrations of H_2SO_4

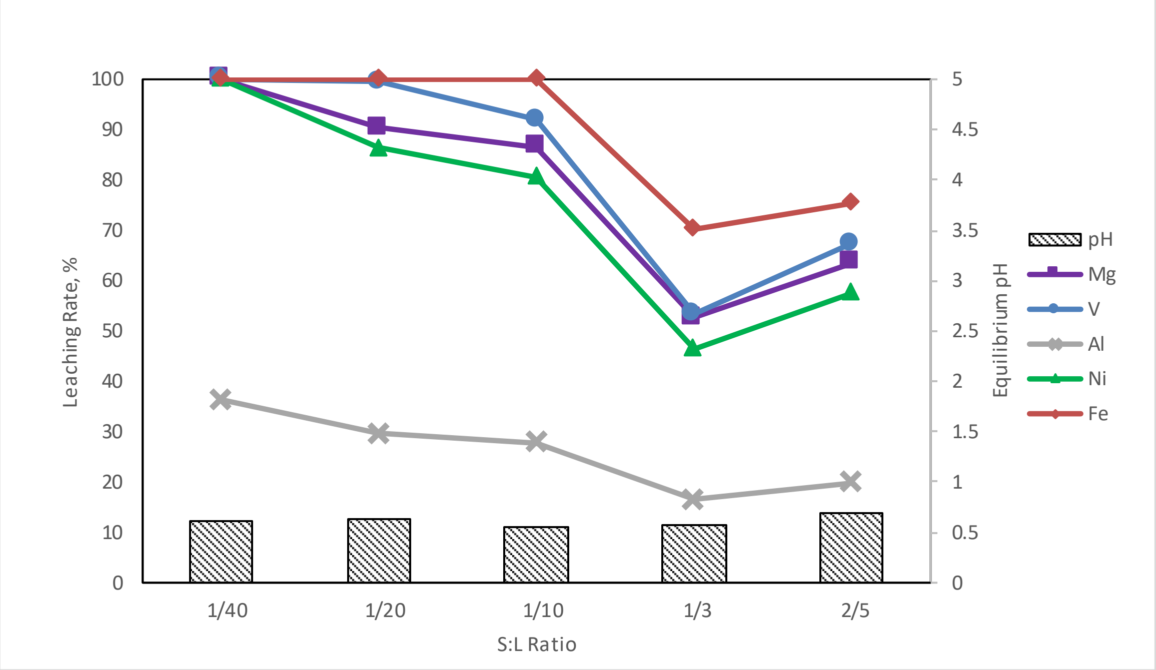

Figure 7 Metal Leaching by Different S:L Ratios of H_2SO_4, 1N, 80°C

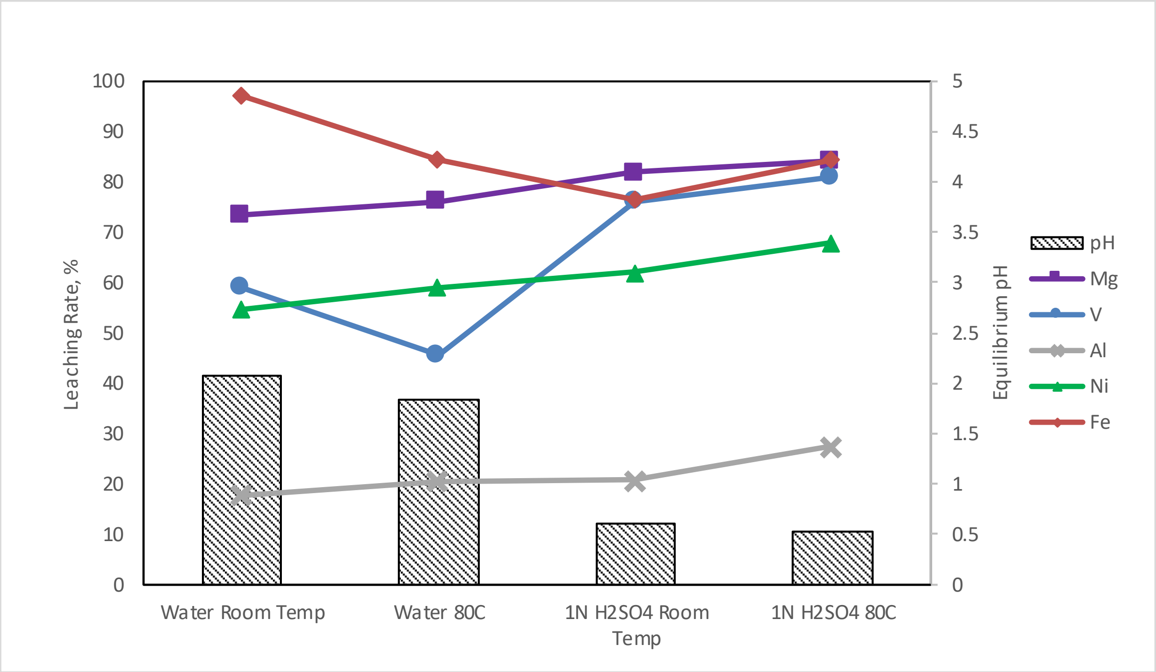

Figure 8 Metal Leaching by Water and 1N H_2SO_4 at Room Temperature and 80°C

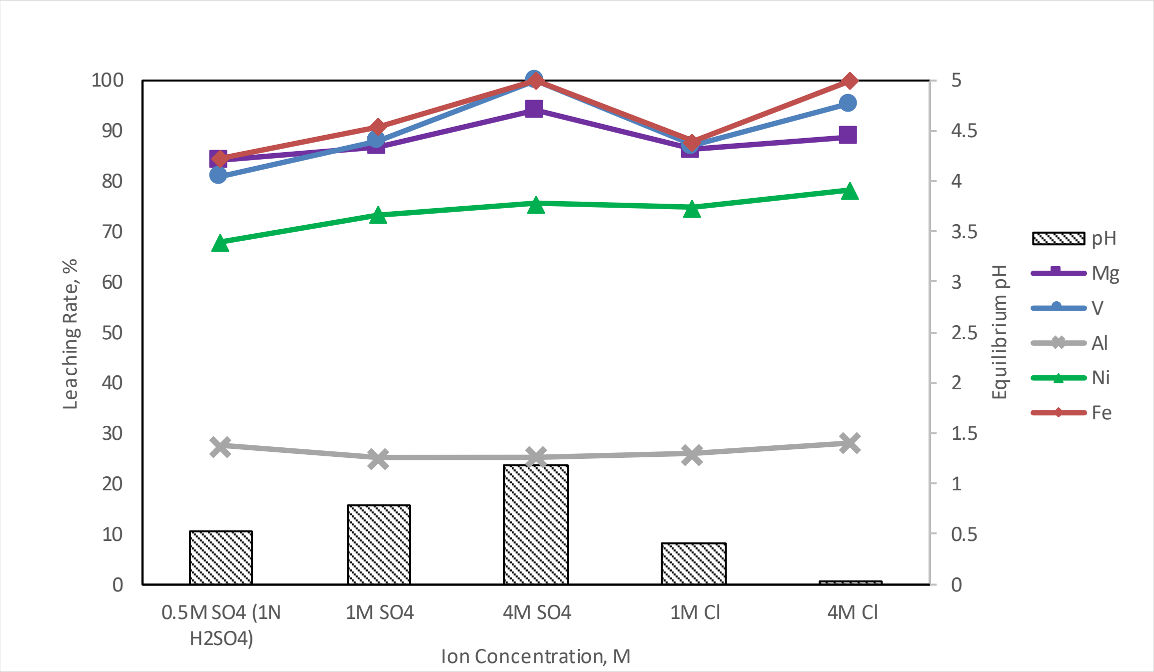

Figure 9 Metal Leaching by 1N H_2SO_4 at Different Anion Concentrations

4.3 Base Leaching

Two types of base solutions were tested in this study: NaOH and NH_4OH, their leaching rates at different concentrations are plotted in Figure 10 and Figure 11. As shown in Figure 10, only V can be leached by NaOH and the leaching rate increases as the NaOH concentration increases but the increasing trend becomes insignificant after the NaOH concentration exceeds 1N. All other metals are not soluble in NaOH solution, except small amount of Al. The results also indicate that NaOH solution has good V selectivity and the pH of the solution should be higher than 13 to maximize the V leaching.

NH_4OH is a weak base and Figure 11 shows that its leaching ability is limited comparing with NaOH and H_2SO_4. Al, Mg and Fe are not leachable by NH_4OH solution but Ni can be leached and the rate increases when the NH_4OH concentration increases. Among three NH_4OH concentrations, V extraction rate reached the highest at 2N, further increasing NH^{4+} concentration decreased the V leaching, possibly due to the formation of insoluble ammonium salt such as NH_4VO_3. This trend agrees with the results of solubility test of NH_4VO_3 in ammonia water conducted by Trypuć and Białowicz (1997), which concluded that the solubility of NH_4VO_3 versus ammonia concentration is not linear due to salting effect.

Figure 12 compares the leachability of each aqueous media, indicating that 1N H_2SO_4 is able to leach out all the metals, while NaOH only extracts V and it is as effective as H_2SO_4. NH_4OH extracts V and Ni but its leaching ability is limited. Based on the leaching test, 1N H_2SO_4 and NaOH can be potentially used for OFA leaching and sequential Ni and V recovery.

4.4 Ion Exchange Resin

The results of batch tests using Lewatit TP 207 (TP207) and Diaion CR11(CR11) were plotted in Figure 13 and Figure 14, which shows that the extraction rate of V and Ni by TP207 was 70% and 45% respectively, when solution pH was lower than 1. Under the same condition, the Ni extraction rate of CR11 was lower, which was about 33% but it had higher V extraction rate, which was 82%. However, once the pH of the solution was increased above 1, both resins almost completely adsorbed all the metals, except Mg. The only difference is that TP207 adsorbed less Mg than CR11.

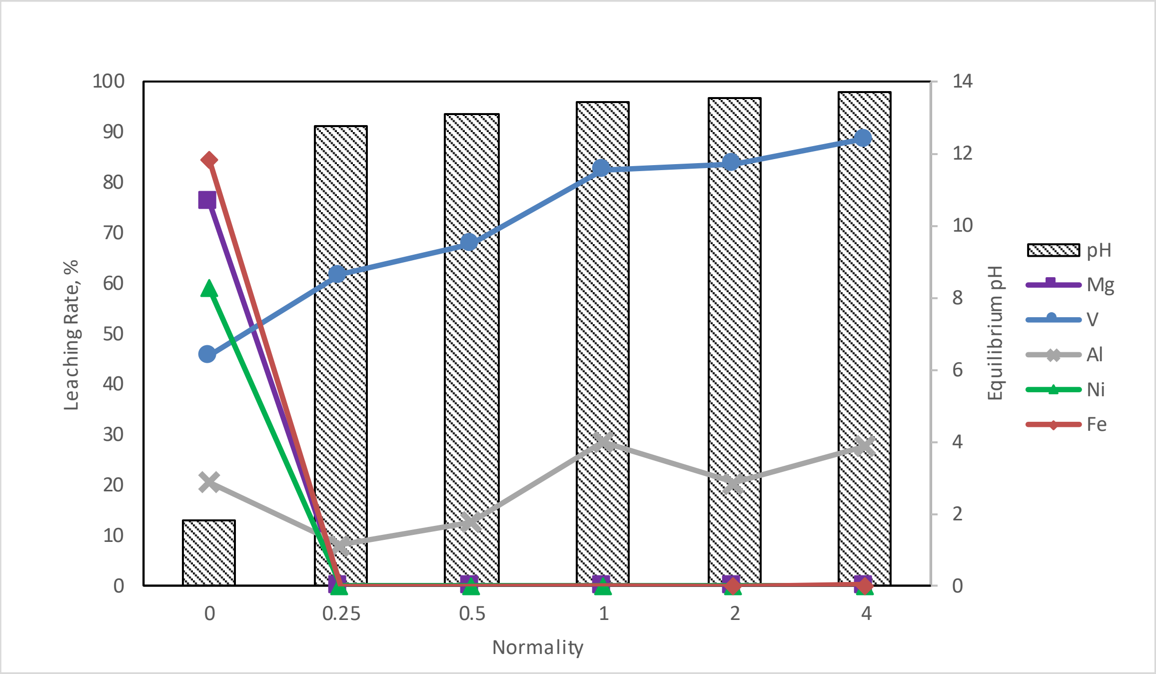

Figure 10 Metal Leaching by Different Concentrations of NaOH

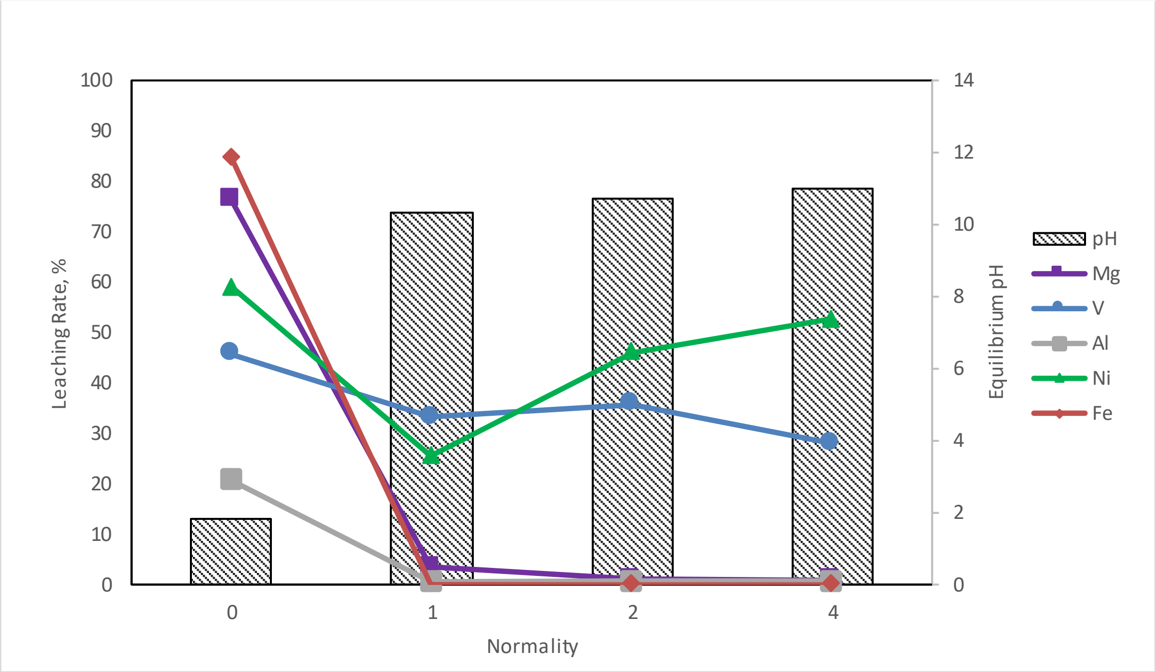

Figure 11 Metal Leaching by Different Concentrations of NH_4OH

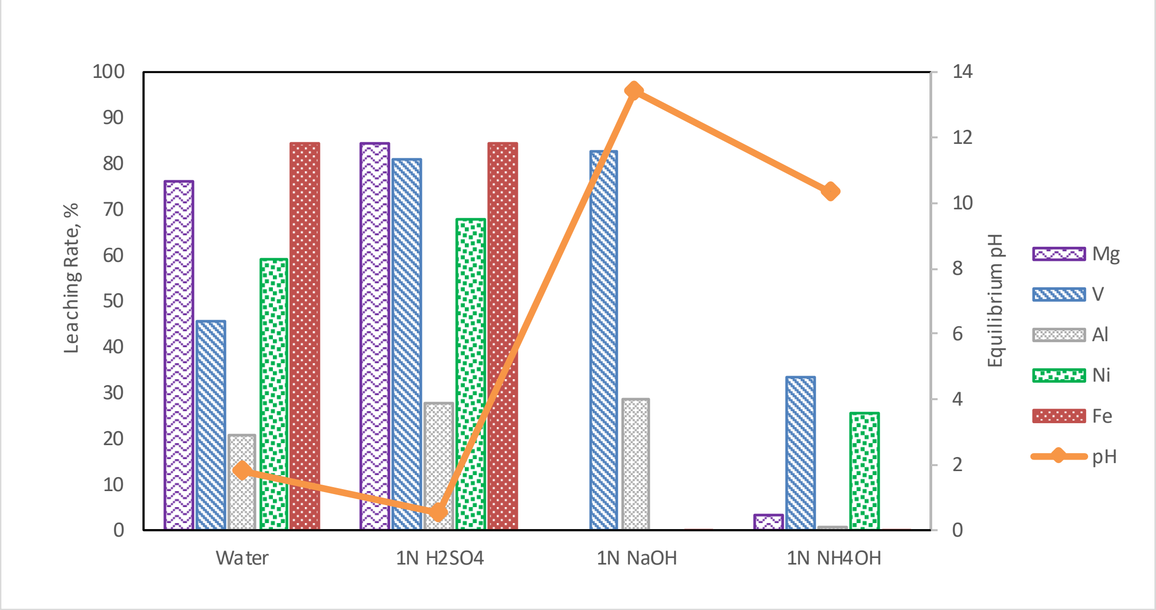

Figure 12 Comparison of the Leachabilities of Different Leaching Agents

For the column test, TP207 was selected because of its good particle integrality and better separation from the metal solutions. When passing the metal solution through the resin column, the residual solution became colorless until the total loaded volume of the treated solution reached approx. 400ml. Figure 15 portrays the changes of metal composition in the residual solution versus loaded volume, indicating complete adsorption of all metals by TP207 until the loaded volume reached 315.5ml. After that, the metal levels started raising, implying that the resin was slowly saturating. Figure 16 shows the accumulated amount of each metal extracted by TP207 versus loaded volume. All the total amount of the adsorbed metals exhibited increasing trend throughout the experiment except Ni and Al that they remained constant after about 370ml, implying that TP207 started saturating at 370ml and the total adsorbed V and Ni was 309.8mg at this point.

Stripping process was carried out by passing 10% H_2SO_4 through the saturated column and Figure 17 shows the changes of the strippant composition, indicating that the stripping process requires less volume than the leaching solution as the process completed when the stripping volume was around 90ml. The concentration of V peaked (1,214 mg/L) at the stripping volume in between 40ml and 60ml. However, all metals were leached out, which concludes that ion exchanges resin is a good technique for metal removal but selective extraction of V and Ni would be limited if the solution contains many other metal impurities. Basically, the metal solution is only "concentrated" after ion exchange resin and the separation of Ni and V is difficult to achieve by this method.

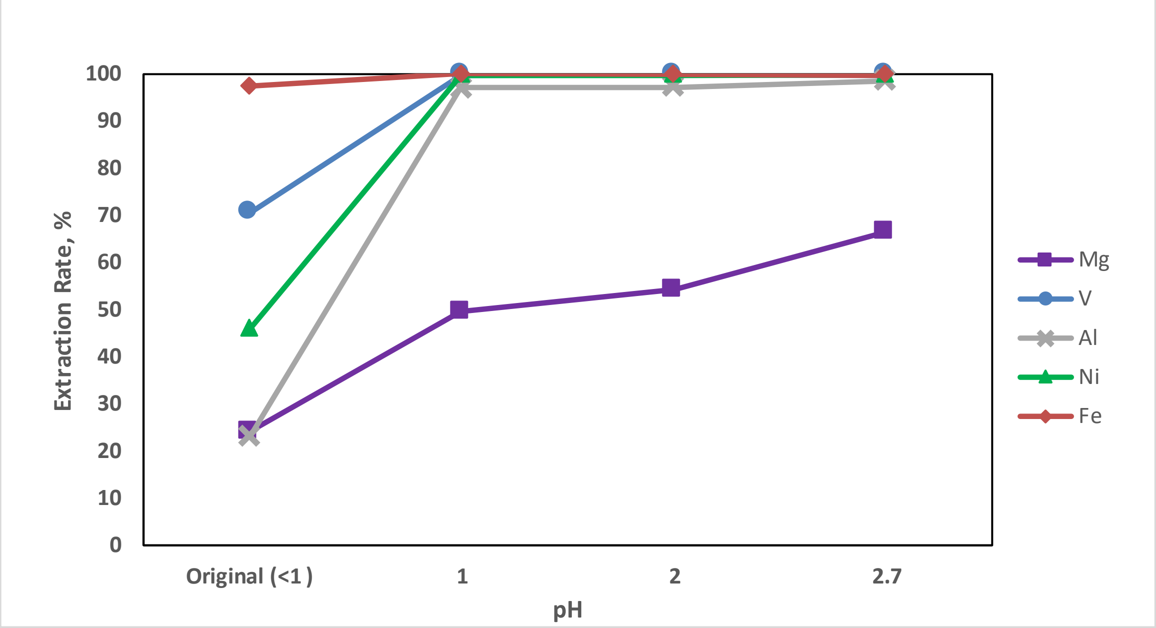

Figure 13 Metal Extraction by Lewatit TP207 at Different pH

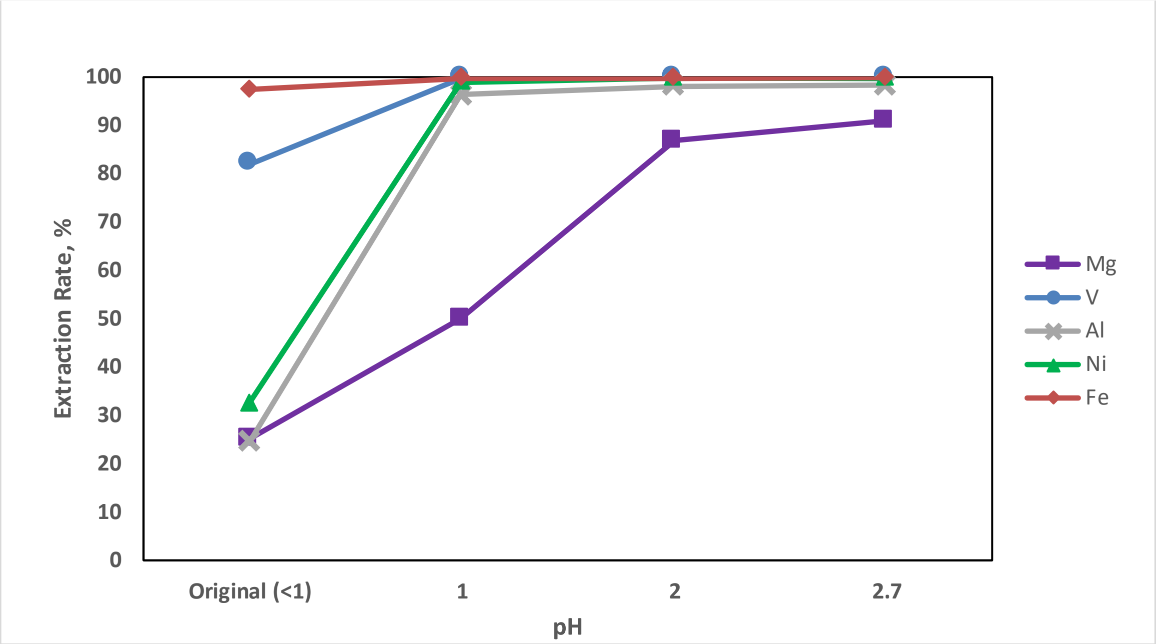

Figure 14 Metal Extraction by Diaion CR11 at Different pH

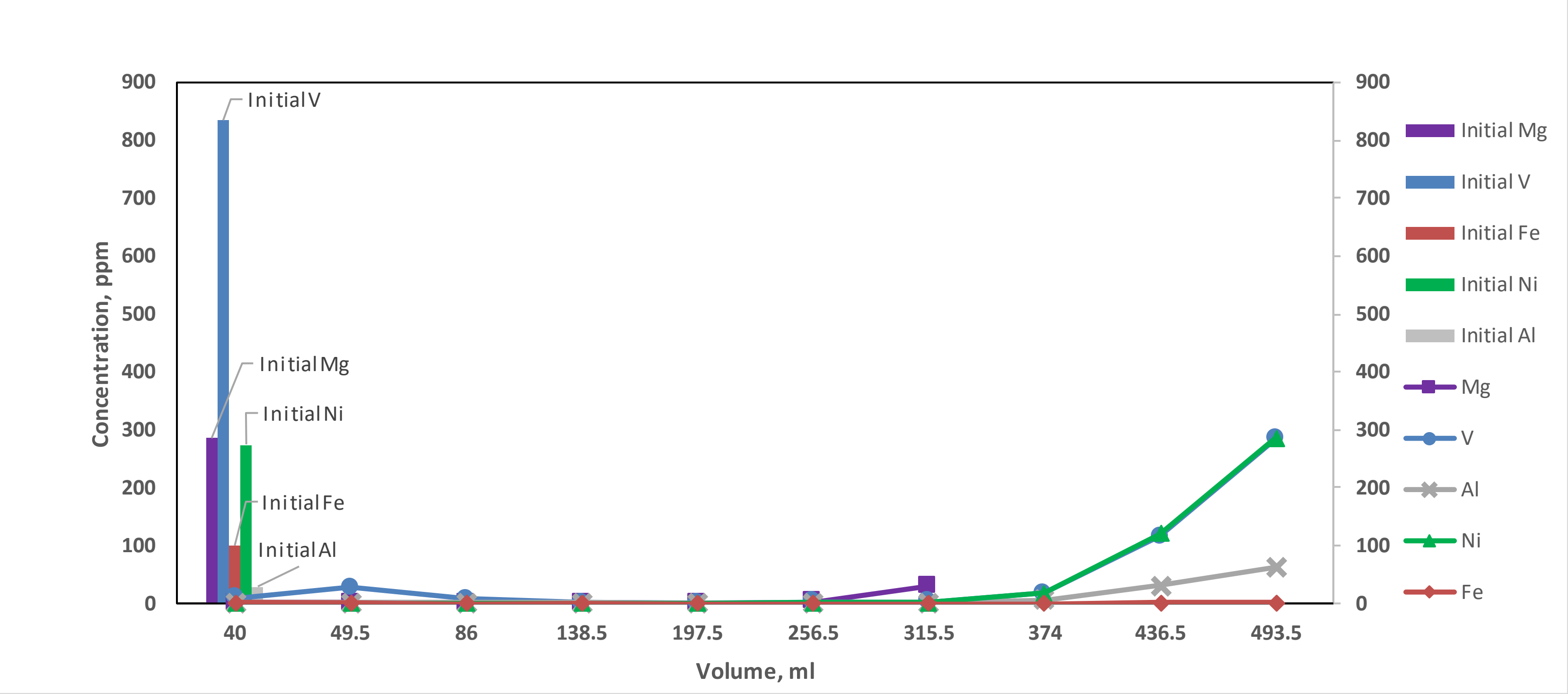

Figure 15 **Metal Concentrations after TP 207 Treatment *Vs* Loaded Volume**

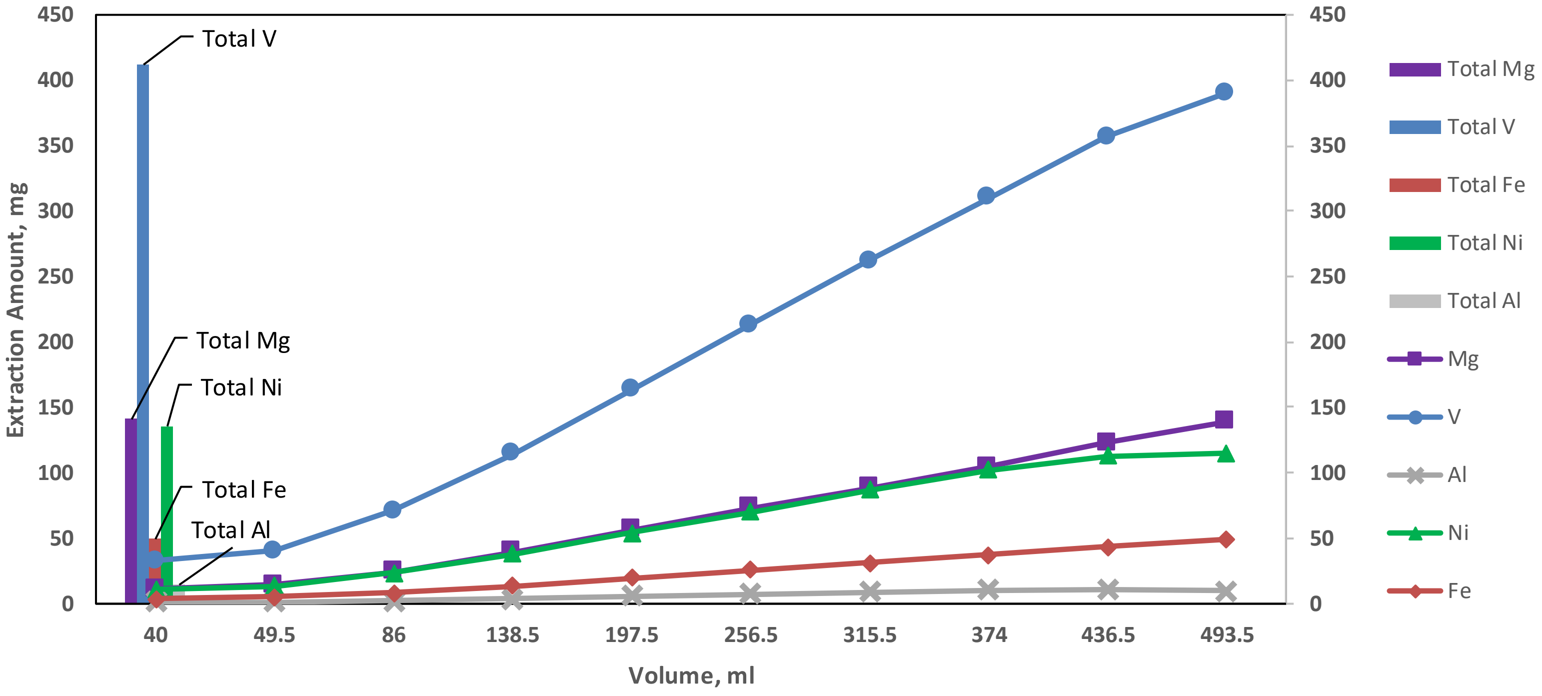

Figure 16 Accumulated Adsorption of Major Metals by TP207 (Resin Volume:41ml)

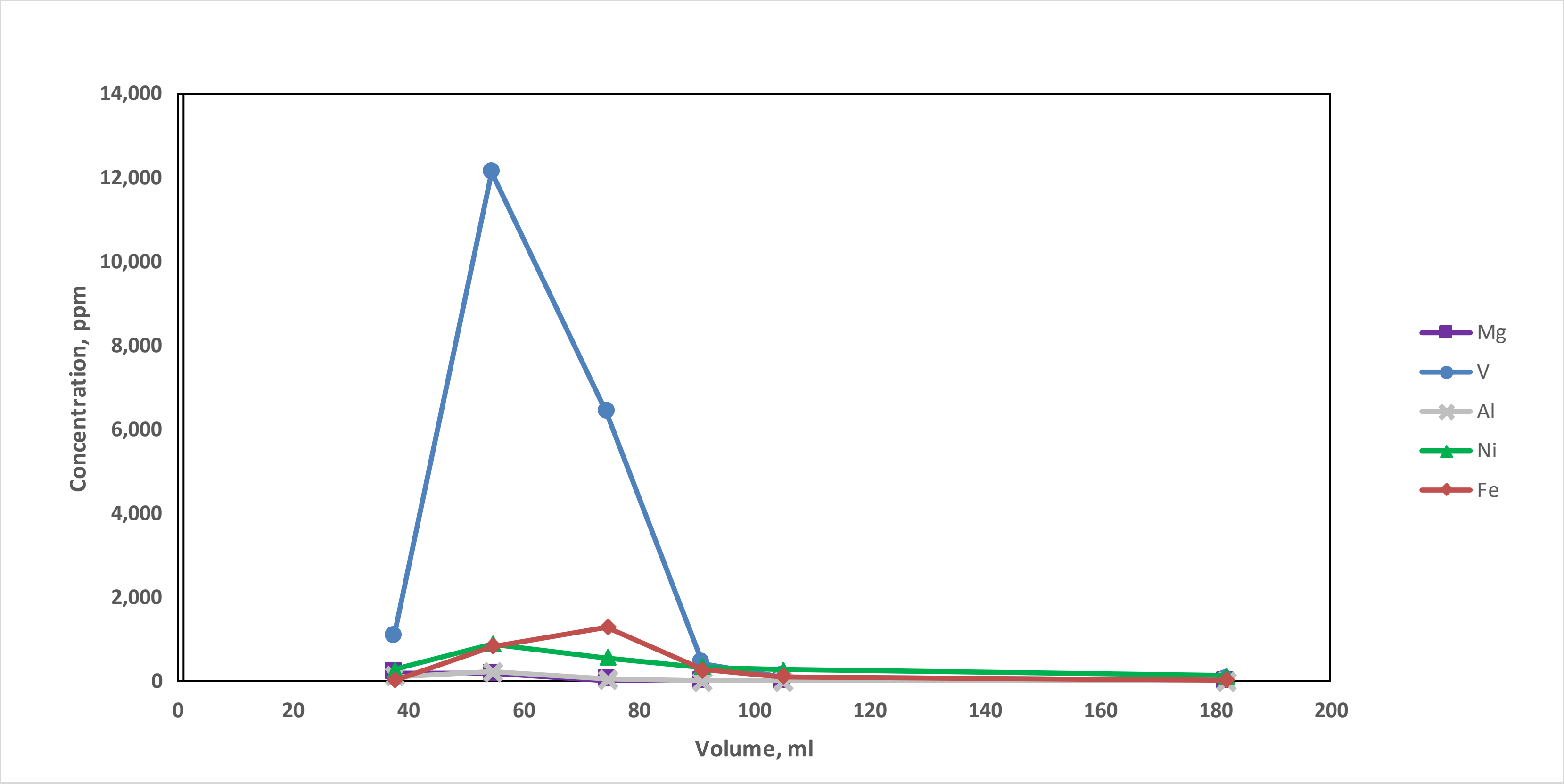

Figure 17 TP207 Stripping by 10% H_2SO_4

4.5 Solvent Extraction

4.5.1 Impact of Vanadium Oxidization State

D2EHPA and TOA were selected for the solvent extraction experiment because D2EHPA has good V(IV) selectivity and its interaction with VO^{2+} is described by Equitation 1. TOA shows good V(V) selectivity (Zhang et al., 2014). The interaction between V(V) and TOA is described by Equitation 4.

In the OFA metal solution, Fe is the most concerned impurity and D2EHPA has a selectivity of Fe(III)>V(IV)>Fe(II). Therefore, the solvent extraction experiment started with a preliminary test to verify the selectivity of D2EHPA and TOA on V(V), V(IV), Fe(III) and Fe(II) by using synthetic metal solutions as listed in Table 8.

The selectivity test of D2EHPA is plotted in Figure 18. Clearly, it proves that D2EHPA extracts V(IV) and Fe(III) effectively and the extraction rates were 76.4% and 99.5% respectively. The extraction of Fe(II) is lower, which was about 44.5%.

As mentioned earlier, V and Fe presented in the OFA are a mixture of V(IV), V(V), Fe(II) and Fe(III), among which V(IV) and Fe(II) are predominant. Thus, Fe(III) and V(V) need to be reduced before D2EPHA extraction in order to improve the selectivity and extraction rate. Na_2SO_3 was selected as the reductant and it was added to synthetic solution firstly to see its effectiveness. It was found that once Fe(III) is reduced to Fe(II), the extraction rate of Fe decreases, while the extraction rate of V increases (see Figure 18).

Figure 19 shows the extraction of Fe and V from synthetic solution by TOA, which proves that TOA does not extract Fe(II), Fe(III) and V(IV), and its extraction rate of V(V) was 71.5%. Once Fe(III) and V(V) are reduced, the extraction rate of TOA drops sharply. Figure 20 compares the extraction rate of D2EHPA (with reduction) and TOA using the same synthetic solution, indicating that D2EHPA has higher V extraction rate than TOA but lower selectivity.

The preliminary test proves that TOA can be used if the OFA leaching solution is oxidized. Therefore, a comparison between D2EHPA after reduction and TOA after oxidization was conducted using the RPP leaching solution and the results are plotted in Figure 21. Without any pre-treatment, about 45% V and 70 % Fe were extracted by D2EHPA, while only around 3 % V and 1% Fe were extracted by TOA, which confirms that V in OFA is mainly V(IV). After reduction by Na_2SO_3, the extraction rate of V by D2EHPA increased to more than 70%, while the Fe extraction rate decreased to below 30%. After oxidization by H_2O_2, the extraction rate of V by TOA was also dramatically increased to 64.1% and Fe was not extracted. The comparison indicates that D2EHPA (with reduction) has better extraction rate than TOA (with oxidization) but it will also extract more unwanted metals such as Fe, Ni and Al, although their quantities are relatively small.

Table 8 V and Fe Concentrations of the Synthetic and the RPP Solution

Element	V, mg/L	Fe, mg/L
Fe(II)+V(IV)	3,344.00	623.87
Fe(III)+V(IV)	3,299.67	479.03
Fe(III)+V(V)	1,979.67	476.53
RPP	8,683.33	1,019.33

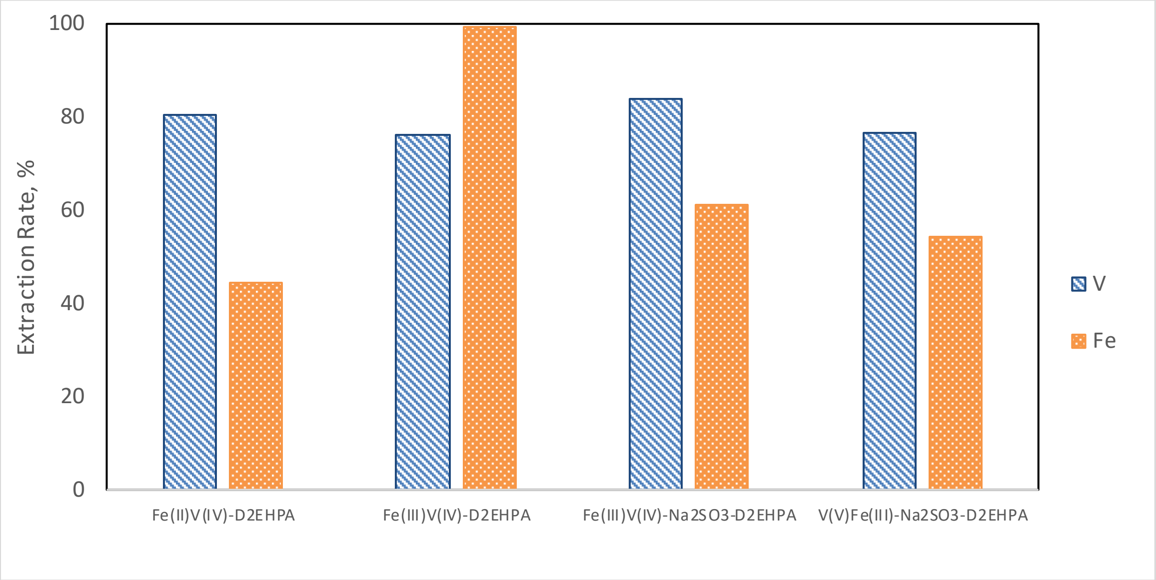

Figure 18 Extraction Rates of Fe and V by D2EHPA from the Synthetic Solution, O:A=1:1, pH=1.3, Room Temperature, 8min Contact Time

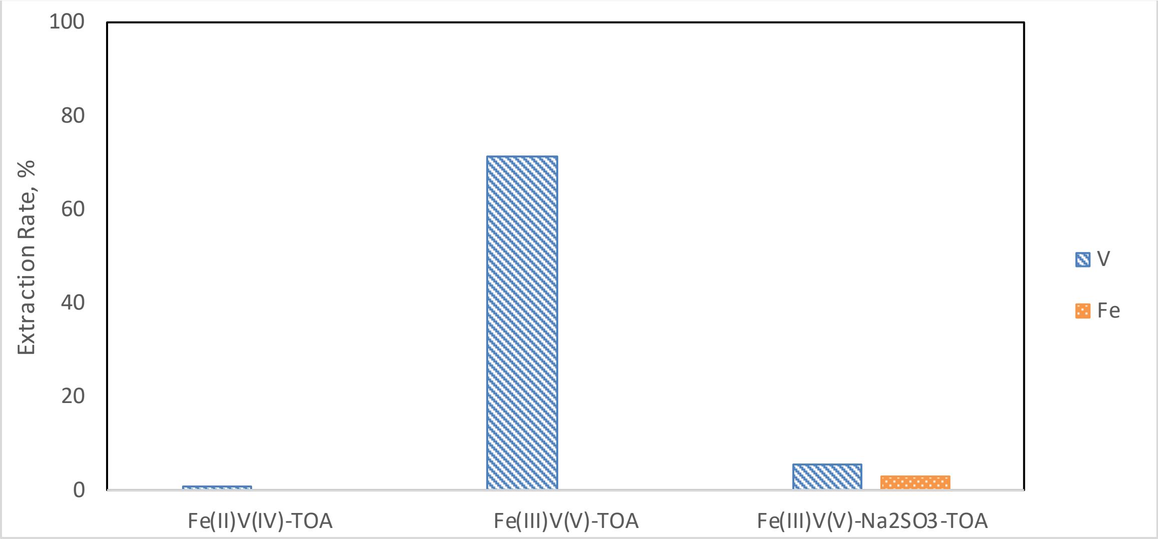

Figure 19 Extraction Rates of Fe and V by TOA from the Synthetic Solution, O:A=1:1, pH=1.3, Room Temperature, 8min Contact Time

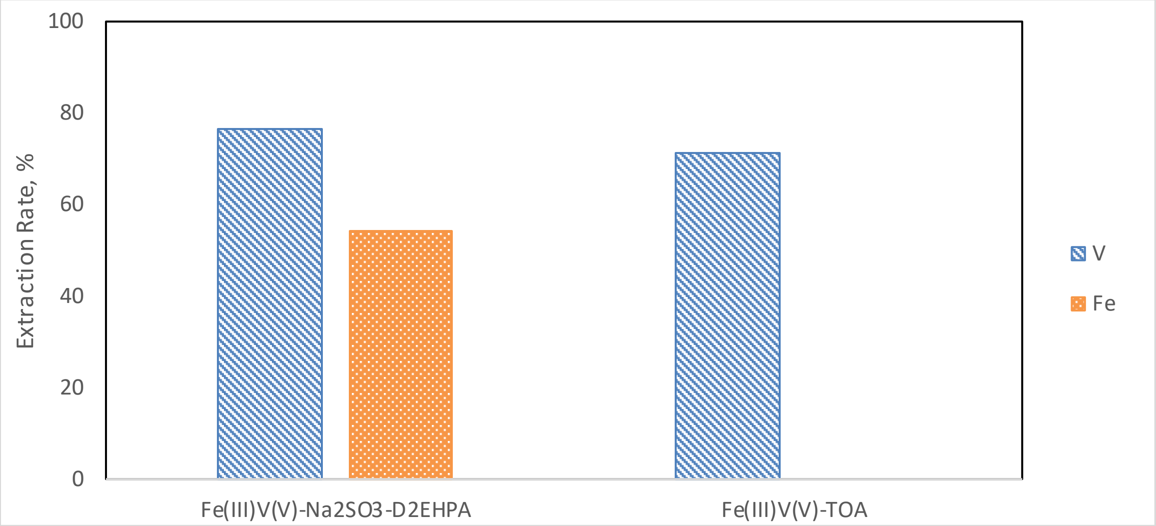

Figure 20 Comparison of V(V) Extraction Rates by D2EHPA (After Reduction) and TOA from the Synthetic Solution

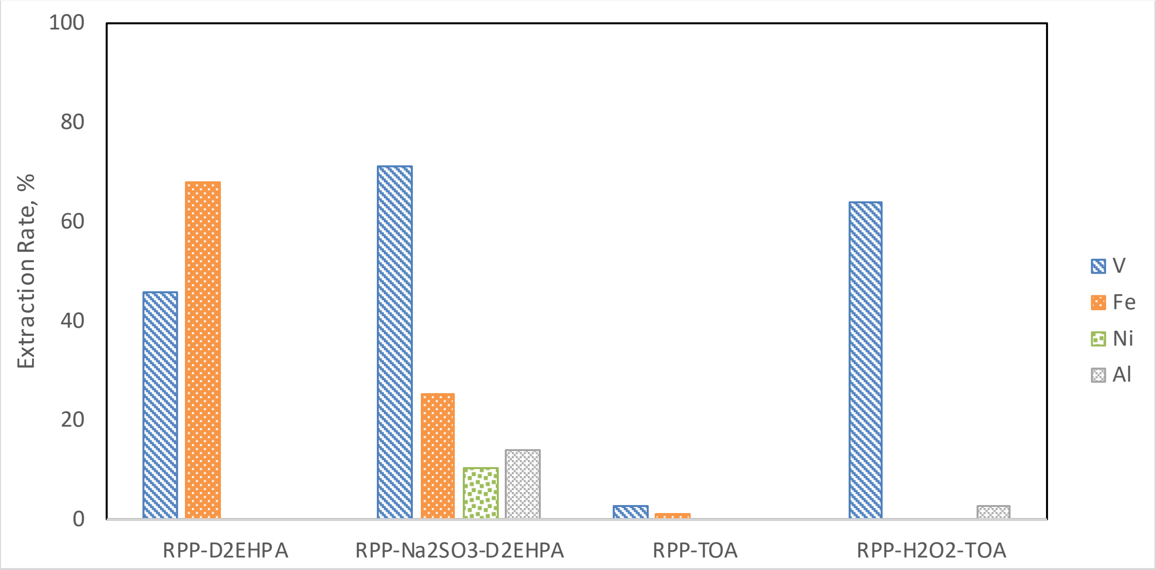

Figure 21 Comparison of Fe and V Extraction by D2EHPA (Before and After reduction) and TOA (Before and After Oxidization) from the RPP Solution, O:A=1:1, pH=1.3, Room Temperature, 8min Contact Time

4.5.2 Impact of pH

The solution pH is one of the most critical factor for solvent extraction and it greatly affects the extraction rate as well as its selectivity. Although, the literatures reported that the optimal pH range for D2EHPA is 2.5 to 3, and around 3 for TOA, optimization of the extraction pH was still tested in this study. Note that the pH range of TOA was limited below 3 because once the solution is oxidized, Fe(III) starts to precipitate when the solution pH is increased above 3 and significant V will be co-precipitated(Navarro et al., 2007).

Figure 22 shows the metal extraction rates of the D2EHPA solvent from the RPP solution at different pH levels, which indicates that the extraction rates of all four metals increase as the pH increases except Ni. The V extraction rate gradually increases when increasing the solution pH, it reached 96.3% when the solution pH was around 5.5. For Fe, the initial extraction rate was high, approximately 92%, and it further increased to almost 100%, when the solution pH was above 2.5. Al was not effectively extracted when the solution pH was lower than 3, only about 3%, however, it suddenly increased to 95.8% at the solution pH 5.5 from 12% (pH 4). The figure also indicates that Ni cannot be extracted in this pH range.

It should note that even the extraction of Al sharply increases at higher pH, it may not greatly affect the purity of V because the original concentration of Al is about 360mg/L, which is relatively small amount comparing with V, which is about 8600mg/L. Although higher is better, the solution pH of 3 is recommended to balance the extraction rate and the selectivity as well as to prevent significant precipitation of Fe and V.

The impact of pH on TOA extraction is portrayed in Figure 23, showing that the extraction rate of V(V) was more than 95% in the pH range from 2 to 3. At pH 2.5, the extraction rate reached highest, which was 99.4%. Al and Ni were not significantly extracted, which was less than 20% and 8% respectively. Fe was not greatly extracted at pH lower than 2.5 but it dramatically increased to 98% once the pH of the solution was increased to 3.

4.5.3 Impact of Stripping

Vanadium was stripped by 1.5 mol H_2SO_4 from the D2EHPA solvent and the results are showed in Figure 24. For the first stage, the V stripping rate was approximate 34% and Fe was not stripped, which indicates that multiple stages of stripping are needed.

For stripping the V enriched TOA solvent, various strippants can be used as mentioned in the previous sections. In this study, three strippants were tested and the results are plotted in Figure 25, indicating that the difference of their efficiencies is insignificant. Among them, 1M NH_4OH+1.5M NH4Cl showed the highest stripping amount, which was 16.2%. In addition, it also eliminates the contamination of Na^+ ion comparing with NaOH and Na_2CO_3, thus, it was selected for the following experiments.

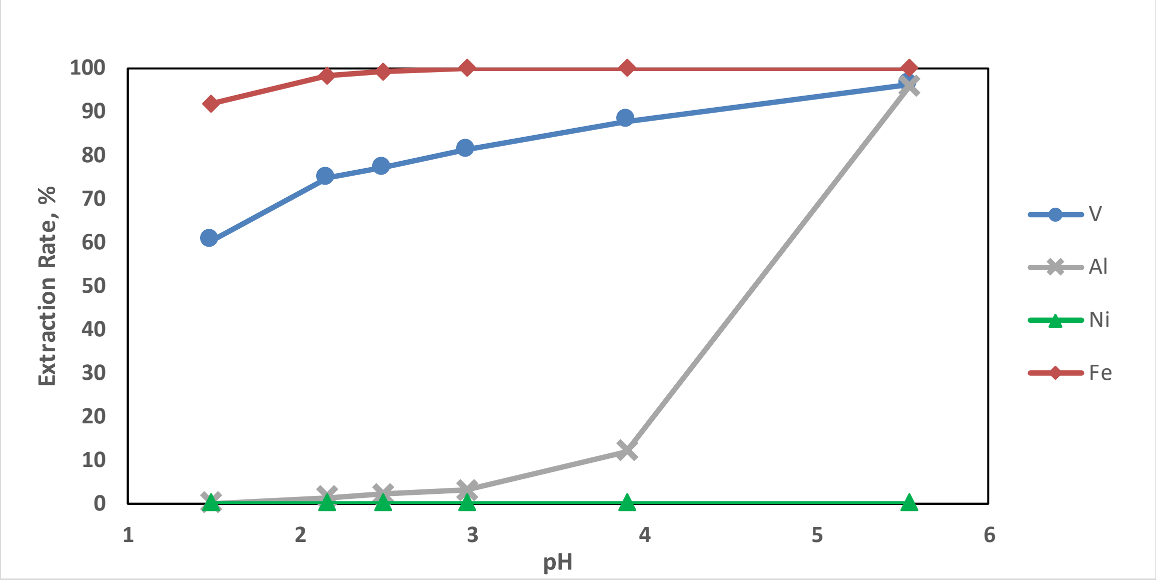

Figure 22 Metal Extraction by D2EHPA from the RPP Solution at Various pH, O:A=1:1, Room Temperature, 8min Contact Time

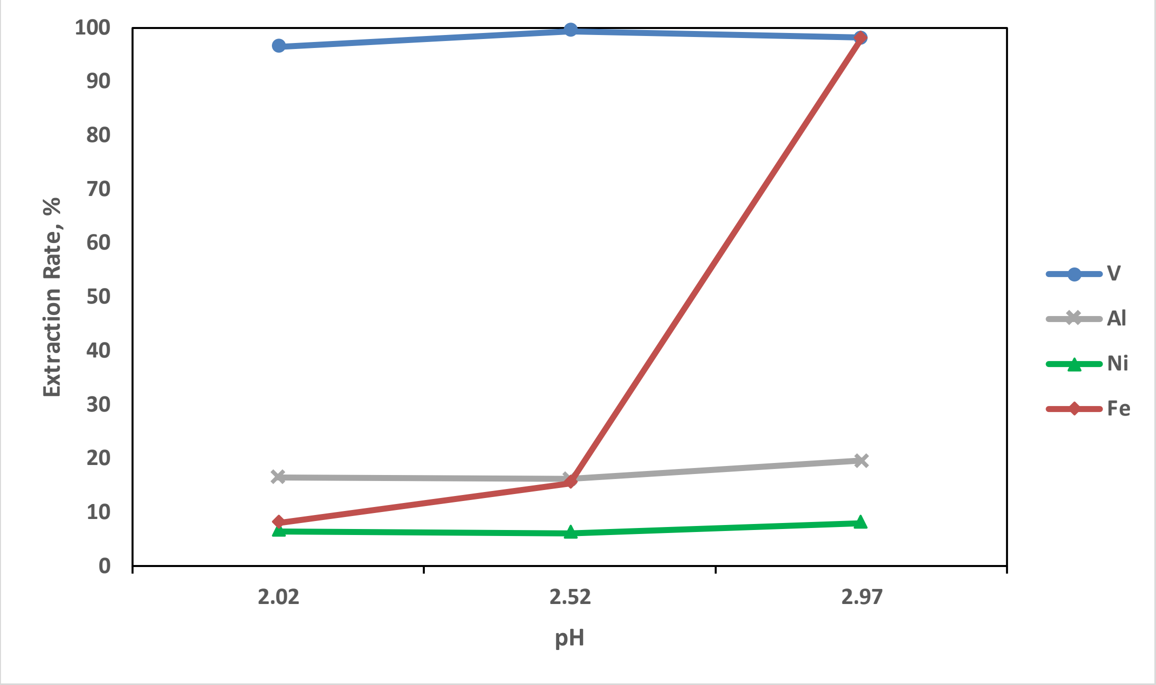

Figure 23 Metal Extraction by TOA from the RPP Solution after Oxidization at Various pH, O:A=1:1, Room Temperature, 8min Contact Time

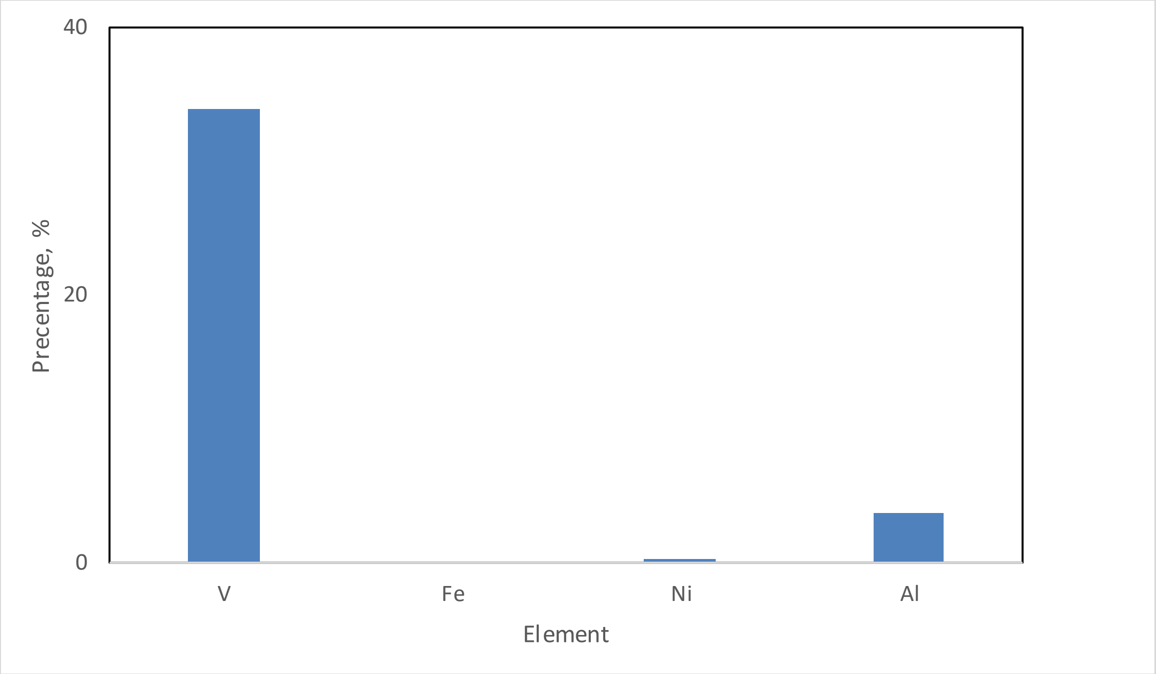

Figure 24 Stripping Rates of the Major Metals by 1.5 mol H_2SO_4 from the V-enriched D2EHPA Sovlent

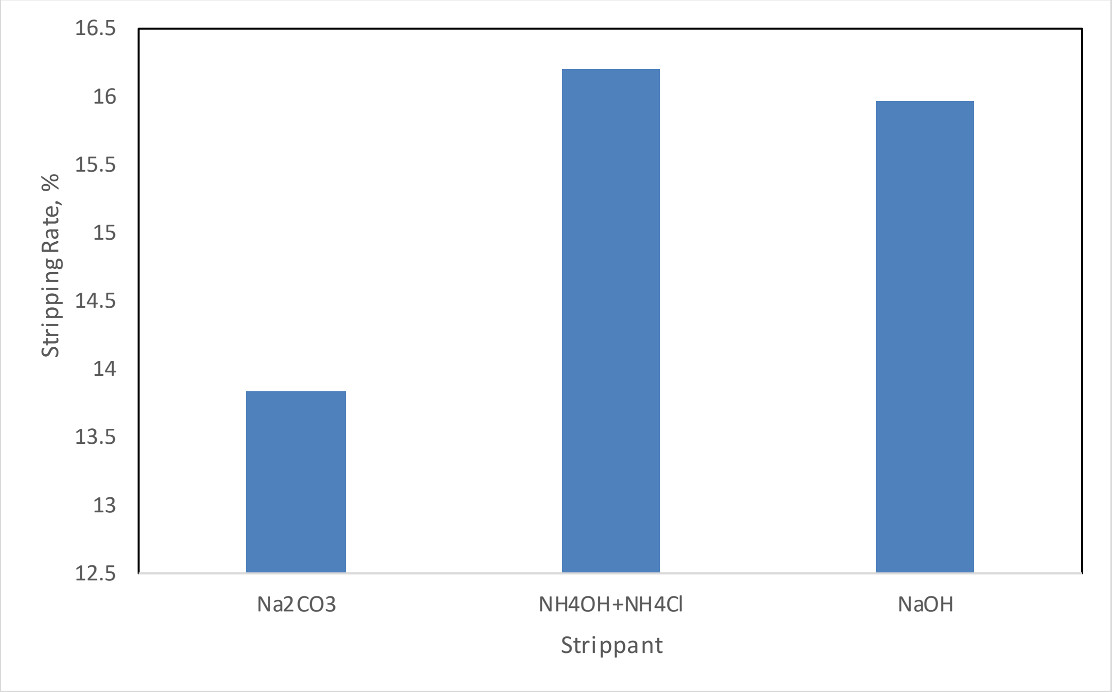

Figure 25 Comparison of Strippants for the V-enriched TOA Solvent

4.6 Integrated Nickel and Vanadium Recovery

Based on above experiments, three possible V and Ni recovery methods were selected: base leaching and followed by chemical precipitation, acid leaching and followed by D2EHPA extraction, and acid leaching followed by TOA extraction. Note that roasting was not considered in this study as the goal of this study is to recover both metal and carbon. To compare the performances of these three approaches, three integrated leaching and recovery processes, as shown in Figures 27 to 29, were conducted using the SPP sample and the mass flows of five major metals (see highlighted labels in the flow chart) were also recorded to calculate the recovery rates.

4.6.1 Base Leaching and Chemical Precipitation

Figure 26 is the flow diagram of the base leaching and chemical precipitation process. The concept is that, among all five major metals, only V can be leached out by NaOH, which leads to good selectivity. Once V is removed, other metals can be leached out again by acid and then selectively precipitated by oxidization and pH adjustment. For example, Fe(III) can be precipitated out at pH around 5 to 6 using NaOH, and then Na_2CO_3 is added to precipitate Ni at pH in between 7 and 8.

In this study, 1N NaOH (1g:10ml) was used to balance the leaching rate as well as minimize the acid consumption for the following leaching for other metals. To precipitate V in the base solution, H_2O_2 was added to oxidize all V(IV) to V(V). After that NH_4Cl was added and the solution pH was reduced to 8-9 by H_2SO_4.

However, no precipitate was collected, possibly because of low concentration of V in the solution. As shown in Table 9, the leaching rate of 1N NaOH was 82.4% and additional 11.3% of V was extracted by water washing. As the ratio of base leaching is 1g:10ml, the V concentration in the base solution was 508.8 mg/L (5087.7mg/kg divided by10ml) which would be too low to be suitable for this process. Therefore, the sequential process was not continued.

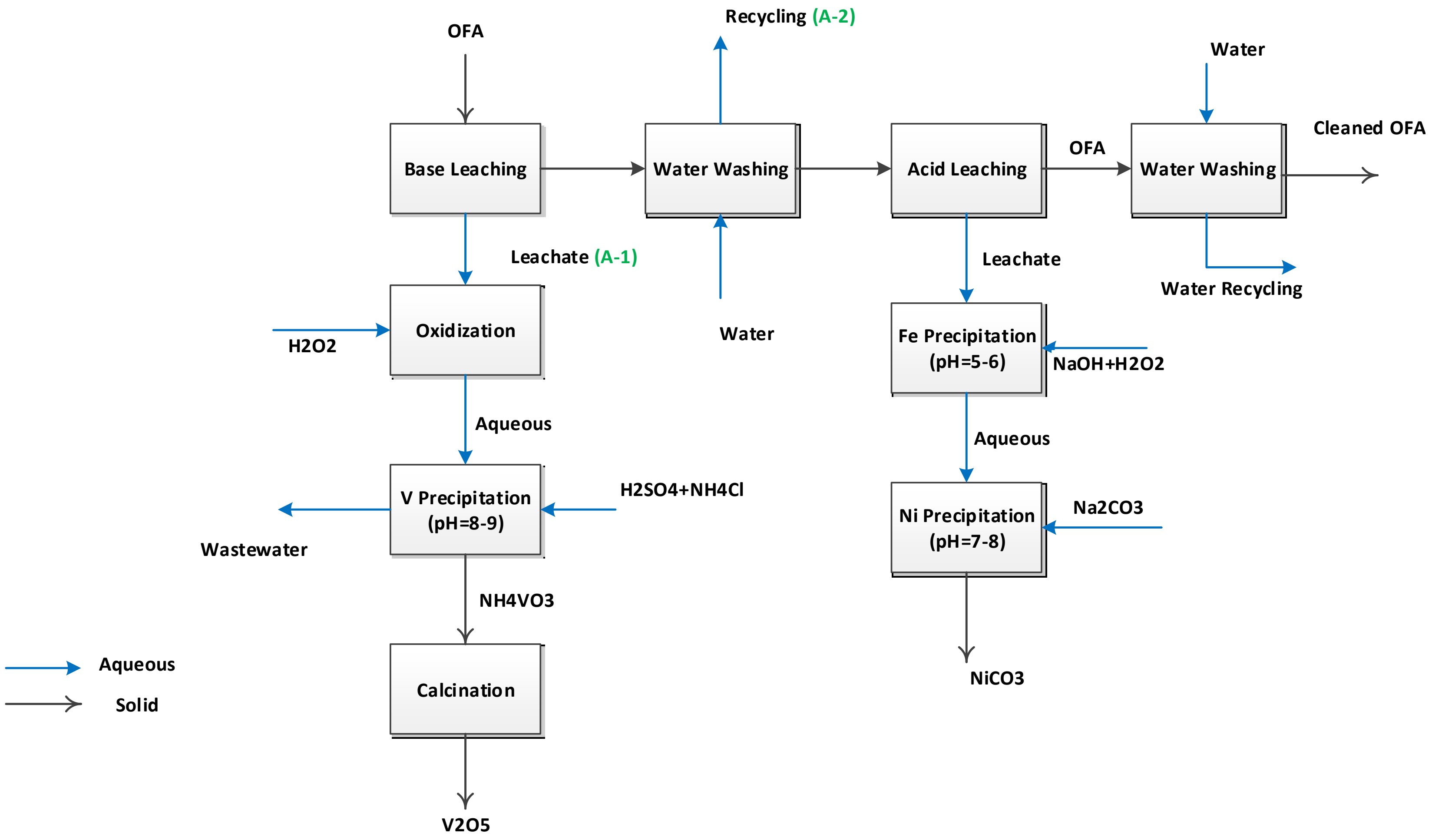

Figure 26 Process Flow Chart of Base Leaching and Chemical Precipitation

Table 9 Mass Balance Sheet of Five Major Metals - Base Leaching Process

Process	V		Ni		Fe		Mg		Al	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Raw	6,170.7	100.0	1,974.6	100.0	7,451.6	100.0	2,619.0	100.0	398.8	100.0
A-1	5,087.7	82.4	0	0	4.7	0.1	0	0	227.0	56.9
A-2	695.3	11.3	0	0	0	0	0	0	32.9	8.2

Note: * Since real volumes of the solutions may be different from the calculated ones due to precipitation or other factors, resulting in approx. 5% variation in calculating the concentrations and percentages

4.6.2 Acid Leaching and D2EHPA Extraction

The second option is to leach out all the metals by acid and then extracts V from the acidic media by D2EHPA. Lastly, Ni is recovered by chemical precipitation. The process flow is shown in Figure 27 and the metal mass flows are recorded in Table 10.

Briefly, the SPP OFA was washed by 1N H_2SO_4 at the S:L ratio of 1g:10ml, then it was rinsed by water at the S:L ratio of 1g:5ml. Although the water leaching solution (A-2) contains metals, it was not mixed with the acidic leachate (A-1), considering that it may dilute the V and Ni concentration, which will affect the efficiency of the sequential recovery process. After leaching, Na_2SO_3 was added to minimize the interference of Fe as well as improve the extraction of V. The pH of the solution was then increased to around 3 by addition of NaOH and V was extracted by D2EHPA at the O:A ratio of 1:1 (v/v). Then, the V enriched solvent was stripped by 1.5M H_2SO_4 at the O:A ratio of 5:1(v/v) with 2 stages. The raffinate after the extraction was oxidized by H_2O_2 and its pH was increased to 5-6 by NaOH to precipitate out Fe, then the raffinate pH was further increased to 7-8 by Na_2CO_3 to precipitate out Ni.

The rates in Table 10 are the unit percentage of the raw SPP sample. The solution concentration can be calculated by dividing the mg/kg value by the volume of the liquid. For example, the unit V and Ni content in the leachate is 5731.8mg/kg and 1834.5 mg/kg, their concentration in solution would be approximately 573.2mg/L and 183.5mg/L as the S:L ratio is 1g:10ml.

After extraction by D2EHPA, the V content dropped from 92.9% to 1.2%, giving an extraction rate of 98.7%. Ni and Mg were not extracted by the solvent but 91.2% Fe and 65.3% Al in the leachate solution were extracted. After oxidization and increasing the pH of the raffinate (B-1), Fe was precipitated out as S-3. Comparing with B-1, most of Fe was removed and it dropped from 8.2% to 0.5%. However, some of Ni and Al were also removed. In S-3, the Fe content is the highest, which is 437.1 mg/kg, followed by Ni 296.4 mg/kg, which indicates that the purity of the Fe precipitate is limited due to low concentration of Fe.

The Ni precipitation by Na_2CO_3 showed good efficiency, 77.6% out of 92.9% Ni in the solution was precipitated. Mg was the major impurity that 10.5% out of 93.6% Mg was precipitated with Ni. Interestingly, in the wastewater stream B-3, the concentrations of all major metals were low except Mg, indicating that recovery of Mg could be possible.

For the V enriched organic solvent, D2EHPA was stripped by 1.5M H_2SO_4 with 2 stages, the total amount of the stripped V was 64.0% out of 92.9% in the solution, meaning that 68.9% of V in the solution was recovered. The major impurity in the strippant was Fe, which was 11.0% out of 93.1%. Fe was removed from the solvent by oxalic acid and the strippant mainly contained Fe and V.

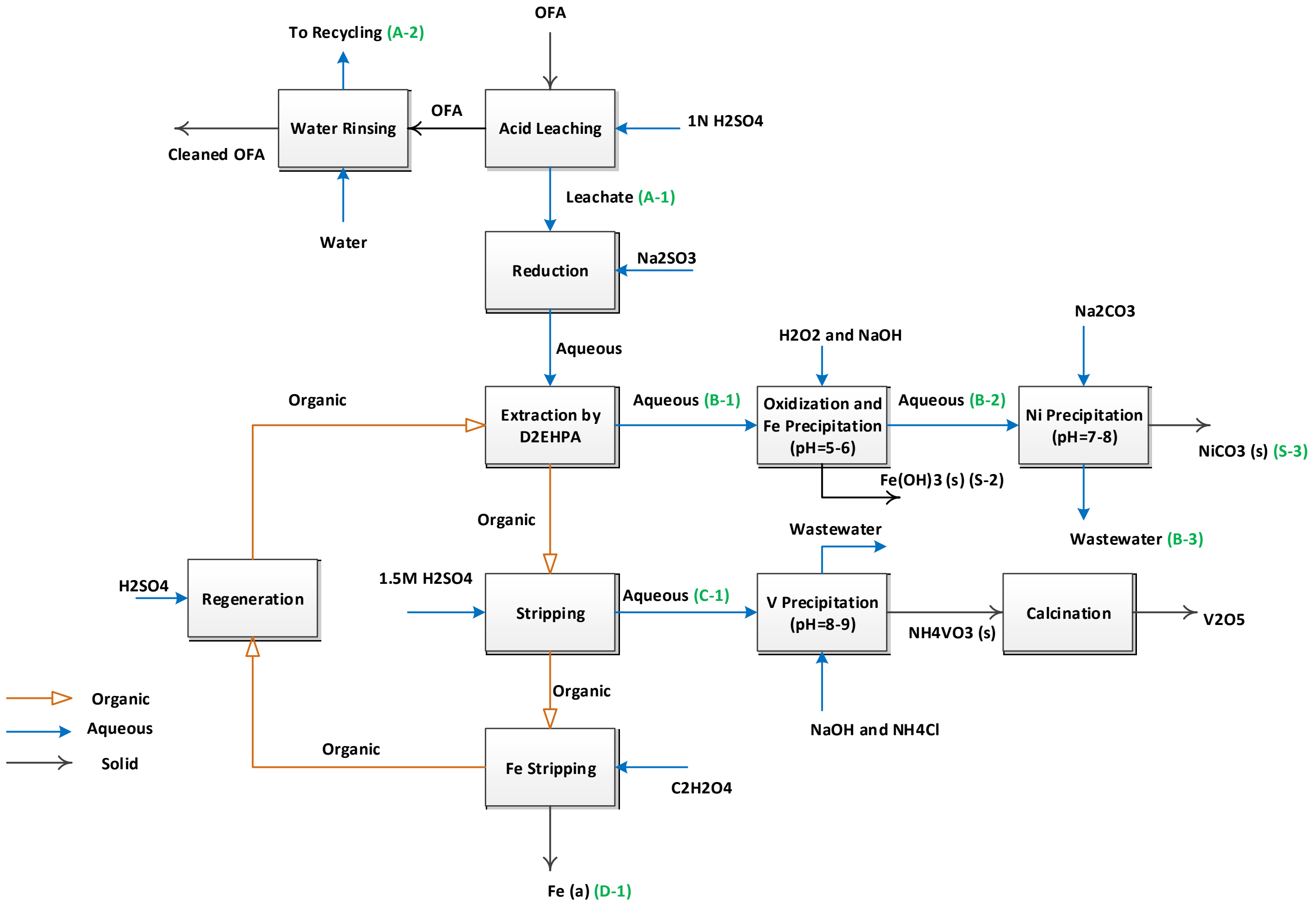

Figure 27 Process Flow Chart of Acid Leaching and D2EHPA Solvent Extraction

Table 10 Mass Balance Sheet of Five Major Metals - Acid Leaching and D2EHPA Extraction Process

D2EHPA	V		Ni		Fe		Mg		Al	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Raw	6,170.7	100.0	1,974.6	100.0	7,451.6	100.0	2,619.0	100.0	398.8	100.0
A-1	5,731.8	92.9	1,834.5	92.9	6,937.9	93.1	2,450.9	93.6	348.0	87.3
A-2	450.5	7.3	147.3	7.5	539.9	7.2	176.6	6.7	35.0	8.8
B-1	73.5	1.2	1,821.8	92.3	609.8	8.2	2,412.7	92.1	120.8	30.3
B-2	53.2	0.9	1,753.6	88.8	38.4	0.5	2,304.7	88.0	5.7	1.4
S-2	0.3	0.0	296.4	15.0	437.1	5.9	214.5	8.2	64.2	16.1
B-3	49.3	0.8	1.5	0.1	0	0	2,155.7	82.3	0	0
S-3	6.4	0.1	1,531.7	77.6	28.6	0.4	273.9	10.5	32.6	8.2
C-1	3,949.2	64.0	0	0	822.8	11.0	21.4	0.8	32.0	8.0
D-1	557.1	9.0	0	0	1,474.5	19.8	0	0.0	72.6	18.2

Note: * Since real volumes of the solutions may be different from the calculated ones due to precipitation and other interferences, resulting in approx. 5% variation in calculating the concentrations and percentages

4.6.3 Acid Leaching and TOA Extraction

In this process, the leaching section is same as the D2EHPA process. After leaching, H_2O_2 was added to oxidize V and Fe and then the pH of the solution was increased to around 2.5 and V was extracted from the solution by TOA. To remove Fe, the pH of the raffinate was increased to 5-6 by NaOH. After that, Ni was removed from the solution by addition of Na_2CO_3 until pH reached 7-8. V enriched solvent was stripped by the mixture of 1M NH_4OH and 1.5M NH_4Cl at ratio of O:A=2:1 with 2 stages.

The mass flows of all five major metals are tabulated in Table 11. Comparing with D2EHPA process, the extraction rate of V was lower, 61.7% out of 92.9% in the solution, giving an extraction rate of 66.4%. However, its selectivity was better, as other metals were not extracted, except small amount of Fe. After precipitation of Fe, the major metal in the precipitate was Fe (5,903.0mg/kg) and V (1478.0mg/kg), indicating co-precipitation effect of V and Fe. In the Ni precipitate, the amount of Ni was 1,771.8mg/kg, accounting for 89.7% of total Ni in the OFA and 96.6% of Ni in the solution. In the strippant, 3,652.5mg/kg V was recovered, which was 59.2% of total V in the OFA, 63.7% in the solution, and 95.9% stripping efficiency.

Between the selected solvents, TOA is preferred over D2EHPA in this case (for SPP sample) as it showed good selective extraction of V over Fe which is the major interfering impurity in this study.

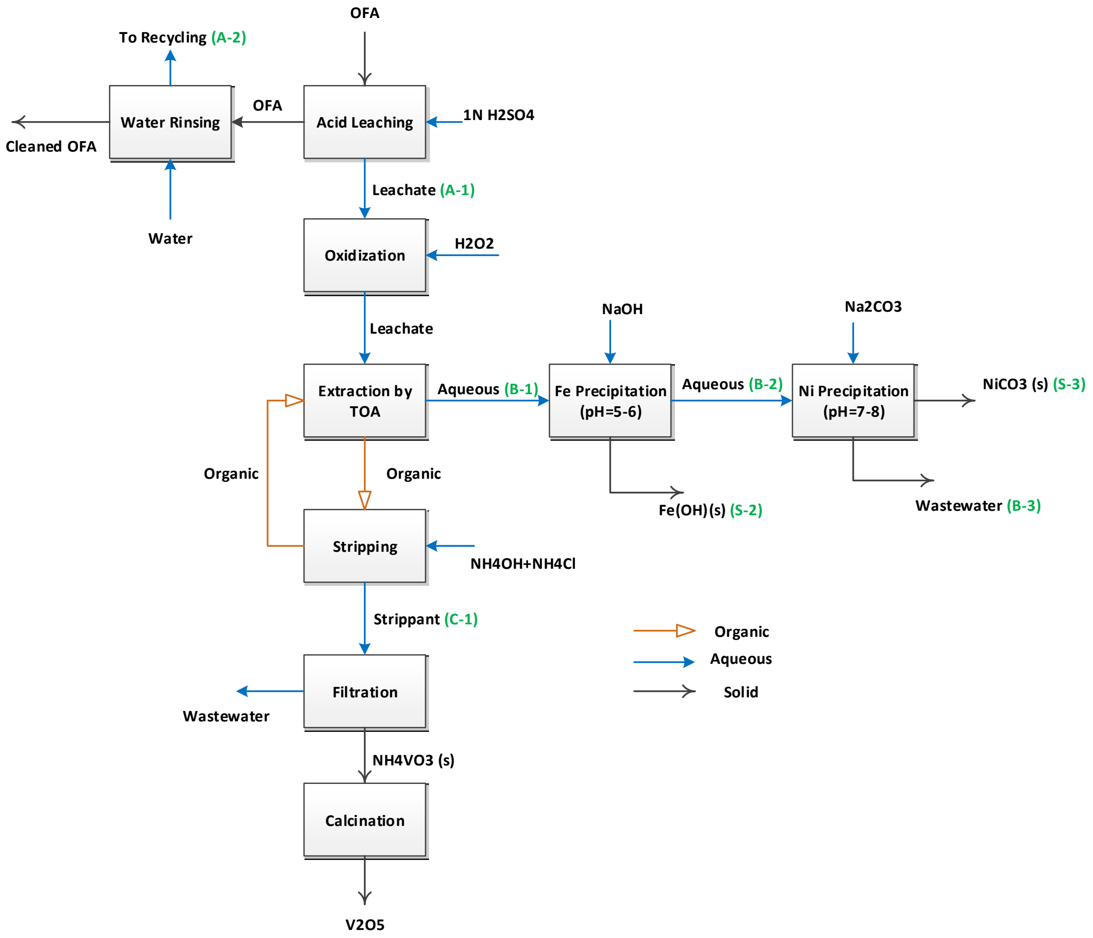

Figure 28 Process Flow Chart of Acid Leaching and TOA Solvent Extraction

Table 11 Mass Balance Sheet of Major Metals - Acid Leaching and TOA Extraction

TOA	V		Ni		Fe		Mg		Al	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Raw	6,170.7	100.0	1,974.6	100.0	7,451.6	100.0	2,619.0	100.0	398.8	100.0
A-1	5,731.8	92.9	1,834.5	92.9	6,937.9	93.1	2,450.9	93.6	348.0	87.3
A-2	450.5	7.3	147.3	7.5	539.9	7.2	176.6	6.7	35.0	8.8
B-1	1,924.1	31.2	1,881.1	95.3	6,557.1	88.0	2,505.6	95.7	355.0	89.0
B-2	56.0	0.9	1,943.7	98.4	108.4	1.5	2,562.0	97.8	97.1	24.3
S-2	1,478.0	24.0	321.0	16.3	5,903.0	79.2	280.0	10.7	184.3	46.2
B-3	7.3	0.1	16.8	0.9	0	0	2,325.8	88.8	0	0
S-3	40.5	0.7	1,771.8	89.7	95.7	1.3	349.4	13.3	110.3	27.7
C-1	3,652.5	59.2	0	0	602.1	8.1	0	0	11.7	2.9

Note: * Since real volumes of the solutions may be different from the calculated ones due to precipitation or other factors, resulting in approx. 5% variation in calculating the concentrations and percentages

5 Conclusions and Recommendations

5.1 Summary

Disposal of OFA raises great environmental concerns due to its acidity and high heavy metal content. However, OFA has high carbon content, which make it a potential precursor for adsorbents. In addition, V and Ni are abundant in OFA and its beneficial reuse can be maximized if these metals can be recovered from the wastewater generated from OFA cleaning.

Through a comprehensive evaluation on the V and Fe leaching and recovery methods, this study developed an integrated metal recovery process for the OFA that has been investigated by our group. More importantly, the mechanism of the process was studied and the linkage between the recovery process and the characteristics of the OFA was understood. Briefly, the findings of this study are summarized as follows:

For metal leaching, both H_2SO_4 and NaOH showed better V extraction than NH_4OH. H_2SO_4 can extract all metals at high efficiency, while NaOH can only leach out V. Higher acid concentration increases the extraction rate but this trend is not linear due to common ion effect that high sulfate concentration inhibits the dissolution of $VOSO_4$ which is the major form of V presented in the OFA. Based on the results, the sulfuric acid concentration should be in the range between 0.5N and 1N.

Increasing temperature moderately improves metal leaching, however, some literatures reported that this trend is also non-linear. The leaching rate decreases when the temperature exceeds 60°C. Solid and liquid ratio plays an important role in the metal leaching process and the results indicated that the unit extraction rate decreases as the S: L ratio increases although the metal concentration increases. It should note that low S:L ratio may consume excess water and acid. In addition, the metal concentration may not be high enough for the sequential metal recovery process. Therefore, the S:L ratio of 1g:10ml was selected to balance the extraction rate and the metal concentration. Salting effect was also studied and found that addition of both common and uncommon salt improves the metal leaching.

For metal recovery, chemical precipitation, ion exchange resin and solvent extraction were evaluated. Since OFA may contains considerable Fe and its precipitation process will remove significant amount of V due to co-precipitation effect. Therefore, direct chemical precipitation may not obtain an acceptable recovery efficiency and selectivity.

Two types of sodium based ion exchange resins, Lewatit TP 207 and Diaion CR11, were evaluated by both batch and column test. The results showed that both resins have good extraction rate but low selectivity. Thus, this technique may not be suitable for this application.

Similarly, two types of solvents, D2EHPA and TOA, were tested for their metal selectivity and efficiency. The preliminary experiment confirmed that D2EHPA has the selectivity order: Fe(III)> V(IV)> Fe(II) and TOA can extract V(V) but not V(IV). Since the OFA metal leachate contains a mixture of V(IV), V(V), Fe(III) and Fe(II), among which V(IV) and Fe(II) are predominant. Therefore, the metal solution needs to be reduced if D2EHPA is used or oxidized if TOA is used. This was confirmed by the solvent extraction experiment using the RPP solution. After reduction by Na_2SO_3, the V extraction by D2EHPA increased from 45.8% to 71.2%, while Fe extraction rate dropped from 68.1% to 25.4%. After oxidization by H_2O_2, the extraction of V by TOA dramatically increased from 2.8% to 64.1%, while Fe was not extracted.

The pH test of D2EHPA showed that its extraction rate increases as the pH increases. However, other metals, such as Al, will also be extracted if the solution pH is higher than 4. Therefore, the preferred pH is 3. For TOA, higher pH will increase the extraction as well, however, it should not exceed 3 due to the co-precipitation of Fe and V. Therefore, pH of 2.5 is preferred.

After identifying the optimal conditions for V and Ni extraction, three integrated processes were proposed. The extraction process using NaOH was unsuccessful as there was no V precipitate obtained due to insufficient concentration of V, indicating that this method is not suitable for the OFA which contains low V. Comparing with D2EHPA, the extraction efficiency of TOA is lower but it showed better separation of V and Fe as well as more recovery of Ni. D2EHPA is more sensitive to the presence of Fe as D2EHPA co-extracts both V and Fe, even though Fe was reduced by Na_2SO_3 before extraction.

Table 12 summarizes the advantages and disadvantages of all the leaching and recovery methods that were included from this study.

Table 12 Summary of the Advantages and Disadvantages of different Vanadium Leaching and Recovery Methods

Processes		Advantages	Disadvantages
Leaching	Roasting	• Reduces the volume of OFA • More concentrated leachate • Reduces the consumption of acid consumption	• Requires fuel input • Major gaseous emissions • Carbon cannot be recycled • Not suitable for high carbon content OFA (low reactivity) • Possible formation of refractory alloy which is hard to be dissolved (direct roasting)
	Acid Leaching	• Good extraction rate • Does not require concentrated acid • Can extract all metals, so carbon can be easily recovered	• No selectivity • Lower metal concentration comparing to roasting

	Base Leaching	• Good leaching rate • Good V selectivity	• Extra acid leaching is required if Ni recovery is needed • Extra acid is needed if carbon need to be recycled
Recovery	Chemical precipitation	• Simple process • Low cost	• Poor selectivity • Low metal purity due to co-precipitation effect
	Ion exchange resin	• Good recovery rate • Fast adsorption and desorption	• Poor selectivity • Resin needs reconditioning
	Solvent extraction, D2EHPA	• High extraction rate • Wide pH range • Fast extraction and stripping • Can be reused	• Interference of Fe • Requires extra stripping of Fe from solvent
	Solvent extraction, TOA	• Good extraction rate • Good selectivity	• Less extraction rate comparing to D2EHPA • Limited pH range

- Fast extraction and stripping
- Can be reused

5.2 Recommendations

Based on the findings of this study, the following improvements can be made in future:

- The V and Ni content in raw OFA and in the leachate solution are critical to the recovery rate, therefore, it is suggested that OFA should be segregated based on its metal content or ash content. High carbon content OFA is more suitable for activated carbon development, while high ash OFA is more suitable for metal recovery.
- The chemical precipitation used in this study for Ni recovery showed good recovery rate but lower purity. To improve the purity of Ni recovery, other methods can be tested such as solvent extraction (e.g. Cyanex 272) and electrolysis.
- Water consumption could be considerable for the metal recovery. To conserve fresh water, seawater leaching (with or without addition of acid) should be tested as the salting effect may improve leaching efficiency according the results of the study
- If the carbon of the OFA is not planning to be recovered, roasting can be considered. The concerns of gaseous emissions can be minimized by pre-water washing prior to roasting as water is able to remove significant amount of the metals and sulfates from the OFA, which will greatly reduce SOx emission.

Bibliography

Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science, 36*(3), 327-363. doi:http://dx.doi.org/10.1016/j.pecs.2009.11.003

Almazán-Ruiz, F. J., Caballero, F., Cruz-Díaz, M. R., Rivero, E. P., Vazquez-Arenas, J., & González, I. (2015). Nickel recovery from an electroplating rinsing effluent using RCE bench scale and RCE pilot plant reactors: The influence of pH control. *Chemical Engineering Research and Design, 97*, 18-27. doi:http://dx.doi.org/10.1016/j.cherd.2015.02.022

Andini, S., Cioffi, R., Colangelo, F., Montagnaro, F., & Santoro, L. (2008). Adsorption of chlorophenol, chloroaniline and methylene blue on fuel oil fly ash. *Journal of Hazardous Materials, 157*(2–3), 599-604. doi:http://dx.doi.org/10.1016/j.jhazmat.2008.01.025

Azhar Uddin, M., Shinozaki, Y., Furusawa, N., Yamada, T., Yamaji, Y., & Sasaoka, E. (2007). Preparation of activated carbon from asphalt and heavy oil fly ash and coal fly ash by pyrolysis. *Journal of Analytical and Applied Pyrolysis, 78*(2), 337-342. doi:http://dx.doi.org/10.1016/j.jaap.2006.09.004

Barik, S. P., Park, K. H., & Nam, C. W. (2014). Process development for recovery of vanadium and nickel from an industrial solid waste by a leaching–solvent extraction technique. *Journal of Environmental Management, 146*, 22-28. doi:http://dx.doi.org/10.1016/j.jenvman.2014.06.032

Blissett, R. S., & Rowson, N. A. (2012). A review of the multi-component utilisation of coal fly ash. *Fuel, 97*, 1-23. doi:http://dx.doi.org/10.1016/j.fuel.2012.03.024

Boyd, C. E. (2015). Review of Basic Chemistry, Solubility, and Chemical Equilibrium *Water Quality: An Introduction* (pp. 41-70). Cham: Springer International Publishing.

Cai, Z., Feng, Y., Li, H., & Zhou, Y. (2013). Selective Separation and Extraction of Vanadium(IV) and Manganese(II) from Co-leaching Solution of Roasted Stone Coal and Pyrolusite via Solvent Extraction. *Industrial & Engineering Chemistry Research, 52*(38), 13768-13776. doi:10.1021/ie401635m

Caramuscio, P., De Stefano, L., Seggiani, M., Vitolo, S., & Narducci, P. (2003). Preparation of activated carbons from heavy-oil fly ashes.

Waste Management, 23(4), 345-351. doi:http://dx.doi.org/10.1016/S0956-053X(02)00118-6

Coman, V., Robotin, B., & Ilea, P. (2013). Nickel recovery/removal from industrial wastes: A review. *Resources, Conservation and Recycling, 73*, 229-238. doi:http://dx.doi.org/10.1016/j.resconrec.2013.01.019

Davini, P. (2002). Flue gas treatment by activated carbon obtained from oil-fired fly ash. *Carbon, 40*(11), 1973-1979. doi:http://dx.doi.org/10.1016/S0008-6223(02)00049-0

Davini, P. (2003). Behaviour of activated carbons obtained from mixtures of oil-fired fly ash and oil refining pitch. *Carbon, 41*(8), 1559-1565. doi:http://dx.doi.org/10.1016/S0008-6223(03)00104-0

Di Pietro, A., Visalli, G., Munaò, F., Baluce, B., La Maestra, S., Primerano, P., . . . De Flora, S. (2009). Oxidative damage in human epithelial alveolar cells exposed in vitro to oil fly ash transition metals. *International Journal of Hygiene and Environmental Health, 212*(2), 196-208. doi:http://dx.doi.org/10.1016/j.ijheh.2008.05.005

Gosselin, P., Naeth, M. A., Plourde, A., Therrien, R., Kraak, G. V. D., & Xu, Z. (2010). *Environmental and Health Impacts of Canada's Oil Sands Industry*. Retrieved from

Holloway, P. C., & Etsell, T. H. (2004). Salt roasting of suncor oil sands fly ash. *Metallurgical and Materials Transactions B, 35*(6), 1051-1058. doi:10.1007/s11663-004-0061-1

Hsieh, Y.-M., & Tsai, M.-S. (2003). Physical and chemical analyses of unburned carbon from oil-fired fly ash. *Carbon, 41*(12), 2317-2324. doi:http://dx.doi.org/10.1016/S0008-6223(03)00283-5

Hu, G., Chen, D., Wang, L., Liu, J., Zhao, H., Liu, Y., . . . Yu, P. (2014). Extraction of vanadium from chloride solution with high concentration of iron by solvent extraction using D2EHPA. *Separation and Purification Technology, 125*, 59-65. doi:http://dx.doi.org/10.1016/j.seppur.2014.01.031

Kurbatova, L. D., Koryakova, O. V., Valova, M. A., & Yanchenko, M. Y. (2015). Examination of Extraction of Vanadium(V) by Trioctylamine from Sulfuric Solutions. *Zeitschrift für anorganische und allgemeine Chemie, 641*(3-4), 617-621. doi:10.1002/zaac.201400426

Kurbatova, L. D., Koryakova, O. V., Valova, M. S., & Yanchenko, M. Y. (2014). Anion exchange extraction of vanadium(V) with trioctylamine. *Russian Journal of General Chemistry, 84*(8), 1636-1637. doi:10.1134/S1070363214080337

Li, C.-x., Wei, C., Deng, Z.-g., Li, M.-t., Li, X.-b., & Fan, G. (2010). Recovery of vanadium from black shale. *Transactions of Nonferrous Metals Society of China, 20*, s127-s131. doi:http://dx.doi.org/10.1016/S1003-6326(10)60026-X

Li, M. T., Wei, C., Zhou, X. J., Qiu, S., Deng, Z. G., & Li, X. B. (2012). Kinetics of vanadium leaching from black shale in non-oxidative conditions. *Mineral Processing & Extractive Metallurgy: Transactions of the Institution of Mining & Metallurgy, Section C, 121*(1), 40-47. doi:10.1179/1743285511Y.0000000012

Li, W., Zhang, Y., Liu, T., Huang, J., & Wang, Y. (2013). Comparison of ion exchange and solvent extraction in recovering vanadium from sulfuric acid leach solutions of stone coal. *Hydrometallurgy, 131–132*, 1-7. doi:http://dx.doi.org/10.1016/j.hydromet.2012.09.009

Liu, F., Ning, P., Cao, H., Li, Z., & Zhang, Y. (2013). Solubilities of NH4VO3 in the NH3–NH4+–SO42—Cl—H2O System and Modeling by the Bromley–Zemaitis Equation. *Journal of Chemical & Engineering Data, 58*(5), 1321-1328. doi:10.1021/je4000873

Liu, Y.-h., Yang, C., Li, P.-y., & Li, S.-q. (2010). A new process of extracting vanadium from stone coal. *International Journal of Minerals, Metallurgy, and Materials, 17*(4), 381-388. doi:10.1007/s12613-010-0330-8

Mofarrah, A. (2014). *Environmental management and potential use of heavy oil fly ash.* (Doctor of Philosophy), Memorial University of Newfoundland. (6493)

Murase, K., Nishikawa, K.-i., Ozaki, T., Machida, K.-i., Adachi, G.-y., & Suda, T. (1998). Recovery of vanadium, nickel and magnesium from a fly ash of bitumen-in-water emulsion by chlorination and chemical transport. *Journal of Alloys and Compounds, 264*(1–2), 151-156. doi:http://dx.doi.org/10.1016/S0925-8388(97)00247-8

Navarro, R., Guzman, J., Saucedo, I., Revilla, J., & Guibal, E. (2007). Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. *Waste Management, 27*(3), 425-438. doi:http://dx.doi.org/10.1016/j.wasman.2006.02.002

Nazari, E., Rashchi, F., Saba, M., & Mirazimi, S. M. J. (2014). Simultaneous recovery of vanadium and nickel from power plant fly-ash: Optimization of parameters using response surface methodology. *Waste Management, 34*(12), 2687-2696. doi:http://dx.doi.org/10.1016/j.wasman.2014.08.021

Noori, M., Rashchi, F., Babakhani, A., & Vahidi, E. (2014). Selective recovery and separation of nickel and vanadium in sulfate media using mixtures of D2EHPA and Cyanex 272. *Separation and Purification Technology, 136*, 265-273. doi:http://dx.doi.org/10.1016/j.seppur.2014.08.038

Parvizi, R., Khaki, J. V., Moayed, M. H., & Ardani, M. R. (2012). Hydrometallurgical Extraction of Vanadium from Mechanically Milled Oil-Fired Fly Ash: Analytical Process Optimization by Using Taguchi Design Method. *Metallurgical and Materials Transactions B, 43*(6), 1269-1276. doi:10.1007/s11663-012-9709-4

Rahman, F., & Skyllas-Kazacos, M. (1998). Solubility of vanadyl sulfate in concentrated sulfuric acid solutions. *Journal of Power Sources, 72*(2), 105-110. doi:http://dx.doi.org/10.1016/S0378-7753(97)02692-X

Rahman, F., & Skyllas-Kazacos, M. (2009). Vanadium redox battery: Positive half-cell electrolyte studies. *Journal of Power Sources, 189*(2), 1212-1219. doi:http://dx.doi.org/10.1016/j.jpowsour.2008.12.113

Rasoulnia, P., & Mousavi, S. M. (2016). V and Ni recovery from a vanadium-rich power plant residual ash using acid producing fungi: Aspergillus niger and Penicillium simplicissimum. *RSC Advances, 6*(11), 9139-9151. doi:10.1039/C5RA24870A

Seggiani, M., Teti, G., & Vitolo, S. (2002). Investigation on the combustion of heavy-oil fly-ashes. *Fuel, 81*(13), 1711-1715. doi:http://dx.doi.org/10.1016/S0016-2361(02)00054-6

Seggiani, M., Vitolo, S., & D'Antone, S. (2006). Recovery of nickel from Orimulsion fly ash by iminodiacetic acid chelating resin. *Hydrometallurgy, 81*(1), 9-14. doi:http://dx.doi.org/10.1016/j.hydromet.2005.09.005

Seggiani, M., Vitolo, S., & De Filippis, P. (2005). Effect of pre-oxidation on the porosity development in a heavy oil fly ash by CO2 activation. *Fuel, 84*(14–15), 1854-1857. doi:http://dx.doi.org/10.1016/j.fuel.2005.02.023

Seggiani, M., Vitolo, S., Pastorelli, M., & Ghetti, P. (2007). Combustion reactivity of different oil-fired fly ashes as received and leached. *Fuel, 86*(12–13), 1885-1891. doi:http://dx.doi.org/10.1016/j.fuel.2006.12.010

Singh, D. K., Yadav, K. K., & Singh, H. (2013). Extraction and Stripping Behavior of Iron (III) from Phosphoric Acid Medium by D2EHPA

Alone and Its Mixtures with TBP/TOPO. *Separation Science and Technology, 48*(10), 1556-1564. doi:10.1080/01496395.2012.753084

Tatár, E., Csiky, G. M., Mihucz, V. G., & Záray, G. (2005). Investigation of adverse health effects of residual oil fly ash emitted from a heavy-oil-fuelled Hungarian power plant. *Microchemical Journal, 79*(1–2), 263-269. doi:http://dx.doi.org/10.1016/j.microc.2004.10.021

Tokuyama, H., Nii, S., Kawaizumi, F., & Takahashi, K. (2003). Process Development for Recovery of Vanadium and Nickel from Heavy Oil Fly Ash by Leaching and Ion Exchange. *Separation Science and Technology, 38*(6), 1329-1344. doi:10.1081/SS-120018812

Trypuć, M., & Białowicz, K. (1997). Solubility of NH4VO3 in Water + Ammonia. *Journal of Chemical & Engineering Data, 42*(2), 318-320. doi:10.1021/je960259q

Tsai, S.-L., & Tsai, M.-S. (1998a). A study of the extraction of vanadium and nickel in oil-fired fly ash. *Resources, Conservation and Recycling, 22*(3–4), 163-176. doi:http://dx.doi.org/10.1016/S0921-3449(98)00007-X

Tsai, S.-L., & Tsai, M.-S. (1998b). A study of the extraction of vanadium and nickel in oil-fired fly ash. *Resources, Conservation and Recycling, 22*, 163–176.

Tsygankova, M. V., Bukin, V. I., Lysakova, E. I., Smirnova, A. G., & Reznik, A. M. (2011). The recovery of vanadium from ash obtained during the combustion of fuel oil at thermal power stations. *Russian Journal of Non-Ferrous Metals, 52*(1), 19-23. doi:10.3103/S1067821211010251

Vitolo, S., Seggiani, M., & Falaschi, F. (2001). Recovery of vanadium from a previously burned heavy oil fly ash. *Hydrometallurgy, 62*(3), 145-150. doi:http://dx.doi.org/10.1016/S0304-386X(01)00193-1

Vitolo, S., Seggiani, M., Filippi, S., & Brocchini, C. (2000). Recovery of vanadium from heavy oil and Orimulsion fly ashes. *Hydrometallurgy, 57*(2), 141-149. doi:http://dx.doi.org/10.1016/S0304-386X(00)00099-2

Zeng, L., & Cheng, C. Y. (2009). A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts: Part I: Metallurgical processes. *Hydrometallurgy, 98*(1–2), 1-9. doi:http://dx.doi.org/10.1016/j.hydromet.2009.03.010

Zhang, J.-h., Zhang, W., Zhang, L., & Gu, S.-q. (2014). A Critical Review of Technology for Selective Recovery of Vanadium from Leaching

Solution in V2O5 Production. *Solvent Extraction and Ion Exchange, 32*(3), 221-248. doi:10.1080/07366299.2013.877753