Vanadium : leaching and solvent extraction

by

Mohammadreza Tavakolikhaledi

B. Sc., Sharif University of Technology, 2005

M. Sc., Sharif University of Technology, 2007

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

The Faculty of Graduate and Postdoctoral Studies

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

May 2014

© Mohammadreza Tavakolikhaledi, 2014

Abstract

The fundamental understanding of vanadium hydrometallurgy was developed in three phases: vanadium (V) leaching, vanadium (III) oxidative leaching, and solvent extraction of vanadium (V&IV).

In the first section, V_2O_5 leaching was studied in three steps. First, vanadium leaching and solubility of VO_2^+ at different pH's and temperatures were investigated in sulfuric acid. Secondly, the kinetics of vanadium leaching in pH 5 and pH 8 solutions, and the reductive leaching of vanadium pentoxide using sodium sulfite were studied. It was shown that the kinetics of acid leaching is rapid but suffers from low solubility of VO_2^+ in solution. Thirdly, the shrinking sphere model was employed to analyze the kinetics of reductive leaching.

In the second step, V_2O_3 oxidative leaching was studied from 30°C to 90°C in sulfuric acid. This study has also been done in three different sections. First, the kinetics of oxidative leaching using oxygen was investigated. It was shown that this oxidative leaching is chemical reaction rate controlled with an activation energy of 69 kJ/mol. In the next step, it was shown that the presence of ferric enhanced kinetics significantly. Finally, oxidative leaching using a constant ferric-ferrous ratio from 1 to 300 was studied. The addition of KMnO₄ solution to the leach reactor was found to be a suitable oxidant for controlling solution potential. The oxidation rate using the constant ferric-ferrous ratio was very sensitive to temperature, with a large activation energy (38 kJ/mol) and the rate was proportional to the Fe(III)/Fe(II) concentration to the power of 0.47. In the third part, purification of synthetic vanadium-containing solutions using the solvent extraction technique was investigated. Various solvent extractants have been tested for vanadium recovery from acid leachates. One of the biggest problems for purification of the vanadium solution is iron separation. Therefore, this research assesses selectivity of vanadium over iron. The extraction of vanadium (V&IV), iron (III&II) with phosphinic acid (CYANEX 272), phosphonic acid (IONQUEST 801), phosphoric acid (D2EHPA) and phosphine oxide (CYANEX 923) extractants is reported. In addition, the extraction reactions for vanadium (V) and (IV) extraction using CYANEX 923 and D2EHPA were also studied.

Preface

This research work was conducted as a part of an NSERC grant awarded to The University of British Columbia. The journal papers listed below have been prepared from work presented in the dissertation. I am the primary contributor for all of them, and the contributing co-authors are as follows: Dr. David Dreisinger (supervisor) and Scott Dornian who contributed to the first paper as a coop student in the summer of 2012. Chapter 4, 5 and 6 of this thesis are based on paper 1, 2 and 3 respectively.

- Tavakoli, M. R., Dornian, S. and Dreisinger, D. B., 2014. The leaching of vanadium pentoxide using sulfuric acid and sulfite as a reducing agent, Hydrometallurgy 141, 59-66.
- 2- Tavakoli, M. R. and Dreisinger, D. B., 2014. The kinetics of oxidative leaching of vanadium trioxide", Hydrometallurgy (Hydrometallurgy, In Press, Accepted).
- 3- Tavakoli, M. R. and Dreisinger, D. B., 2014. Separation of vanadium from iron by solvent extraction using acidic and neutral organophosphorus extractants, Hydrometallurgy 141, 17-23.

	Abstract		ii
	Preface		iv
	Table of	f Contents	v
	List of T	Tables	ix
	List of F	igures	X
	Nomencl	ature	xiv
	Acknowl	edgments	xvi
	Dedicatio	0n	xvii
1	Intro	duction	1
1	1111100	Juction	1
	1.1 F	listory	2
	1.2 P	roperties of vanadium	
	1.3 P	rimary and secondary sources and vanadium products	
2	Litera	ature review	6
	2.1 A	Aqueous chemistry	7
	2.2 I	Leaching and metallurgical processes	12
	2.2.1	Roasting	
	2.2.2	Leaching	
	2.2.2	2.1 Oil and combustion ashes	16
	2.2.2	2.2 Spent catalysts	21
	2.2.2	2.3 Kinetic studies	
	2.2.3	Summary	
	2.3 S	separation and purification: solvent extraction	
	2.3.1	Solvent extraction of vanadium in industry	

Table of Contents

		2.3.	.2.1 Solvent extraction using cation extractants	31
		2.3.	.2.2 Solvent extraction using anion extractants	41
		2	2.3.2.2.1 Problems with using amines	47
	2.4	5	Summary	. 47
	2.5	(Objectives	. 48
3	ł	Expe	rimental	, 49
	3.1	l	Leaching	. 50
	3	8.1.1	Vanadium (V)	. 50
		3.1.	.1.1 Material	50
		3.1.	.1.2 Experimental procedure	50
	3	3.1.2	Vanadium (III)	. 52
		3.1.	.2.1 Material	
		3.1.	.2.2 Experimental procedure	52
	3.2	5	Solvent extraction	. 54
	3	3.2.1	Materials	. 54
	3	3.2.2	Experimental procedure	. 55
	3.3	I	Magnitude of errors in the experiments	. 56
4	ľ	Vana	$\Delta dium (\Lambda^2)$ loophing	59
4		v alla	autum (v) reaching	. 30
	4.1		Thermodynamics of the vanadium –water system	. 59
	4.2	S	Solubility	. 60
	4.3]	Leaching of vanadium in pH 5-8 solution	. 68
	4.4]	Reductive leaching	. 70
	4	4.4.1	Effect of temperature	. 72
	4	4.4.2	Effect of particle size	. 76
	4	1.4.3	Effect of stirring speed	. 77
	4	1.4.4	Effect of sodium sulfite concentration	. 79

	4.4.5	Effect of pH	
	4.4.6	Chemistry and electrochemistry of the reaction	
5	Van	adium (III) leaching	88
5	5.1	V ₂ O ₃ leaching using oxygen	89
	5.1.1	Effect of particle size	
	5.1.2	Effect of stirring speed	
	5.1.3	Effect of sulfuric acid concentration	
5	5.2	V ₂ O ₃ leaching using oxygen and ferric	100
	5.2.1	Effect of initial ferric concentration	101
	5.2.2	Effect of temperature	101
	5.2.3	Effect of pH	102
5	5.3	Vanadium trioxide leaching using ferric-ferrous solutions	103
	5.3.1	Effect of temperature	104
	5.3.2	Effect of particle size	107
	5.3.3	Effect of ferric-ferrous ratio	108
6	Solv	ent extraction	114
6	5.1	Extraction of vanadium (V) in the presence of iron (III)	115
	6.1.1	Effect of pH value on selectivity	115
	6.1.2	Effect of contact time	116
	6.1.3	Vanadium (V) extraction mechanism using CYANEX 923	117
	6.1.4	Stripping vanadium from CYANEX 923	121
	6.1.5	Role of sulfate on vanadium (V) solvent extraction	
6	5.2	Extraction of vanadium (IV) in the presence of iron (III)	124
	6.2.1	Effect of pH on selectivity	
6	5.3	Extraction of vanadium (IV) in the presence of iron (II)	124

6.	B.1 Effect of pH on selectivity	
6.	8.2 Vanadium (IV) extraction mechanism using D2EHPA	127
7 C	onclusions and recommendations for future work	
7.1	Conclusions	131
7.2	Recommendations for future work	
Refere	nces	

List of Tables

Table 1.1. Physical properties of vanadium
Table 1.2. Vanadium world annual production (metric tonne) by country
Table 2.1. Characteristics of some vanadium species in aqueous solutions 9
Table 2.2. Thermodynamic data for aqueous vanadium species at standard state
Table 2.3. Roasting condition for vanadium recovery
Table 2.4. The analysis of the used ashes 19
Table 2.5. Percentage of materials dissolved on water leaching of roasted catalysts 23
Table 2.6. Summary of Vanadium leaching studies 29
Table 2.7. Scrub of V, Fe, and Al from the loaded solvent
Table 2.8. Strip of Mo from the scrubbed solvent (CYANEX272)
Table 2.9. Strip of vanadium from loaded solvent (CYANEX272) 37
Table 2.10. Stripping of vanadium from TOMAC and TOA solutions with various
aqueous media
Table 2.11. Influence of stripping agent and concentration on vanadium stripping from
loaded organic phase
Table 2.12. Extraction of V (V) 1 g/L from alkaline NaOH solution (pH 12.8) using
various extractants
Table 3.1. Chemicals used and composition of the synthetic feed solution 54
Table 4.1. Thermodynamic data for equation 4.1 64
Table 5.1. Thermodynamics data for reaction 5.1 89
Table 5.2. Thermodynamic data for reaction 5.3 100
Table 6.1. Strip of Vanadium (V) from the loaded solvent 123
Table 6.2. Strip of Vanadium (IV) from the loaded solvent 129

List of Figures

Figure 1.1. Consumption of vanadium in various end use categories
Figure 2.1. Stability relationships of vanadium ions and the compounds in aqueous media
at 25°C
Figure 2.2. Vanadium species in water as a function of pH with a total VO^{2+}
concentration of 14.3 mM 10
Figure 2.3. Treatment of vanadium raw materials
Figure 2.4. Extraction yield of vanadium versus the molarity of the H ₂ SO ₄ leaching
solution at room (white circles) and boiling temperature (black circles) with a liquid/solid
ratio of 3 mL/g
Figure 2.5. Metallurgical processes for spent HDS catalysts involving acid leaching 23
Figure 2.6. Metallurgical processes for spent HDS catalysts involving caustic leaching 24
Figure 2.7. Chemical structures and pKa values of the commercial extractants
Figure 2.8. Percentage of extraction of metals from sulfate solutions as a function of
equilibrium pH with 20% CYANEX 272 dissolved in Exxsol D80
Figure 2.9. Percentage of extraction of metals from sulfate solutions as a function of
equilibrium pH with 20% PIA-8 dissolved in Exxsol D80
Figure 2.10. Percentage of extraction of metals from sulfate solutions as a function of
equilibrium pH with 20% PC-88A dissolved in Exxsol D80 34
Figure 2.11. Percentage of extraction of metals from sulfate solutions as a function of
equilibrium pH with 20% TR-83 dissolved in EXXSOL D80
Figure 2.12. Effect of the solution pH on the percent extraction of vanadium from
Na ₂ CO ₃ -synthesized solution; TOA (tri-n-octylamine), TOMAC (tri-n-
octylmethylammonium chloride)
Figure 2.13. pH dependence on the extraction of individual metal ions from sulfuric acid
solutions by 20 vol% LIX63 dissolved in Exxsol 80 40
Figure 2.14. Effect of pH on the extraction of metal values with 0.5M LIX63 in Shellsol
D70 at an A/O ratio of 1:1 and 40°C
Figure 2.15. Effect of pH on the solvent extraction of V(V)
Figure 2.16. pH influence of vanadium extraction for different extractants

Figure 2.17. Effect of Aliquat-336 concentration on the extraction of Vanadium (1 g/L)
from 3 M HCl solution at 25°C and phase ratio O/A=1 46
Figure 3.1. The experimental set up for solvent extraction tests
Figure 4.1. Speciation of vanadium (V) in aqueous media at 25°C 59
Figure 4.2. The effect of solid to liquid ratio on V ₂ O ₅ leaching; (a) vanadium extraction,
(b) vanadium molarity
Figure 4.3. The effect of pH on vanadium leaching at 30°C
Figure 4.4. The effect of pH on vanadium leaching at 50°C
Figure 4.5. The effect of pH on Vanadium leaching at 70°C
Figure 4.6. The effect of pH on vanadium leaching at 90°C
Figure 4.7. The effect of different solvent and adding different salts on vanadium
Eigen 4.8 Demon aposto for usualium solution to confirm usualium complemention in
the presence of sulfate (7
Eigene 4.0. The effect of terms are used diver leaching.
Figure 4.9. The effect of temperature on vanadium leaching
Figure 4.10. The effect of temperature on variadium leaching $\frac{1}{10}$
Figure 4.11. The effect of temperature on vanadium reductive leacning
Figure 4.12. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various temperature test; (b) Plot of
$(1-(1-X)^{\frac{2}{3}})$ versus time for various temperature tests
Figure 4.13. Arrhenius plot for activation energy calculation for reductive leaching 75
Figure 4.14. SEM image for (a) the initial particle; (b) after 20 minutes of leaching at
30°C; (c) after 20 minutes of leaching at 90°C
Figure 4.15. The effect of particle size on vanadium reductive leaching
Figure 4.16. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various particle sizes (b) The effect of
particle size on the rate of dissolution of vanadium78
Figure 4.17. The effect of stirring speed on vanadium reductive leaching
Figure 4.18. The effect of sulfite concentration on vanadium reductive leaching
Figure 4.19. Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various sulfite concentration tests
Figure 4.20. The effect of initial sulfite concentration on the rate of dissolution of
vanadium

rigure 4.21. The effect of pir on vanadium reductive reaching	52
Figure 4.22. Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various pH	37
Figure 5.1. The effect of temperature on vanadium leaching	0
Figure 5.2. (a) Plot of $(1-(1-x)^{\frac{1}{3}})$ versus time for various temperature test; (b) Plot of	of
$(1-(1-X)^{\frac{2}{3}})$ versus time for various temperature test	13
Figure 5.3. Arrhenius plot for activation energy calculation for oxidative leaching usin oxygen	ıg 94
Figure 5.4. The effect of particle size on the rate of vanadium oxidative leaching9.	95
Figure 5.5. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various particle sizes (b) The effect of	of
particle size on the rate of dissolution of vanadium	96
Figure 5.6. The effect of stirring speed on vanadium oxidative leaching	97
Figure 5.7. The effect of sulfuric acid concentration on vanadium oxidative and no	n
oxidative leaching	8
Figure 5.8. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various particle sizes; (b) The effect of	əf
particle size on the rate of dissolution of vanadium	9
Figure 5.9. The effect of initial ferric concentration on the kinetics of vanadium oxidativ	<i>i</i> e
leaching)1
leaching 10 Figure 5.10. The effect of temperature on vanadium oxidative leaching 10)1)2
leaching10Figure 5.10. The effect of temperature on vanadium oxidative leaching10Figure 5.11. The effect of temperature on vanadium oxidative leaching10)1)2)5
leaching)1)2)5
leaching)1)2)5 of
leaching10Figure 5.10. The effect of temperature on vanadium oxidative leaching10Figure 5.11. The effect of temperature on vanadium oxidative leaching10Figure 5.12. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various temperature tests; (b) Plot of $(1 - (1 - X)^{\frac{2}{3}})$ versus time for various temperature test10Figure 5.13. Arrhenius plot for activation energy calculation)1)2)5)5)6)7
leaching)1)2)5)5)6)7
leaching)1)2)5)5)6)7)8)5
leaching)1)2)5)5)6)7)8)7)8)5
leaching	01 02 05 05 06 07 08 017 08 017 09 0
leaching)1)2)5)5)6)7)8)7)8)7)8)7)9 0 m

Figure 5.18. The effect of stirring speed on vanadium oxidative leaching 112
Figure 5.19. Effect of pH on vanadium oxidative leaching
Figure 6.1. Extraction of V (V) and Fe (III) from sulfate solution as a function of
equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-ORFOM12 115
Figure 6.2. Percentage of extraction of V (V) and Fe (III) from sulfate solution as a
function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-
ORFOM12
Figure 6.3. Effect of mixing time on the extraction yield of vanadium with 40%
CYANEX 923 in SX-ORFOM 12 at pH 2 117
Figure 6.4. Effect of CYANEX 923 concentration on vanadium extraction 118
Figure 6.5. Percentage of extraction of V (IV) and Fe (III) from sulfate solution as a
function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-
ORFOM12
Figure 6.6. Percentage of extraction of V (IV) and Fe (III) from sulfate solution as a
function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-
ORFOM12
Figure 6.7. Percentage of extraction of V (IV) and Fe (II) from sulfate solution as a
function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-
ORFOM12
Figure 6.8. Percentage of extraction of V (IV) and Fe (II) from sulfate solution as a
function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-
ORFOM12
Figure 6.9. Effect of pH on distribution coefficient (D2EHPA and vanadium (IV)) 128
Figure 6.10. Effect of D2EHPA concentration on vanadium (IV) extraction 129

Nomenclature

A	Anion monomeric
b	Stoichiometric coefficient of the reaction
С	Concentration of H^+ in the bulk solution (mol/L)
(C _{aq}) _I	Solubility of oxygen (molal)
d	Particle size (m)
D	Distribution coefficient
De	Diffusion coefficient (m^2/s)
E	Potential (mV)
Ea	Activation energy (kJ/mol)
E _m	Mixed potential (mV)
F	Faraday constant (A/mol)
i	Current density (A/m ³)
K _e	Equilibrium constant
ks	Rate constant (1/min)
n	Number of electrons
<i>R</i> ∘	Average radius of spherical particle (µm)
t	Time (min)
Т	Temperature (K)
Х	Fraction of particle converted

Ζ	Number of electron transfer in charge transfer process
α	Charge transfer coefficient
β	Complexation equilibrium constant
ρ	Density (kg/m ³)
τ	Time to complete dissolution (min)

Acknowledgments

I am very thankful to my supervisor, Dr. David Dreisinger, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. Thanks are also given to Dr. David Dixon and Dr. Berend Wassink for their helpfulness and many useful discussions. I also acknowledge the rest of my thesis committee as well for their assistance. (Dr. Akram Alfantazi and Dr. Warren Poole).

I also thank Scott Dornian for his help in running experiments in the summer 2012. I wish to thank Dr. Robin Stoodley and Paula Parkinson for their assistance in using the ICP instrument for chemical analysis.

It has been a great privilege to spend these years of graduate studies in the Department of Materials Engineering at the University of British Columbia. Its members and memories will always remain in my mind. Special thanks to all colleagues and officemates for providing a friendly environment that was always a pleasure to work in.

Special thanks are owed to my family for all the love, encouragement and support the have provided throughout my life.

Dedication

To my beloved family

1 Introduction

1.1 History

In 1801, Manuel Del Rio discovered vanadium in a Mexican lead vanadate ore. Vanadium metal was first produced in powder form by Roscoe in 1867-1869 by reduction of vanadium dichloride with hydrogen. The first major application of vanadium was in 1905 by Henry Ford who recognized the advantages of vanadium steel and promoted its use in automobile construction (Habashi, 1998).

The beneficial addition of vanadium to iron and steel has maintained vanadium as an industrially-important metal. Another major and important metallurgical application of vanadium was developed in the 1950s and that was vanadium becoming the vital constituent of the multi-component titanium alloys for aerospace applications. Other applications such as catalysts, photo catalysts, biological applications and fuel cells have increased the importance of vanadium recently (Radosevich, 2007)



Figure 1.1. Consumption of vanadium in various end use categories (Habashi, 1998)

1.2 Properties of vanadium

Vanadium belongs to the group VB in the periodic table and is a body centered cubic (bcc) metal. Table 1.1 shows some important physical properties of vanadium.

Atomic number	23
Atomic weight	50.94
Density (g/cm ³)	6.11
Melting point (°C)	1910
Boiling point (°C)	3409
Latent heat of fusion (KJ/mol)	16.74
Entropy (J/mol.K)	28.95

Table 1.1. Physical properties of vanadium (Habashi, 1998)

1.3 Primary and secondary sources and vanadium products

Vanadium is present in over 50 different minerals and is the 22nd most abundant element in the Earth's crust (Moskalyk and Alfantazi, 2003). Vanadium is used in metal alloys with iron to produce high-strength steels which have a wide range of uses, including structural applications such as reinforcing bars in building and construction, gas and oil pipelines, tool steel, the manufacturing of axles and crankshafts for the motor vehicle industry, and in jet engines for the aircraft industry. Non-steel uses include welding and alloys in nuclear engineering and superconductors. Other applications such as catalysts, biological applications and fuel cells have increased the importance of vanadium recently. To summarize, vanadium is known as an important element and it can be anticipated that its importance will be expanded in the future because:

1- It is extremely important in the use of high-strength steel. High-strength, low-

alloy steel uses very small amounts of vanadium. About 0.5% of vanadium content approximately doubles the strength of steel and therefore could lead to less use or weight of steel for sensitive applications. Therefore, the amount of iron ore and energy consumption needed for the manufacturing of steel decreases as well.

2- Besides all of its non-steel uses, vanadium may be used for mass storage redox batteries. The only really good long-term, cost-effective solution for mass storage energy is vanadium mass-storage batteries. The vanadium redox flow battery is a type of rechargeable flow battery that employs vanadium ions in different oxidation states to store chemical potential energy. The vanadium redox battery exploits the ability of vanadium to exist in solution in four different oxidation states and uses this property to make a battery that has just one electroactive element instead of two. The main advantages of the vanadium redox battery are that it can offer almost unlimited capacity simply by using larger storage tanks. It can be left completely discharged for long periods with no ill effects, it can be recharged simply by replacing the electrolyte if no power source is available to charge it, and if the electrolytes are accidentally mixed, the battery suffers no permanent damage. The main disadvantages with vanadium redox technology are a relatively poor energy-to-volume ratio and the system complexity in comparison with standard storage batteries.

As shown in Table 1.2, about 74 thousand tonnes per annum of vanadium are produced in the world by different countries (http://minerals.usgs.gov).

Country	2008	2009	2010	2011	2012
China (thousand tonnes)	26	29	32	36	39
United States (tonnes)	520	230	1060	590	272
Russia (thousand tonnes)	14.5	14.5	15	15	15
South Africa (thousand tonnes)	23.3	22.6	23.7	23.5	20
Total (thousand tonnes)	61.1	58	71	74	74
Japan, petroleum residues, ash spent catalysts (tonne)	560	560	560	560	560
Grand total (thousand tonnes)	62	59	72	74	74

Table 1.2. Vanadium world annual production by country (http://minerals.usgs.gov)

Vanadium is a relatively abundant trace element and occurs in a large number of minerals and deposits. Vanadium is not only produced from primary resources, but is also obtained from secondary production, or processing of steelmaking slag, oil and coal residues, spent catalysts and uranium co-products. Characteristics of vanadium in secondary resources are completely different and depend on the sources (Das et al., 2007); the average concentration of vanadium varies in different sources.

In addition of source variety, vanadium usage has been expanding to different industries, such as the battery industry. This requires better understanding of the hydrometallurgy of vanadium to overcome complexities involved in its recovery process. Therefore, building a fundamental understanding for vanadium leaching and solvent extraction can help us to plan for increased vanadium production from new and varied sources.

2 Literature review

2.1 Aqueous chemistry

The chemistry of vanadium in aqueous solutions is complex. The most common oxidation states for vanadium are +2, +3, +4, and +5. In an aqueous system, the oxidation state of vanadium can be +3, +4, and +5. The vanadium (II) oxidation state is not stable in aqueous solutions. The redox potential of vanadium (II)_(aq) is such that hydrogen ions will be reduced to hydrogen (gas) and vanadium (III)_(aq) forms.

Since most of the vanadium products have been produced as vanadium (V), the most important cation in the chemistry of vanadium production is VO_2^+ . Moreover, aqueous vanadium (IV) exists in various ionic states depending on the pH including $VO(H_2O)_5^{+2}$, $VO(OH)(H_2O)^+$, and the dimer, $(VOOH)_2(H_2O)_n^{+2}$. In this cationic form, which occurs under acidic conditions, V (IV) is highly water-soluble. However, under mildly acidic conditions, about pH 4, where it is largely non-ionic, it forms a hydrous oxide $VO_2.nH_2O$ (Ksp~10⁻²²), thus limiting the solution concentration to low values. Under basic conditions, the oxide can be redissolved to form the anionic species (Tracey and Crans, 1998; Tracey et al., 2007).

Figure 2.1 is a diagram showing the equilibrium Eh-pH diagram for the vanadium-water system. In this figure, five solid substances are considered (V, V₂O₂, V₂O₃, V₂O₄ and V₂O₅). A total of 10 aqueous species appear on the diagram at the concentration level of around 1 g/L vanadium species (V⁺², V⁺³, V(OH)⁺², VO⁺², V₄O₉⁻², VO₂⁺, H₂V₁₀O₂₈⁻⁴, HV₁₀O₂₈⁻⁵, V₄O₁₂⁻, V₂O₇³⁻) (Pourbaix, 1949).



Figure 2.1. Stability relationships of vanadium ions and the compounds in aqueous media at 25°C (Pourbaix, 1949)

Table 2.1 summarizes a variety of complex speciation and oxidation states in aqueous solutions. Vanadium (V) exists in a series of polyanions such as decavanadate $V_{10}O_{28}^{6-}$, or metavanadate $V_4O_{12}^{4-}$, that are partially protonated according to the pH value. Vanadium speciation in solution depends on its concentration and the pH value of solution (Zeng and Yong Cheng, 2009).

Oxidative state	Species	Medium	Colour
V(II)	$[V(H_2O)_6]^{+2}$	Acidic	Purple
V(III)	$[V(H_2O)_6]^{+3}$	Acidic	Green
V(IV)	VO^{+2}	Acidic	Blue
	VO_4^{-4}	Acidic	
V(V)	VO_4^{-3}	pH>12.6	Achromaticity
	$V_2 O_7^{-4}$	pH=9.6-10	Achromaticity
	VO ₃ ⁻	pH=7-7.5	
	$V_{3}O_{9}^{-3}$	pH=7-7.5	Achromaticity
	$V_4O_{12}^{-4}$	pH=7-7.5	
	$V_{10}O_{28}^{-6}$	pH=2-6.5	Orange-Red
	$\mathrm{VO_2}^+$	pH=1-2	Yellow

Table 2.1. Characteristics of some vanadium species in aqueous solutions (Zeng and

Yong Cheng, 2009)

Olazabal et al (1992) presented the distribution diagram (Figure 2.2) of vanadium (V) species in water as a function of the pH by computer simulation based on the ISP software package. This program (made at the Royal Institute of Technology in Sweden) solves the mass balance equations of the different components of a chemical system in terms of equilibrium and stoichiometric formation constants. The cationic vanadium (V) species is predominant at pH<2. Polynuclear anionic species are predominant at pH>9.



Figure 2.2. Vanadium speciation in water as a function of pH with a total VO²⁺ concentration of 14.3 mM (Olazabal et al., 1992)

It is apparent from the account given above that vanadium has many chemical forms in solution. The controlling of vanadium speciation by changing the pH is essential in the processing of vanadium, especially in the purification and precipitation recovery steps. Table 2.2 shows some available thermodynamic data of the aqueous species of vanadium (V), (IV), and (III).

	ΔH°_{f}	ΔG°_{f}	S°			
Formula	(kJ/mol)	(kJ/mol)	(kJ/mol.K)			
V (V)						
$\mathrm{VO_2}^+$	-649.8	-587	-42.3			
VO ₃ ⁻	-888.3	-783.7	50			
VO_4^{-3}	-	-899.1	-			
HVO_4^{-2}	-1159	-974.9	17			
$H_2VO_4^{-2}$	-1174	1020.9	121			
H_3VO_4	-	-1040.3	-			
$V_2O_7^{-4}$	-	-1720	-			
$HV_{2}O_{7}^{-3}$	-	-1792	-			
$H_3V_2O_7$	-	-1864	-			
$V_{3}O_{9}^{-3}$	-	-2356	-			
$V_4O_{12}^{-4}$	-	-3202	-			
$V_{10}O_{28}^{-6}$	-	-7675	-			
$HV_{10}O_{28}^{-5}$	-8694	-7708	1544			
$H_2V_{10}O_{28}^{-4}$	-	-7729	-			
$VO_2.H_2O_2^+$	-	-746.4	-			
$\mathrm{VO.H_2O_2}^{+3}$	-	-523.4	-			
V (IV)						
VO^{+2}	-486.6	-446.4	-133.9			
VOOH^+	-	-657	-			
$(\text{VOOH})_2^{+2}$		-1331	-			
$V_4O_9^{-2}$	-	-2784	-			
V (III)						
V^{+3}	-259	-251.3	-230			
VO^+	-	-451.8	-			
VOH^+	-	-471.9	-			

Table 2.2. Thermodynamic data for aqueous vanadium species at standard state (Barner and Scheueman, 1978; Evans and Garrels, 1958; Wanty and Goldhaber, 1992)

2.2 Leaching and metallurgical processes

There are many processes to treat vanadium raw materials. Figure 2.3 illustrates many of the processes which have been used for the recovery of vanadium.



Figure 2.3. Treatment of vanadium raw materials (Habashi, 1998)

On the left side of this figure, the processes for primary vanadium recovery are shown. Pyrometallurgy, hydrometallurgy, and pyro-hydro metallurgy methods have been used for the recovery of vanadium. Since vanadium has a high melting point (1910°C), pyrometallurgy methods are not feasible to reduce vanadium oxide to elemental vanadium. Hydrometallurgy and pyro-hydrometallurgy processes are popular methods to extract vanadium from different resources. Either direct leaching as a hydrometallurgy method or salt roasting and leaching together as a pyro-hydrometallurgy method has been used for vanadium recovery. Salt roasting of vanadium oxides, which have low solubility, make metavanadate phases, which have more solubility. All of the conditions for roasting and acidic or basic leaching of different vanadium resources, as illustrated in Figure 2.3 will be discussed in this chapter.

2.2.1 Roasting

Salt-roasting changes the mineral of vanadium to an oxide anion in its maximum valence state. Vanadium in the feed materials converts on roasting with a source of sodium under oxidizing conditions to form soluble sodium salts (Gupta, 1992; Zhang et al., 2012):

$$2NaCl + O_2 + H_2O + V_2O_3 = 2NaVO_3 + 2HCl$$
(2.1)

Or

$$2NaCl + V_2O_5 + H_2O = 2NaVO_3 + 2HCl$$
(2.2)

Or

$$2NaCl + V_2O_3 + 3/2O_2 = 2NaVO_3 + Cl_2$$
(2.3)

The formation of sodium metavanadate by reaction 2.3 is slow; so, in practical conditions, reaction 2.1 for the lower valent vanadium and reaction 2.2 for the pentavalent vanadium oxide occur predominantly.

Some other sources of sodium for salt roasting have been used such as sodium carbonate and sodium sulfate (Gupta, 1992; Geyrhofer et al., 2003; Hukkanen and Walden, 1985; Rohrmann, 1985):

$$Na_2CO_3 + V_2O_5 = 2NaVO_3 + CO_2$$
(2.4)

$$Na_2SO_4 + V_2O_5 = 2NaVO_3 + SO_3$$
 (2.5)

In general, it can be mentioned that the temperature of salt roasting of vanadium due to vanadium characteristics and additive reagent can be varied between 700°C and 1200°C. Roasting can be done in a rotary kiln or multiple hearth furnace (Geyrhofer et al., 2003)

The role of roasting on the increasing of vanadium leaching efficiency from different sources of vanadium has been shown in various reports. This happens because of changing vanadium composition to the more soluble vanadium component.

Holloway and Etsell (2004) reported that the optimum roasting conditions for processing "carbon-free¹" ash from oil sands were determined to be 2 to 3 hours of roasting at 850°C to 900°C with NaCl additions of 20 to 30%. This condition resulted in vanadium extractions of 75 to 85% for all of the tested samples from Suncor's oil sands which contained 2.86 to 3% V, Al, Ca, Fe, Mo, Ni, Si, Ti and different amount of carbon and sulfur. Moreover, Li and Xie (2012) reported that increasing temperature from 500°C to 850°C increases vanadium recovery by leaching; however, it was revealed that increasing the temperature to more than 850°C can decrease vanadium recovery because of sintering.

¹ - Carbon (and sulfur) were removed from the fly ash samples prior to salt roasting by heating as-received fly ash at 500°C to constant weight in a muffle furnace

However, Shelwit and Alibrahim (2006) reported more than 90%wt of sulfur and 60%wt of vanadium could be extracted by the salt-roasting treatment using about 25%wt of NaCl or Na₂CO₃ at a temperature of 400°C for 1 hour followed by Na₂CO₃ leaching at a temperature of 70-80°C. They used a low range of temperature for removing vanadium from petroleum coke. This low range of temperature is generally not a suitable range for vanadium roasting.

It was shown that increasing the temperature in the roasting of spent catalysts from 450°C to 800°C could lead to an increase of vanadium leaching from 45% to about 85% (Chen et al., 2006). In addition, Tavakoli et al (2010) confirmed the significant effect of temperature in the roasting of bottom ashes; moreover, they studied the effect of adding sodium carbonate and sodium chloride as an additive for roasting and reported sodium carbonate can increase vanadium recovery more than sodium chloride.

Table 2.3 shows the summary of the roasting conditions for vanadium recovery.

Material	Additive	Additive amount (%wt)	Temperature (°C)	Roasting Time (Hours)	References
Vanadium content	NaCl, Na ₂ CO ₃ , Na ₂ SO ₄ (Rarely ¹)	25-40	70 - 1100	1-3	(Biswas et al., 1985; Chen et al., 2006; Gomez- Bueno et al., 1981; Holloway and Etsell, 2004; Tavakoli et al., 2010; Zeng and Cheng, 2009)

Table 2.3. Roasting condition for vanadium recovery

 $^{^{\}rm l}$ - Because of the cost of sodium sulfate and higher temperature needed for roasting compared other additives

2.2.2 Leaching

The methods of vanadium dissolution used in vanadium source processing include:

1- Water leaching of the salt-roasted vanadium source

2- Acid leaching of the salt-roasted vanadium source

3- Basic leaching of the salt-roasted vanadium source

4- Direct acid pressure or atmospheric leaching

5- Direct basic pressure or atmospheric leaching

Roasting of vanadium sources is an effective method for vanadium extraction; however, roasting needs a high temperature and a lot of additives to make sodium metavanadate. Therefore, there is a rational interest to dissolve vanadium directly.

The past reports for vanadium leaching and solvent extraction were studied carefully and are summarized below.

2.2.2.1 Oil and combustion ashes

Fuel oil and petroleum coke burned in power stations produce two types of waste ash: bottom ash and fly ash. The characteristics of ash depend on the type and origin of the fuel used as well as the boiler conditions. Fly ash consists of inorganic, incombustible matter and during combustion some of the components partially transform into a glassy, amorphous structure. Fly and coal ashes damage the environment and cause some serious human health problems. Some research (Cenni et al., 1998; Fernandez et al., 2003; Gavett et al., 1997; Pritchard, 1996; Veranth et al., 2000) showed that inhaling fly ashes by mice resulted in lung damage. On the other hand, fly ashes can be a good secondary resource for vanadium and nickel. As an example, it was reported that more than 420 tonnes of fly ash that contains vanadium, nickel and magnesium is produced by Jordan power stations every year (Abdel-latif, 2002; Al-Ghouti et al., 2011). The gross reserve of vanadium in stone coal is 118 million tonnes in terms of V_2O_5 in China, which accounts for more than 87% of the domestic reserve of vanadium (Lan Yao-Zhong, 2005; Zhu et al., 2010).

Okuwaki et al (1988) investigated vanadium recovery from electrostatic precipitator ash. The vanadium extraction was 88% or greater with $0.5M H_2SO_4$ at 60-90°C, with an extraction time of 45 minutes and H_2SO_3 as a reducing agent.

Akita et al (1995) reported that 22.7% of vanadium from oil fly ash was extracted by 2M HCl at 50°C. The vanadium leaching efficiency was low in this case but Ni, Fe, Al and Mg were also co-extracted. The reagents Na₂CO₃, $(NH_4)_2CO_3$ and NH₄Cl were then tested for vanadium leaching. It was shown that 2M Na₂CO₃ dissolves 60% of the vanadium at 70°C after 7 hours while the leaching of other metals is suppressed. NH₄Cl leached nickel and magnesium preferentially and about 20% of vanadium was leached as well. In the case of leaching by $(NH_4)_2CO_3$ leaching, vanadium was not leached at all. It seems that ammonium solutions cannot leach vanadium but alkaline solutions can leach vanadium selectively.

Tsai and Tsai (1998) showed that the extraction of vanadium from fly ash in ammonia water (around 40%) appears to be less than that of leaching in either 2M sulfuric acid or 2M sodium hydroxide (more than 90% at room temperature for 2 hours). They suggested the two-stage leaching method for nickel and vanadium: in the first stage, the soluble

nickel compounds are leached in an ammoniacal solution; in the second stage the residue left from the extraction of nickel is leached in an alkaline solution to recover vanadium.

Figure 2.4 shows four kinds of fly ash (Table 2.4) leached in different concentrations of sulfuric acid by Vitolo et al (2000). They showed that the yield of extraction increased with the acidity of the leaching solution but it had a higher effect on samples B and C than on A. In addition, the effect of liquid to solid ratio was studied. Generally, an increase in the L/S ratio led to an increase in the extraction yield, however, different behavior was observed in different samples. An increase in L/S from 2 to 3 mL/g had no effect on the extraction yield of sample A, whilst an increase in the yield of 5% and 15.5% was observed for samples B and C respectively. This result may be related to the wettability of the fly ashes, which decreases with carbonaceous fraction. This means that a higher L/S ratio is necessary for ashes with a high carbonaceous fraction to ensure an adequate contact between the solid and the liquid phases. They reported different behaviours of vanadium leaching in different types of ashes in other research as well (Vitolo et al., 2001; Vitolo et al., 2000).

Main constituents of the fly ashes (%wt)					
	Oil fly ashes				
	А	В	С	Orimulsion fly ashes	
Moisture	1.9	0.9	1.5	5.2	
С	33.1	39.6	79.1	7.1	
V	2.6	3.3	1.3	11.7	
Fe	3.5	3.9	4	0.6	
Na	2.3	2.4	0.2	1.1	
Κ	0.2	0.2	0.1	not revealed	
Ni	1.3	1.2	0.7	2.5	
Si	2.5	0.7	0.8	not revealed	
Al	2.1	0.4	0.6	3.2	
Ti	0.1	Traces	Traces	0.1	
S	12.6	11.3	11.6	13.2	
Р	0.1	0.1	0.1	traces	

Table 2.4. The analysis of the used ashes (Vitolo et al., 2000)



Figure 2.4. Extraction yield of vanadium versus the molarity of the H_2SO_4 leaching solution at room (white circles) and boiling temperature (black circles) with a liquid/solid ratio of 3 mL/g (Vitolo et al., 2000)
In other research, the mobility of water-soluble major and trace elements in six fly ashes was studied at 90°C. They reported that the leaching rate of the different trace impurities in the six different fly ashes can be sorted, in decreasing order, $B \ge Mo \ge Se \ge Li >$ $Sr \ge Cr \ge As = Ba = Cd = V > Sn > Rb = Zn \ge Cu = Ni > Pb > U > Co >$

Mn (Querol et al., 2001). It was shown by Choi et al (2002) that chemical composition of the fly ashes is size-dependent for most elements. Some of the elements are associated with the surfaces of particles and some others are incorporated in the glassy form. Generally, the fractions incorporated in the glass matrix might be dissolved more slowly compared with readily-leachable elements associated with surfaces.

Extraction of Egyptian boiler ash containing 20% vanadium was also considered by pressure leaching and leaching following roasting. Amer (2002) compared pressure leaching and pyro-hydrometallurgical treatment for extraction of vanadium. He claimed consumption of sulfuric acid (10%) is cheaper than the amount of soda required for alkali roasting (50%). In addition, the selectivity of the processing is achieved where both vanadium and nickel are leached as sulfates while the other impurities which are mainly represented by iron are precipitated as jarosite. However, leaching of vanadium after the alkali roasting forms soluble sodium vanadate while the precipitate contains both the nickel and iron which needs further techniques for nickel removal. So, the pyrohydrometallurgical approach is technically feasible, but it is not cost effective in comparison to the pressure leaching because of the salt consumption, energy demanded, and selectivity.

Guibal et al (2003) reported that both acidic and alkali leaching are effective for the leaching of vanadium from fly ash. They reported almost the same recovery for high L/S

ratios, while Navarro et al (2007) reported that extraction efficiency with the alkaline procedure is lower than that reported with an acidic treatment. However, the alkaline process is significantly better in terms of selective recovery of vanadium. Direct acid leaching of vanadium from heavy oil and combustion ashes was studied. The researchers investigated direct acid leaching and leached more than 75% of vanadium.

There is a wide range of contradictory results for the effect of additives on vanadium leaching. It is claimed that both reductive and oxidative agents can increase leaching. Li et al (2009) reported that more than 90% of vanadium from black shale was leached by 350 g/L sulfuric acid at 180°C with a liquid/solid ratio of 1.2 mL/g for 3 hours. Moreover, the effect of FeSO₄ as an additive was studied as a reducing agent and no significant effect on vanadium leaching was reported while they reported that adding FeSO₄ increased vanadium recovery by about 7.7% in another study (Li et al., 2010c). However, NaClO as an oxidative agent on vanadium leaching in their paper in 2010 (Li et al., 2010) was studied and it was shown that the recovery of vanadium increased from 80% to 85.1% by adding 1 g/L NaClO at 95°C, 87.5 g/L H₂SO₄, 15 g/L HF and a liquid/solid ratio of 4 mL/g for 6 hours. Moreover, Chen et al (2010) studied the effect of an additive reagent on vanadium ore (V₂O₅: 1.09%). They suggested MnO₂ and H₂O₂ could increase vanadium recovery by about 5% while FeSO₄ decreased it by about 2%.

2.2.2.2 Spent catalysts

The petroleum refining industry and sulfuric acid plants are using some special catalysts containing vanadium and molybdenum. These catalysts have limited life cycles, and after utilization, are generated as spent catalysts (Kar et al., 2005). This kind of spent catalyst forms an important secondary source of many valuable metals. A spent hydro-refining

catalyst mainly consists of 10–30% Mo, 0–12% V₂O₅, 0.5–6% NiO, 6–8% CaO, 8–12% S, 10–12% carbon and the balance is Al_2O_3 (Marafi and Stanislaus, 2003; Sun et al., 1998; Sun et al., 2001).

There are two main routes to process spent catalysts in the acid stage. One is direct acid leaching under pressure or high temperature; the other one is roasting around a temperature of 500-700°C followed by acid leaching with or without pressure and high temperature. Pre-treatments of the recovery processes such as roasting and washing the catalysts have been used to remove sulfur and carbon from the catalysts and increase the recovery. In direct leaching, sulfuric, hydrochloric, and nitric acids and some organic acids such as oxalic and citric acids are used for leaching-spent catalysts. Some solvents such as oxalic and citric acid were used as a complexing agent to selectively extract vanadium from the spent catalyst (Lee et al., 1992). The same amount of vanadium extraction for both oxalic and citric leaching was reported, however, it was revealed that citric acid is not as selective as oxalic acid for vanadium over molybdenum and nickel. Dilute sulfuric acid leaching usually gave low recoveries of metal values of spent catalysts. Biswas et al (1985) investigated the effects of the temperature and the flowing gas on the leaching of spent catalysts in water after salt roasting at 850°C. Table 2.5 shows that more than 80% of vanadium was leached at 100°C.

Flow	Leaching	Pe	ercentage o	f material	dissolved	
gas	Temperature (°C)	V	Мо	Al	Co	Ni
N ₂	100	81.85	81.78	0.25	0.05	0.31
N_2	80	78.52	73.9	0.25	0.04	0.18
N_2	52	76.54	65.1	0.22	0.09	0.12
N_2	35	69.2	58.05	0.22	0.08	0.1
Air	100	70.32	65.7	0.42	0.13	3.33
H_{2}	100	14.95	63.66	1.47	0.15	1.8

Table 2.5. Percentage of materials dissolved on water leaching of roasted catalysts (Leaching time 1hour; roasting temperature 850°C; gas flow rate during 1 l L/minute; water vapour pressure 0.253 bar; S/L ratio 1/10.66 g/mL) (Biswas et al., 1985)

Figure 2.5 summarized all of the processes which have been used for acidic vanadium leaching from spent catalysts.



Figure 2.5. Metallurgical processes for spent HDS catalysts involving acid leaching (Zeng and Cheng, 2009)

Figure 2.6 illustrates the processes for spent HDS catalysts (Hydrodesulfurization) involving caustic leaching. Alkali leaching can be used for HDS catalysts. It also dissolves some aluminum but leaves nickel, cobalt, and iron in the residue to some degree.



Figure 2.6. Metallurgical processes for spent HDS catalysts involving caustic leaching (Zeng and Cheng, 2009)

In the case of roasting/leaching, Villareal et al (1999) used the spent petroleum catalyst containing 27.28% V_2O_5 and 1.92% MoO₃ to recover vanadium and molybdenum. After some pre-treatment procedures such as washing by ethanol and heating for 24 hours at 450°C to remove carbon and sulfur, vanadium and molybdenum leaching was tested by NaOH and NH₃. It was shown that both solvents can leach vanadium more than 90% at temperatures around 95°C. In addition, they concluded that an NH₃ solution is more useful for the selective extraction of vanadium than NaOH. Moreover, Chen et al (2006) reported that more than 90% of vanadium and molybdenum could be extracted by roasting with sodium carbonate at 750°C followed by caustic leaching at a pH of 10.5.

The main routes for direct leaching, which are dilute, or concentrated atmospheric or pressure leaching were studied as well. Yasuhara (1982) could leach over 95% of vanadium with a 4% caustic solution in an autoclave while Grzechowiak et al (1987) used a high sulfuric acid concentration and high temperature (around 180°C) to leach that amount of vanadium.

In the case of NaOH/NaAlO₂, leaching was performed at high temperature in the range of 150-250°C and sodium aluminate was used to convert molybdenum and vanadium to sodium molybdate and sodium vanadate (Wiewiorowski et al., 1986).

Mishra et al (2010) tried to compare alkali leaching using $(NH_4)_2CO_3$ and acidic leaching by H₂SO₄. They reported that 20 g/L of $(NH_4)_2CO_3$ can leach 34% of vanadium while 20 g/L of sulfuric acid can extract 60% of vanadium at a temperature of 30°C, pulp density 10% (w/v) for 1 hour. They also observed that the kinetics of dissolution of vanadium increased by increasing the pulp density from 10 to 40% but they did not mention any reason for this result.

Moreover, there are many other resources for vanadium production from primary vanadium ores (Gupta and Krishanmurphy, 1992). A similar technique for vanadium production has been applied for these different resources. As an example, carnotite $(K_2(UO_2)_2(VO_4)_2\cdot 3H_2O)$ can be considered for vanadium and uranium production. This ore is mostly found in United States, Australia, Congo and Kazakhstan (www.wikipedia.org). Both roasting-leaching and direct leaching using caustic or acidic solution have been tried for leaching of this kind of ore. It seems that high recovery of uranium and vanadium in leaching was obtained using different methods; however, the

problem is separation of uranium and vanadium in the solution (Fischer, 1942). Different methods such ion exchange for removing uranium (Bibler, 1990), selective loading using different extractants such as amines and D2EHPA (El-Enein et. al., 2014) or selective stripping after loading by D2EHPA (Crouse and Brown, 1959) have been offered to complete the flowsheet.

2.2.2.3 Kinetic studies

Few researches have been reported to investigate the kinetics of vanadium leaching. Aarabi et al (2010) studied the kinetics of vanadium leaching from an LD (Linz-Donawitz) converter slag of a steelmaking plant. Based on their kinetic results, two leaching stages for vanadium leaching were reported. During stage one (the first 15 minutes), a sharp increase in the amount of vanadium extracted was observed (fast leaching rate) and during stage two (more than 30 minutes), a slower leaching rate was encountered. The rate of leaching of vanadium is controlled by chemical reaction at low temperature whereas it is controlled by diffusion through the solid product layer at higher temperature. Amer (1994) showed that the most favorable conditions for the extraction of 95% of the vanadium present as vanadium trioxide in the black shale are: temperature 180°C, acid concentration 10% by weight, grain size 61-88 µm and leaching time 40 minutes. It was indicated that the kinetics of vanadium dissolution is under mixed control and the overall activation energy of the reaction was reported around 30 kJ/mol. Li et al (2012) observed that oxidative conditions can increase leaching efficiency from black shale containing a mixture of vanadium (V) and (III) oxides. The activation energy for the kinetics study was reported to be 40.1 kJ/mol. Pressure oxidation of pure vanadium trioxide in sulfuric acid was studied (Zhou et. al., 2012). It was shown that vanadium trioxide can be completely leached in about 20 minutes by 1M sulfuric acid, oxygen partial pressure 1MPa, and 140°C. A reaction control mechanism was reported with an activation energy of 43.46 kJ/mol. However, a shrinking core model was used for pure vanadium trioxide while no ash layer was reported. Qiu et al (2011) investigated the pressure oxidative leaching of vanadium trioxide using sodium hydroxide. They found that about 90% of vanadium can be dissolved in 2M sodium hydroxide, oxygen partial pressure 500 kPa, and 130°C in about 40 minutes. They offered two stage kinetic models for the leaching: the chemical control regime for the initial step and the diffusion mechanism for the later stage. Unfortunately, they also applied the shrinking core model for starting pure materials without mentioning any ash layer or showing the constant particle size through the leaching. Wang-Xing et al (2010) studied the kinetics of calcium vanadate containing 65.5% vanadium by Na₂CO₃ leaching. They claimed that the reaction rate constant increases with increasing pH and stirring speed and an activation energy of 38.98 kJ/mol was obtained.

2.2.3 Summary

From the literature review, the important parameters for leaching are temperature, solvent concentration, S/L ratio, time of leaching and additive reagents. Table 2.6 summarizes all of the important reports about vanadium leaching but, as it was shown, there is a wide range of contradictory results for the impact of different parameters in vanadium leaching.

In most of the reports, temperature and solvent concentration have a prominent effect on the recovery of vanadium in leaching. However, Li et al (2010) reported the optimum concentration for sulfuric acid for vanadium leaching. In some other parameters such as S/L ratio or additive reagents, a wide range of contradictory results have been reported. For instance, some other researchers (Li et al., 2011; Navarro et al., 2007; Vitolo et al., 2001; Vitolo et al., 2000) suggested that by decreasing the S/L ratio, the efficiency of leaching decreases. However, Li et al (2009) and Arabi et al (2010) without clarifying with any proper reason, reported the optimum condition for solid to liquid ratio to obtain maximum vanadium recovery in leaching. Mishra et al (2010) observed the kinetic of dissolution of vanadium increased by increasing the pulp density from 10 to 40%. Generally, increasing the S/L ratio would increase the extraction of vanadium, and this is limited by the concentration of protons available in the solution.

In addition, there is a similar story for the effect of oxidizers and reducers on vanadium leaching in literature. Li et al (2009) and Chen et al (2010) investigated NaClO and MnO₂, respectively, as oxidizers to increase the vanadium recovery in leaching; while Okuwaki (1988) and Li et al (2010) studied H_2SO_3 and $FeSO_4$, respectively, as reductive agents to increase the leaching recovery. Moreover, Li et al (2009) showed that $FeSO_4$ has no effect on vanadium leaching while Chen et al (2010) reported $FeSO_4$ decreases vanadium recovery.

No	Source	Vanadium Content (%)	Extraction (%)	Solvent	Solvent Conc.	Temp. (°C)	S/L ratio (g/L)	Time (min)	Ref.
1	HDS Catalyst	15	81.8	H ₂ O	-	Boiling	-		(Biswas et al., 1985)
2	EP ash	1.93 - 3.36	95	$\mathrm{H}_2\mathrm{SO}_4$	0.5 M	70	0.125	45	(Okuwaki et al., 1988)
3	Fly ash	1.8	63	Na ₂ CO ₃	2 M	25	0.2	420	(Akita et al., 1995b)
			10	NH4Cl	2 M	25	0.2	420	(Akita et al., 1995b)
			20	(NH ₄) ₂ CO ₃	2 M	25	0.2	420	(Akita et al., 1995b)
4	Fly ash	0.41 & 1.91	95	H_2SO_4	2 M	30	0.2	120	(Tsai and Tsai, 1998)
			75	NaOH	2 M	30	0.2	120	(Tsai and Tsai, 1998)
			48	NH4OH	2 M	30	0.2	120	(Tsai and Tsai, 1998)
5	Spent petroleum Catalyst	27.28 (V ₂ O ₅)	90	NH ₃	15 M	95	100	1440	(Villarreal et al., 1999)
			90	NaOH	pH=8	95	100	1440	(Villarreal et al., 1999)
6	Fly ash	1.3 - 3.3	80 - 95	$\mathrm{H}_2\mathrm{SO}_4$	2 M	Boiling	333.34	30	(Vitolo et al., 2000)
7	Fly ash	3.8 (19wt% after burning)	97	$\mathrm{H}_2\mathrm{SO}_4$	2 M	Boiling	142.85	60	(Vitolo et al., 2001)
8	Boiler ash	20	98	$\mathrm{H}_2\mathrm{SO}_4$	0.6 M	220	0.5	30	(Amer, 2002)

Table 2.6. Summary of vanadium leaching studies

9	Fly ash	0.93	80	NaOH	5 M		100	5760	(Guibal et al., 2003)
		0.93	90	$\mathrm{H}_2\mathrm{SO}_4$	0.5 M	Ambient	100	1440	(Guibal et al., 2003)
10	Spent Catalyst	0.42	90.1	Water	-	80-90	0.5	15	(Chen et al., 2006)
11	Fly ash	1.6	98	$\mathrm{H}_2\mathrm{SO}_4$	0.5 M	Ambient	250	1440	(Navarro et al., 2007)
			56	NaOH	2 M	Ambient	250	1440	(Navarro et al., 2007)
			60	Na ₂ CO ₃	0.66 M	Ambient	250	1440	(Navarro et al., 2007)
12	Black Shale mine	3.26 (V ₂ O ₅)	75	$\mathrm{H}_2\mathrm{SO}_4$	2 M	180	833.34	240	(Li et al., 2009)
13	Black Shale Mine	0.56 (V ₂ O ₅)	86	$\mathrm{H}_2\mathrm{SO}_4$	0.87 M	95	250	8640	(Li et al., 2010)
14	Stone coal	1.09	85	$\mathrm{H}_2\mathrm{SO}_4$	1 M	95	333.34	120	(Chen et al., 2010)
15	Steel Slag	8.46 (V ₂ O ₅)	90	NaOH	0.4 M	240	500	350	(Xiao et al., 2010)
16	LD convertor Slag	1.97 (V2O5)	90	$\mathrm{H}_2\mathrm{SO}_4$	3 M	70	0.067	140	(Aarabi-Karasgani et al., 2010)
17	Black Shale Mine	6.15 (V ₂ O ₅)	70	$\mathrm{H}_2\mathrm{SO}_4$	2 M	150	14.28	60	(Li et al., 2010)
18	Calcium vanadate	65.5 (V ₂ O ₅)	95	Na ₂ CO ₃	1.2 M	80	40	60	(Wang-xing et al., 2010)
19	Spent petroleum Catalyst	9	80	H_2SO_4	1 M	30	0.1	120	(Mishra et al., 2010)
20	Stone coal	1.82	91	H_2SO_4	0.3 M	150	0.833	240	(Deng et al., 2010)

2.3 Separation and purification: solvent extraction

2.3.1 Solvent extraction of vanadium in industry

Liquid-liquid extraction (solvent extraction) refers to the distribution of a solute between two immiscible liquid phases in contact with each other. The whole process essentially consists of three steps: extraction, scrubbing and stripping.

Because of different kinds of species of vanadium in solution, different solvent extractants have been used to extract vanadium. Solutions containing vanadium in the feed solution to solvent extraction may be neutral, basic, or acidic. Acid or alkali leaching solutions can contain impurities such as iron, chromium, and molybdenum, in addition to vanadium, depending upon the vanadium source treated.

Many extractants have been used for vanadium solution purification. Among these, Di-2-ethylhexyl phosphoric acid (D2EHPA) and amines have been used in plant operations while the others have been essentially confined to laboratory or pilot scale studies.

2.3.2 Recent researches

Since vanadium solution in different concentration and pH's make different species (Figure 2.2), different kinds of solvents have been used for solvent extraction under different conditions. In the sections below, some recent studies for solvent extractions of vanadium will be considered.

2.3.2.1 Solvent extraction using cation extractants

Inoue and Zhang (1995) studied liquid-liquid extraction of vanadium (V) in sulfuric acid using some commercial acidic organophosphorus reagents such as TR-83, PC-88A, PIA-8, and CYANEX 272 (Figure 2.7). Figure 2.8 to Figure 2.11 show the experimental results for vanadium recovery at different pH values.



Figure 2.7. Chemical structures and pKa values of the commercial extractants (Zhang et al.,

pKa = 4.02

1995)



Figure 2.8. Percentage of extraction of metals from sulfate solutions as a function of equilibrium

pH with 20% CYANEX 272 dissolved in Exxsol D80 (Zhang et al., 1995)



Figure 2.9. Percentage of extraction of metals from sulfate solutions as a function of equilibrium pH with 20% PIA-8 dissolved in Exxsol D80 (Zhang et al., 1995)



Figure 2.10. Percentage of extraction of metals from sulfate solutions as a function of equilibrium pH with 20% PC-88A dissolved in Exxsol D80 (Zhang et al., 1995)



Figure 2.11. Percentage of extraction of metals from sulfate solutions as a function of equilibrium pH with 20% TR-83 dissolved in EXXSOL D80 (Zhang et al., 1995)

They concluded that CYANEX 272 and PIA-8 are likely to be suitable extractants for the selective separation and recovery of molybdenum and vanadium from aluminum, cobalt, and nickel from sulfuric acid media at low pH. However, vanadium, iron, and small amount of aluminum co-extracted together with molybdenum into the solvent phase. Since Mo cannot strip by sulfuric acid, they tried to use sulfuric acid for scrubbing the solution. Table 2.7 shows the result of scrubbing tests.

Table 2.7. Scrub of V, Fe, and Al from the loaded solvent

(The organic solvent was 40% CYANEX 272 and the metal loading was (ppm): 2870 Mo, 760 V, 35 Fe, 40 Al) (Zhang et al., 1995)

scrub reagent		% scrub	of metals	
(H_2SO_4, M)	Mo	V	Fe	Al
2.75	0.1	68.3	100	100
2.15	0.07	62.1	100	100
1.45	0	54.5	74.3	100

Stripping of molybdenum from the loaded solvent is a key problem in the recovery of molybdenum by extraction with acidic organophosphorus compounds. Because molybdenum gives rise to anionic species with an acidic organophosphorus extractant in alkaline solutions and it is a requirement to recover it as ammonium molybdate for its reuse, aqueous ammonia was chosen as the strip reagent and its optimum concentration for stripping was determined. As Table 2.8 shows, the strip performance of molybdenum is largely dependent upon the content of ammonia. On the other hand, when the content of ammonia solutions was greater than 7%, the formation of a second organic phase was observed and the viscosity in both phases increased, making phase separation difficult. It was observed that good phase separation was obtained in the range of 5-7% ammonia (Table 2.8).

NH4OH	strip	solution (p	opm)	% strip	nhase senaration
(v/v, %)	pН	Мо	V	of Mo	phase separation
2	-	-	-	-	aq white turbid
4	-	-	-	-	aq white turbid
5	8.21	2590	80	90.2	clear, good
5.5	8.27	2580	86	89.9	clear, good
6	8.3	2590	94	90.2	clear, good
7	8.43	2640	110	92	clear, good
8	-	-	-	-	third phase, viscous
10	-				third phase, viscous
15	-	-	-	-	third phase, viscous
20	-	-	-	-	third phase, viscous

Table 2.8. Strip of Mo from the scrubbed solvent (CYANEX272) (Zhang et al., 1995)

Vanadium can then be further recovered from the scrub solution containing iron and aluminum with 40% CYANEX 272 in Exxol D80 and the pH was adjusted to around 1.5 by adding calcium hydroxide powder. Therefore, 92% of vanadium and nearly 100% of iron were extracted while aluminum was not extracted at all under the selected conditions. They tried to separate iron and vanadium by using NH₄OH as a stripping agent. Table 2.9 shows that stripping with 2.75 molar in H₂SO₄ solution recovered only 82.7% of the vanadium and most of the co-extracted iron. However, 92.6% stripping of vanadium could be achieved with 6% aqueous ammonia solution and, in addition, the small amount of co-extracted iron was not stripped at all.

,. ,	strip			
strip agent	Мо	V	Fe	- V strip, %
2.75 M H ₂ SO ₄	0	330	24	82.7
6% NH4OH	2.0	384	0	96.2

Table 2.9. Strip of vanadium from loaded solvent (CYANEX272) (Zhang et al., 1995)

(Solvent loading (ppm): 2 Mo, 399 V, 29 Fe)

Giavarini (1982) showed that a D2EHPA-TBP mixture is less effective than D2EHPA under similar conditions to extract vanadium from fly ash leach liquor. Extraction of vanadium by trin-octylamine (TOA) and tri-n-octylmethylammonium chloride (TOMAC) is shown in Figure 2.12 and stripping results are shown in Table 2.10. Alkaline solutions provide favorable characteristics for the stripping: NaOH is more effective compared with Na₂CO₃ and NH₄Cl whereas aqueous solutions of salt (NaC1) and acid (HCl) were not suitable for the stripping (Akita et al., 1995).



Figure 2.12. Effect of the solution pH on the percent extraction of vanadium from Na₂CO₃synthesized solution; TOA (tri-n-octylamine: white circles), TOMAC (tri-noctylmethylammonium chloride: dark circles) (Akita et al., 1995)

Table 2.10. Stripping of vanadium from TOMAC and TOA solutions with various aqueous

			% stripping		
	NaOH	Na ₂ CO ₃	$NH_4Cl + NH_4OH$	NaCl	HC1
	2M	2M	3M (pH 9.8)	1M	2M
TOMAC	87.6	85.1	68.3	27.9	-
TOA	98.5	86.4	63.4	28.4	17.3

media (Akita et al., 1995)

 $V_{w}=20 \text{ cm}^{3}, V_{\circ}=20 \text{ cm}^{3}, [V]=179 \text{ ppm}, 4 \text{ hours}$

The kinetics of solvent extraction was studied by some researchers and they claimed that the kinetics of extraction of V (IV) by D2EHPA is in the chemical reaction rate control regime (Hughes and Biswas, 1991; Ipinmoroti and Hughes, 1990). Ipinmoroti and Hughes (1990) reported a rate constant of 2.8×10^{-3} mol^{1/2}/S for the extraction of vanadium (IV) by D2EHPA at 28°C.

However, the kinetics of extraction of the forward extraction of VO²⁺ from the sulfate-acetate medium by D2EHPA in toluene was studied and it was found that the reaction $VO^{2+} + A^- \rightarrow$ $VOA^+(A^- \text{ is anion of monomeric D2EHPA})$ occurred at the aqueous film of the interface or in the bulk aqueous phase as the rate-determining step. It was shown that at higher temperature, $E_a < 20$ kJ/mol and so the process becomes diffusion-controlled (diffusion of A⁻ to the bulk aqueous phase or to the aqueous film of the interface becomes slow). However, at lower temperature, $E_a > 50$ kJ/mol indicating the process is chemical reaction rate controlled (Biswas and Mondal, 2003).

Furthermore, Deng et al (2010) also used Na_2SO_3 to reduce ferric to ferrous in a solution containing iron and vanadium. Using 10% P204 (di(2-ethylhexyl) phosphoric acid), 5% TBP, and 85% kerosene, the authors extracted 94% vanadium and 4.91% iron at pH 2.3, A/O=2 and contact time 10 minutes.

The extraction of various elements using LIX 63 has been reported by Zhang et al (1996). Figure 2.13 shows that an increase in pH enhanced the extraction of vanadium (IV) and percentage extraction reached almost 100% when the pH rose to approximately 2, whereas aluminum (III), cobalt (II), and nickel (II) were still not extracted. The extraction of iron (III) was also negligible while molybdenum (VI) and vanadium (IV) can be accomplished by simultaneous extraction. A pure vanadium (IV) product can be recovered as a sulfate by selectively stripping vanadium (IV) from the loaded solvent by 2 M sulfuric acid solution (Zhang et al., 1996).



Figure 2.13. pH dependence on the extraction of individual metal ions from sulfuric acid solutions by 20 vol% LIX63 dissolved in Exxsol 80 (Zhang et al., 1996)

Furthermore, solvent extraction of molybdenum and vanadium from sulfuric acid solution of spent catalysts was investigated. Both molybdenum (VI) and vanadium (V) can be selectively extracted over iron (III), aluminum (III), nickel (II), and cobalt (II) from the catalysts using 0.4 M LIX63 in the pH range of 1-2. Over 99.9% of Mo (VI) and V (V) were extracted in a single contact with only 28 mg/L Al being extracted. The extraction pH isotherm of vanadium (IV) in Figure 2.13 was quite different from V (V) in Figure 2.14. At pH 1, over 50% of vanadium (IV) was extracted, while over 97%V was extracted for V (V) (Zeng and Cheng, 2010).



Figure 2.14. Effect of pH on the extraction of metal values with 0.5M LIX63 in Shellsol D70 at an A/O ratio of 1:1 and 40°C (Zeng and Cheng, 2010)

Mishra et al (2010) also studied the recovery of metal values from spent catalysts. They observed that after the extraction of Mo by LIX-84I (10%), vanadium could be extracted to greater than 80% at an A/O ratio of 1/5 in 2 stages.

2.3.2.2 Solvent extraction using anion extractants

Vanadium (V) can form the anion species in the mildly acidic and basic range of pH; therefore, anion extractant solvents are popular in this range. Much research has been done using anion extractants for vanadium solvent extraction (Meawad et al., 2010). Amines being cations in character extract vanadium from solution as an anionic complex. As only pentavalent vanadium forms anionic complexes, it is necessary to oxidize all the vanadium in the solution to the pentavalent state prior to solvent extraction by amines. The oxidation of V (IV) to V (V) can be accomplished by oxidants such as H_2O_2 and the reaction can be written as:

$$2 \text{ VO}^{+2} + \text{H}_2\text{O}_2 = 2 \text{ VO}_2^+ + 2\text{H}^+$$
(2.1)

The VO_2^+ formed is solvated according to the reaction:

$$2 \text{ VO}_2^+ + 3\text{H}_2\text{O} = \text{H}_3\text{V}_2\text{O}_7^- + 3 \text{ H}^+$$
(2.2)

and extracted by amine. Except in strongly acidic solutions, anionic vanadium complexes exist over a wide pH range. So it is important to include many results published in the field of the extraction of vanadium by amines. Secondary, tertiary, and quaternary amines have been used for vanadium extraction. Tertiary amines (Alamine 336) extract better than the quaternary amine (Aliquat 336) in the mild acidic pH around 2 to 3. In this section, some of the recent publications about vanadium extraction using amines will be studied.

Olazabal et al (1992) reported a quantitative extraction of vanadium using different amine extractants dissolved in Toluene. Vanadium (V) can be extracted by Alamine 336/Toluene in a wide pH range where mono and polynuclear species of vanadium are present. In addition, Aliquat 336/Toluene quantitatively extracted vanadium in the range 3.5<pH<9. The extraction with quaternary ammonium salt is favoured in the region where aqueous polynuclear species are predominant.

Moreover, Nekovar and Schrotterova (2000) claimed vanadium (V) polymerized at low pH (within the approximate pH range 2-6) to form polyanions $V_{10}O_{28-n}$ (OH)_n⁽⁶⁻ⁿ⁾⁻(n=0, 1, 2) and Primene JMT can extract vanadium in this range effectively.

Figure 2.15 illustrates the percentage of vanadium extracted from leach solutions (3.88 g/L V (V)) with organic phase made up of amine (5% v/v), isodecanol (5% v/v) as a modifier, and kerosene using O/A ratio of 1. It can be seen that Primene 81R allows a broad pH range for the extraction of V (V). However, Alamine 336 is restricted to pH values below 4. pH50 values for Alamine 336 and Primene 81R were obtained as 4.67 and 7.98, respectively. The authors

postulated that the extracted species for vanadium at pH 4.5 is $(H_{2-x}V_{10}O_{28})^{x-6}$ with x= 0, 1, 2 while at pH 8, they suggested the extracted vanadium anion species consist of several vanadates: $(V_4O_{12})^{4-}$, $(V_2O_7)^{4-}$, and $(VO_4)^{3-}$. Extraction isotherms showed that the loading capacity for the primary amine is six times greater than for the tertiary amine and the primary amine can be used in the broad pH range (Lozano and Godínez, 2003).



Figure 2.15. Effect of pH on the solvent extraction of V(V) (Lozano and Godínez, 2003)

Bal et al (2004) showed that V (V) in the acidic range as decavanadate species is rapidly extracted by Aliquat 336 in kerosene modified by n-decanol according to a mechanism of anion exchange, but the reddish extracted species turns olive green within a few days at room temperature while a black-greenish solid precipitated. This solid third phase is composed of mixed-valence decavanadate compounds such as $(R_3R'N)_4(HV_3^{IV}V_7^{V}O_{26})$ and/or $(R_3R'N)_4(HV_7^{IV}V_3^{V}O_{24})$ and when cyclohexanol and ethyl-4-phenol were used as phase modifiers instead of n-decanol, the precipitation of mixed-valence decavanadates is no longer observed.

Figure 2.16 shows the effect of pH for vanadium extraction using a primary amine (Primene JMT), a secondary amine (Amberlite LA-2), a tertiary amine (Alamine 304, Alamine 336), and quaternary ammonium salt (Aliquat 336). Aliquat 336 showed increasing vanadate recovery efficiency with increasing pH while the other extractants showed a sharp optimum pH. Moreover, it was shown that 20 mM of Aliquat 336, Primine JMT, Alamine 336, Amberlite LA2 and Alamine 304 could extract about 100, 75, 85, 95, and 70% of vanadium, respectively. So they concluded Aliquat 336 is more appropriate for vanadium extraction (Navarro et al., 2007).



Figure 2.16. pH influence of vanadium extraction for different extractants (Navarro et al., 2007)

Table 2.11 compares the stripping efficiency of different chemical agents for vanadium recovery from the loaded organic phase. In the case of Amberlite LA-2, vanadium recovery was readily achieved using alkaline media (NaOH, ammonia) and mixed media (ammonia and ammonium salt) with quantitative recovery of the metal. In the case of Aliquat 336, the stripping was much more difficult and a severe selection of the stripping agent was required. The quantitative recovery of vanadium was only achieved using a concentrated mixed solution of ammonia and ammonia and ammonia salt ($1.5M NH_3 + 1.5M NH_4NO_3$ or NH_4Cl). However, Al was simultaneously and

partially extracted with V and the difficulty in stripping V and Al from the loaded organic phase strongly limits the possibility of the using amine extractants for the treatment of alkaline and acidic leachates (Navarro et al., 2007).

Table 2.11. Influence of stripping agent and concentration on vanadium stripping from loaded organic phase (Navarro et al., 2007)

Stripping agent	Stripping efficiency (%)			
	Aliquat 336	Amberlite LA-2		
NH ₄ Cl/NH ₃ (1.5 M each)	100	94		
NH ₄ Cl/NH ₃ (1 M each)	50	Not determined		
NH ₄ NO ₃ /NH ₃ (1.5 M each)	94	100		
NH ₄ NO ₃ /NH ₃ (1 M each)	48	Not determined		
NaOH (1 M)	28	98		
NH ₃ (0.5 M)	Not determined	98		
NH ₃ (1 M)	3	100		
NH ₃ (2 M)	Not determined	100		
H_2SO_4 (1 M)	2	5		

In another research (El-Nadi et al., 2009), a comparative study of the solvent extraction of vanadium (V) of spent catalysts from hydrochloric acid and sodium hydroxide media (Table 2.12) was separately carried out using an Aliquat-336 extractant dissolved in kerosene containing 10% n-octanol as a phase modifier. The results indicated that the extraction from the sodium hydroxide solution is better than from the hydrochloric acid media. However, the acidic route of leaching and extraction avoids the complication of molybdenum being present in most of the spent catalysts as an interfering metal.

Extractant	Concentration, M	Extraction (%)
Cupferron	0.1	14
8-Hydroxyquinoline	0.1	24
Thenoyltrifluoroacetone	0.1	5.4
Aliquat-336	0.1	45.6
CYANEX 301	0.1	0
CYANEX 302	0.1	0

Table 2.12. Extraction of V (V) 1 g/L from alkaline NaOH solution (pH 12.8) using various extractants (El-Nadi et al., 2009)

It was shown in Figure 2.17 that the slope of the log-log linear relationship between Aliquat 336 concentrations with the corresponding distribution ratios is around four, which indicates the participation of four molecules of the extractant in the extracted V (V) species in the investigated system.





2.3.2.2.1 Problems with using amines

Pentavalent vanadium species can oxidize amines easily. This limits the use of amines for V (V). Amines extract rapidly but phase separation is slow. As compared to D2EHPA, the time required for the amine phase disengagement is large. Stripping of vanadium from amines has to be controlled as well. Vanadium is stripped from the amine solvents using ammonium solutions. Stripping with an ammonium salt converts the extracted decavanadate into a metavanadate species. The low aqueous solubility of ammonium metavanadate (NH_4VO_3) may results in crystallization in the aqueous strip liquor (Gupta, 1992).

2.4 Summary

Since vanadium forms different species at different pH, different extractants have been used for its solvent extraction. Vanadium forms anionic species in a broad range of pH from mildly acidic to basic; therefore, anionic extractants are popular for vanadium purification. However, amines have some problems as well. On the other hand, some other cationic extractants showed poor selectivity, especially with respect to iron, aluminum, and molybdenum. It seems that understanding the behavior of different vanadium valences (V and IV) and extractants along with studying the extraction chemistry of iron can make a key contribution to the solvent extraction processes of vanadium.

2.5 Objectives

Considering the literature review, this research has been based on two categories: leaching and solvent extraction.

Due to the lack of consistent results for vanadium leaching and the lack of deep understanding in previous research, the goal of the leaching work was identified. It was planned to investigate the chemistry and kinetics of vanadium leaching over a range of pH values using pure vanadium oxides as starting material. To reach the goals, the following investigations have been carried out:

- Studying vanadium (V₂O₅) atmospheric leaching at different pHs to understand the leaching efficiency in different media as well as the kinetics of leaching
- Investigating the impact of reductive agents on vanadium (V₂O₅) leaching kinetics at acidic pH
- Studying vanadium (V₂O₃) oxidative leaching in sulfuric acid using different additives

The goals of the solvent extraction work are elaborated as follows:

- Study of the extraction chemistry of V (V) and V (IV) and different acid and solvating extractants
- Investigation of separation factors for V (V) and V (IV) over Fe (III) and Fe (II) under a range of extraction conditions.
- Study of extraction stoichiometry of V (V) and V (IV) in the acidic pH range
- Study of stripping of metals from loaded solvent.

3 Experimental

3.1 Leaching

Considering the literature review and the lack of consistent results for vanadium leaching in various reports, chemical grades of vanadium oxides have been selected to study the behavior of vanadium leaching by aiming to understand its fundamental hydrometallurgy. Vanadium pentoxide and vanadium trioxide are the most known and available sources of vanadium oxide. Therefore, investigating the effect of different parameters on leaching efficiency as well as the kinetics of leaching could possibly lead to better processes.

3.1.1 Vanadium (V)

3.1.1.1 Material

Chemical grade vanadium pentoxide (V_2O_5) from Fisher Scientific was used for leaching experiments. The purity of vanadium pentoxide was greater than 99.6% with low levels of iron (0.01% max), aluminum (0.03% max), silicon dioxide (0.01% max), sulfur (0.01% max), and phosphorus (0.01% max). The effect of impurities was not considered in our experiments. Chemical grade sodium sulfite was used for reductive leaching. The vanadium pentoxide was screened to various particle size fractions for the study. The -106+75 µm fraction was used for leaching and solubility studies.

3.1.1.2 Experimental procedure

The experiments to measure leaching rates and vanadium solubility were performed in a Pyrex reactor equipped with a magnetic stirrer and a reflux condenser. A water bath was used for controlling the temperature. The final solution was filtered using ashless syringe filter paper and analyzed for vanadium content with Inductively Coupled Plasma spectroscopy (ICP, PerkinElmer model Optima 7300). The pH was controlled and recorded via a data acquisition

system connected to a computer. The pH was kept constant (± 0.01) during the leaching process by the addition of concentrated sulfuric acid from an acid stock tank on a digital scale connected to an accurate pump and controller. The vanadium extraction was confirmed using mass balance by weighing the remaining solid after each test and calculating the extent of leaching. Solubility of vanadium in different solvents at pH 1 and 30°C was studied. Vanadium species was also investigated by Raman spectroscopy. The final vanadium solution after leaching pure vanadium pentoxide in HCl, H₂SO₄, and H₂SO₄ with 0.55 Na₂SO₄ at pH 1 and 30°C was analyzed by Raman spectroscopy. Raman spectra of each sample using a Raman micro-spectrometer that fibre-couples an IPS 300 mW, 785 nm diode laser to an Olympus BX-51 microscope. This system collects backscattered light with a six-around-one fibre bundle. The bundle exit, arranged as a vertical fibre stack, forms a 100 micrometer slit at the entrance of an Acton 300 mm monochromator coupled to a Princeton instruments PIXIS back-illuminated CCD detector. A laboratory computer reads the CCD, and bins the pixels in each column, t, from 1 to 1400 to form a spectrum of scattered-light intensity versus Raman shifted wavelength. Samples were prepared for analysis by filling a 100 microliter aluminum well plate. Spectral acquisitions combine the signals recorded from five accumulations using a 5 s exposure time for each.

In the second phase, the kinetics of vanadium pentoxide leaching by weak acid solution (pH 5) and dilute sodium hydroxide solution (pH 8) was studied. In these tests, pH was kept constant by adding sodium hydroxide during the experiment. Vanadium (V) concentration was also analyzed by ICP. It should be clarified that in all of the experiments, kinetics of the overall reaction was investigated and mechanism of the reaction was not considered.

In the last step, the kinetics of the reductive leaching of vanadium (V) using sodium sulfite was investigated. The effects of pH, temperature, and sulfite concentration on the kinetics were

studied. For this part of the project, UV-spectroscopy (PerkinElmer model Lambda 35) was applied to analyze vanadium (IV) concentration in the leach solution samples (Kanamori et al., 1999; Yang and Gould, 2003). UV spectroscopy showed a suitable accuracy for vanadium (IV) standard solutions in sulfuric acid.

3.1.2 Vanadium (III)

3.1.2.1 Material

Chemical grade vanadium trioxide (V_2O_3), iron (III) sulfate pentahydrate and iron (II) sulfate heptahydrate made by Fisher Scientific were used for experiments. The vanadium trioxide was screened to various particle size fractions for the study. The -106+75 µm fraction was used for leaching studies.

3.1.2.2 Experimental procedure

The procedure involved leaching vanadium trioxide in 0.5 L sulfuric acid solution in a 1 L Pyrex reactor equipped with a magnetic stirrer for agitation and a reflux condenser to prevent water loss. The pH was also controlled in these experiments. The pH was monitored using a glassy pH electrode from Applisens (model: Z001023551) connected to the controller. The pH was calibrated using standard buffer of 1.68, 4 and 7 with temperature adjustment. At 30°C, 94 g/L of sulfuric acid made a solution of pH 0. For experiments at higher temperature, higher sulfuric acid concentrations were added to keep an initial pH of 0. The reactor was immersed in a water bath to control the temperature. Samples of solution were withdrawn with time to follow the kinetics of leaching. The final slurry was filtered using ashless syringe filter paper and analyzed for vanadium content with ICP or UV spectroscopy (Kanamori et al., 1999; Yang and Gould, 2003). The leaching kinetics were investigated in three steps. First, the acid oxidation leaching of

vanadium trioxide using oxygen was studied. A flow of 480 mL/min of oxygen with a purity of more than 99.5% was injected into the solution containing 1 g/L of V_2O_3 in sulfuric acid. The effects of temperature, pH, particle size, and stirring speed on the leaching of vanadium were studied. Secondly, a mixture of ferric and oxygen as oxidative agents was used for oxidative leaching of vanadium. For these experiments, 180 mL/min of oxygen was applied during these experiments, again at 1 g/L of vanadium trioxide. The effects of the initial ferric concentration, temperature, and pH were then studied. Finally, in the third step, a constant potential (Bouffard et al., 2006) was applied to study the kinetics of vanadium oxidative leaching. This technique involves adding a solution of potassium permanganate to maintain a constant ferric/ferrous ratio in leaching. For these experiments, 1 g/L of vanadium trioxide was leached in sulfuric acid solution at pH 0. Leaching tests were performed under constant potential conditions which involved the control of every relevant variable during leaching. The addition of 0.5 M potassium permanganate solution was controlled to a constant potential (ferric/ferrous ratio) set point using a controller connected to ORP electrode. The ORP electrode was a single junction platinum electrode with an Ag/KCl internal reference electrode which was made by Analytical Sensors & Instruments as a special electrode for UBC (Model: R0DM-0006). Since the ferric-ferrous redox reaction is reversible on the platinum surface, it can be assumed that potential is controlled by that ratio. Hence by maintaining constant potential, the ferric/ferrous ratio was maintained constant. The mass of the oxidant solution was continually monitored via a digital scale connected to a computer for continuous data capture. Potassium permanganate is highly soluble in acidic media and rapidly re-oxidizes the ferrous ion to ferric ion. Permanganate has simple aqueous chemistry in pH ≤ 2 solutions and generates five electron-moles of oxidation per mole of reduced permanganate. The use of permanganate for constant potential leaching tests has been

demonstrated by a number of researchers (Bouffard et al., 2006; Kametani and Aoki, 1985; Zheng et al., 1986). During the experiments reported in this work, the potassium permanganate was consumed rapidly and was able to keep the potential constant through the process. The potential varied by no more than ± 3 mV from the initial value in all the tests. The vanadium concentration for each sample was adjusted to account for the volume of the added sodium permanganate solution to the reactor and the withdrawal of samples during the test. The vanadium concentration change in solution was also confirmed with reference to the amount of potassium permanganate added.

3.2 Solvent extraction

3.2.1 Materials

Aqueous solutions were prepared using chemical grade materials. Table 3.1 shows the starting materials used for the solvent extraction tests. Vanadium and iron concentrations in the solution were about 1 g/L in all feed solutions.

Flement	Chamical	Metal Concentration
Element	Chemical	(g/L)
Vanadium (V)	V_2O_5	1
Vanadium (IV)	VOSO ₄ .nH ₂ O	1
Iron (III)	$Fe_2(SO_4)_3.5H_2O$	1
Iron (II)	$Fe(SO_4).7H_2O$	1

Table 3.1. Chemicals used and composition of the synthetic feed solution

All of the extractants (CYANEX 272, IONQUEST 801, D2EHPA, and CYANEX 923) were used as-received without any further purification. ORFOM SX-12 supplied by Chevron Phillips was used as a diluent of the organic phase in the experimental program.

3.2.2 Experimental procedure

Extraction studies were carried out by mechanical stirring of the aqueous and organic solutions in a glass reactor at 30°C with a stirring speed of 900 rpm for 20 minutes (Figure 3.1). The pH was stable after the first few minutes for all cases. All of the reported points for the extraction were obtained by running a single batch-single element experiment. The pH was kept constant by adding 2M sulfuric acid or 4M sodium hydroxide. After extraction, phase separation was performed using separatory funnels at room temperature. The aqueous solutions were then filtered through Whatman 3 filter paper and analyzed by Inductively Coupled Plasma (ICP) or Atomic Absorption Spectroscopy (AAS). The organic phase was filtered through Whatman 1PS filter paper for stripping tests. Only the metal concentrations in aqueous samples were analyzed and the extraction was calculated from the initial and final aqueous solution concentrations. For each test, 100 mL of organic and 100 mL of aqueous solution were mixed together. Nitrogen was injected into the ferrous solution before the solvent extraction to remove oxygen from the solution. Since precipitation of ferric occurred above pH 2, solvent extraction tests were conducted below pH 2.


Figure 3.1. The experimental set up for solvent extraction tests

3.3 Magnitude of errors in the experiments

Error was minimized in the experimental work because pure materials were used for this project, and the experimental conditions were carefully controlled.. However, the following errors should be considered:

1- 1- All of the results were reported using analytical techniques such as ICP, AA and UVspectroscopy. For these techniques, it is expected that an error of \pm 3-5% in analysis can take place. This typically means that leach extractions and solvent extraction recovery values are accurate within the same range of values. There are some error involved in pH measurement for strong acidic solution in high temperature. However, it was attempted to minimize this error by calibration using acidic buffer solutions at different temperatures. A range of error of \pm 0.1 pH units might be expected for the experiments completed. 2- Particle size of the starting materials was obtained using different mesh sizes. The analyses were reported for an average particle size in a round shape. This error should not have any significant contribution on the total error.

Repeat analyses of solutions and measurements of vanadium extraction showed errors in the ranges cited above.

4 Vanadium (V) leaching

4.1 Thermodynamics of the vanadium –water system

Vanadium has a wide range of stable oxidation states with the most common states being +2, +3, +4, and +5. Vanadium can form a variety of complex species and oxidation states in aqueous solutions (Barner and Scheueman, 1978; Gupta, 1992; Tracy et al., 2007).

In order to understand vanadium leaching, it is important to examine vanadium chemistry. Vanadium (V) species versus pH was depicted in Figure 4.1 using Medusa software (Puigdomenech, 2004). It can be seen below that vanadium (V) ion has a very complex chemistry in aqueous solution. A pentavanadyl cation VO_2^+ forms at low pH, and, at higher pH values a variety of anions are present.



Figure 4.1. Speciation of vanadium (V) in aqueous media at 25°C

4.2 Solubility

The kinetics of V_2O_5 leaching at different solid to liquid ratios was studied. As Figure 4.2 shows, the kinetics of vanadium (V) leaching is rapid at 90°C. However, at a high solid to liquid ratio, the leaching halted abruptly after a short time, apparently because the vanadium solution had reached its solubility limit. In fact, the solution has been saturated by vanadium to the same concentration for the experiments performed at 5 and 10 g/L solid to liquid ratio. This means that when there is enough sulfuric acid in the solution, the leaching can be completed quickly. However, acid concentration must be kept high through the leaching process. This suggests that the final leach solution will have significant amounts of sulfuric acid which should be neutralized by sodium hydroxide before the purification step.

The solubility of VO_2^+ was studied at different pHs from 0.3 to 1.4 and at varying temperatures. Figure 4.3 through Figure 4.6 illustrate vanadium extraction versus time at different pH's at 30, 50, 70, and 90°C. The limiting concentration reached in each experiment represents the solubility of pentavalent vanadium in each leach solution at the temperature used for leaching.



Figure 4.2. The effect of solid to liquid ratio on V_2O_5 leaching; (a) vanadium extraction, (b) vanadium molarity (60g/L H₂SO₄, 90 °C, 90 μ m, and 600 rpm)



Figure 4.3. The effect of pH on vanadium leaching at 30°C

(at 10 g/L V₂O₅, 90 μm , and 600 rpm)



Figure 4.4. The effect of pH on vanadium leaching at 50°C

(at 10 g/L V₂O₅, 90 μ m, and 600 rpm)



Figure 4.5. The effect of pH on Vanadium leaching at 70°C





Figure 4.6. The effect of pH on vanadium leaching at 90°C

(at 10 g/L $V_2O_5,\,90~\mu m,$ and 600 rpm)

The results show that the vanadium leaching to VO_2^+ is rapid but this species suffers from low solubility. Thermodynamic data were studied for comparison with the experimental results and clarification. Table 4.1 shows the thermodynamic data for the following reaction, which can be expected to occur in acidic media. It should be mentioned that for solubility calculations, the activity coefficients for the aqueous species of vanadium was assumed to be 1.

$$V_2O_5 + 2H^+ = 2VO_2^+ + H_2O$$
(4.1)

Table 4.1. Thermodynamic data for equation 4.1 (Barner and Scheueman, 1978; Evans and Garrels, 1958; Wanty and Goldhaber, 1992)

Temperature	ΔH°	ΔS°	ΔG°		Calculate	ed Vanadiu	m Solubili	ty (mM)
(°C)	(kJ)	(J/K)	(kJ)	K	pH 0.3	pH 0.6	pH 1	pH 1.4
30	-35.18	-147.73	9.60	2.21×10 ⁻²	74.57	37.37	14.87	5.92
50	-38.06	-156.95	12.65	9.01×10 ⁻³	47.56	23.83	9.49	3.77
70	-40.70	-164.89	15.87	3.83×10 ⁻³	31.03	15.55	6.19	2.46
90	-43.34	-172.35	19.24	1.70×10 ⁻³	20.68	10.36	4.13	1.64

As shown, the solubility of this cation is affected significantly by temperature and pH. Considering thermodynamic data and Le Chatelier's principle, it would be expected that, by decreasing pH and temperature, the solubility of VO_2^+ increases. However, the experimental data reported higher values for solubility than that presented in Table 4.1. This can be explained with reference to the complexation of vanadium in sulfate media. In a solution containing sulfate/bisulfate anions, a mono sulfate or mono bisulfate complex may be formed according to the following reactions:

$$VO_2^{+} + SO_4^{-2} = VO_2SO_4^{-1} \qquad \beta_1 = K_1 = \frac{[VO_2SO_4^{-1}]}{[VO_2^{+}][SO_4^{-2}]}$$
(4.2)

$$VO_2^+ + HSO_4^- = VO_2HSO_4$$
 $\beta_1 = K_1 = \frac{[VO_2HSO_4]}{[VO_2^+][HSO_4^-]}$ (4.3)

The equilibrium constant ($Log \beta_1$) for reaction 4.2 has been reported as 0.98 (Ivakin, 1966), 1.3 (Rakib and Durand, 1996), and 1.72 (Puigdomenech, 2004). Besides, the equilibrium constant (Log β_1) for reaction 4.3 was also reported -0.136 (Ivakin, 1966). In fact, in non-complexing aqueous acidic solution, the pentavanadyl ion (VO_2^+) is the only dominant cation in the solution. However, the formation of the vanadium sulfate complex can increase solubility of vanadium in sulfuric acid media. To investigate in more detail, the solubility of vanadium in different acid media and the effect of ionic strength and complexation have been studied. Figure 4.7 shows vanadium solubility in sulfuric acid, nitric acid, and hydrochloric acid. The results after 2 hours leaching were depicted because vanadium had reached its solubility limit in all the experiments. Moreover, each test was continued for 8 hours to make sure that the solubility number did not change significantly. It can be seen that the solubility of vanadium in nitric and hydrochloric acid is almost the same at pH 1 and 30°C. However, the solubility of vanadium in sulfuric acid is greater. To investigate the effect of added salt on vanadium solubility considering ionic strength and complexation (Butler, 1998), the solubility of vanadium in hydrochloric acid was studied by adding 0.33 and 1.65 molar sodium chloride and 0.11 and 0.55 molar sodium sulfate separately. The results shown in Figure 4.7 confirm that by increasing the sulfate concentration in solution, the solubility of vanadium increases. This is believed to be due to the complexation of the vanadyl ion by sulfate.



Figure 4.7. The effect of different solvent and adding different salts on vanadium solubility

(at 10 g/L V₂O₅, 90 µm 30°C, pH 1, and 600 rpm)

Some techniques have been developed to study speciation in solution. Raman spectroscopy is one of the well-known methods for this purpose. This technique has been used to detect different cations in vanadium solutions formed with various acids and complexing salt additions (Bal et al., 2004; Chagnes et al., 2010; Hurley et al., 2011; Tomikawa and Kanno, 1998; Tracy et al., 2007). The final solutions after leaching at pH 1 by hydrochloric acid with no salt and 0.55 M sodium sulfate as well as sulfuric acid with no additives were characterized by Raman spectroscopy. As Figure 4.8 shows, when the matrix is hydrochloric acid, soluble vanadium only appears as one cation, VO_2^+ . However, when sulfate is available in the solution, vanadium has been confirmed to complex as $VO_2SO_4^-$. Lastly, with the addition of sodium sulfate to the hydrochloric acid solution, the formation of $VO_2SO_4^-$ appears on the Raman spectra.



Figure 4.8. Raman spectra for vanadium solution to confirm vanadium complexation in the presence of sulfate

As discussed above, acid leaching of vanadium pentoxide suffers from the low solubility of vanadium. However, it was shown that by increasing the sulfate concentration in the system, the vanadium solubility will increase due to complexation. Two alternate strategies for overcoming the low solubility of vanadium have been investigated. Leaching at higher pH and reductive leaching have been applied to change the vanadium species in solution in an attempt at increasing solubility.

4.3 Leaching of vanadium in pH 5-8 solution

The kinetics of vanadium leaching using mildly acidic or mild basic solution was investigated. According to Figure 4.1, vanadium (V) can form decavanadate anion in solution at pH 5. The formation of decavanadate can proceed by the following reaction:

$$5V_2O_5 + 5OH^2 = HV_{10}O_{28}^{-5} + 2H_2O$$
 $\Delta G_{298K}^{\circ} = -648.02 \text{ kJ/mol}$ (4.4)

This reaction is highly favorable. The decavanadate species has a high solubility in water. Therefore, solubility limits should not impede leaching of vanadium under conditions designed to form decavanadate. During the leaching process, the pH was kept constant by adding sodium hydroxide to the solution. Figure 4.9 shows the effect of temperature on vanadium leaching. Temperature has a significant effect on vanadium leaching. Vanadium pentoxide was nearly completely leached in 90 minutes at 90°C. However, less than 40% of the vanadium was leached in that same time at 30°C.



Figure 4.9. The effect of temperature on vanadium leaching (at pH 5, 10 g/L, 90 μm, and 600 rpm)

Moreover, leaching at higher pH has also been studied. Reactions 4.5 and 4.6 show the chemical reactions that form the two anion species that dominate at pH 8 (Pourbaix, 1949; Puigdomenech, 2004):

$$3V_2O_5 + 6OH^2 = 2V_3O_9^{-3} + 3H_2O$$
 $\Delta G_{298K}^\circ = -221.9 \text{ kJ/mol}$ (4.5)

$$2V_2O_5 + 4OH^2 = V_4O_{12}^{-4} + 2H_2O$$
 $\Delta G_{298K}^{\circ} = -208.6 \text{ kJ/mol}$ (4.6)

According to the thermodynamic data, all of these anion species in the solution have high solubility. Therefore, the effect of temperature on the kinetics of vanadium leaching in mildly basic media was investigated. Figure 4.10 represents the effect of temperature on vanadium leaching. It was observed that the temperature has a significant effect on vanadium leaching in mildly basic media. Moreover, the molar ratio of sodium hydroxide consumption to vanadium pentoxide was determined to be 2.09 for leaching at pH 8 and 90°C. This value is very close to the ratio from reactions 4.5 and 4.6. In addition, it was shown that by increasing the pH from 5 to 8, the kinetics of vanadium leaching improved drastically. For instance, at 90°C, the leaching was completed in one hour at pH 8; while it required 2 hours at pH 5. At other temperatures, the time to obtain similar recovery for vanadium was almost double at pH 5 compared with pH 8.



Figure 4.10. The effect of temperature on vanadium leaching

(at pH 8, 10 g/L, 90 µm, and 600 rpm)

4.4 Reductive leaching

Since vanadium (IV) has higher solubility than vanadium (V) in acidic media (Puigdomenech, 2004), reductive leaching can be applied to increase vanadium extraction at a modest pH and hence decrease acid consumption in the leaching and vanadium recovery process. The kinetics of reductive vanadium pentoxide leaching using sodium sulfite was investigated. The effects of varying temperature, particle size, stirring speed, pH, and sodium sulfite concentration were studied. For the kinetic study, since pure vanadium pentoxide was used and all spherical particles were shrunk through the leaching process (without formation of an "ash layer"), the shrinking sphere model was applied to describe the reductive leaching of vanadium. For the reaction of this kind, the following three steps occurring in succession:

Step1. Diffusion of the reactant from the bulk solution through the film layer to the surface of the solid

Step2. Reaction on the surface between reactant and solid

Step3. Diffusion of the reaction products from the surface of the solid through the film layer back to the bulk solution

The leach model has been defined by evaluating the thermal function k(T), the chemical function f(C) surrounding sulfite concentration, and the topological function g(1-X) indicating the changing vanadium pentoxide grain topology in the following generalized topological leach model and X is fraction of unreacted solid:

$$\frac{dX}{dt} = k(T). f(C). g(1 - X)$$
 (4.7)

For the kinetic study, when the chemical reaction is the rate-controlling step, the rate is proportional to the available surface of unreacted core. Thus, the fraction of vanadium reacted at any time can be predicted by (Levenspiel, 1999):

$$\frac{t}{\tau} = 1 - (1 - X)^{\frac{1}{3}}$$
 and $\tau = \frac{\rho R_{\circ}}{b k_s C}$ (4.8)

where R_{\circ} is the average initial radius of the spherical particles, ρ is the molar density of the sample, b is the stoichiometric coefficient of the reaction, k_s is the rate constant for surface reaction, and C is representative as a concentration function.

Film resistance at the surface of a particle is dependent on numerous factors, such as the relative velocity between particle and fluid, size of particle, and fluid properties. By assuming round

particles in the same size, R_{\circ} , equations 4.9 can be obtained. This equation represents the fraction of vanadium reacted at any time when the resistance to diffusion through the hydrodynamic film controls the rate of the reaction (Levenspiel, 1999):

$$\frac{t}{\tau} = 1 - (1 - X)^{\frac{2}{3}}$$
 and $\tau = \frac{\rho R_{\circ}^2}{2bD_e C}$ (4.9)

where ρ , R_o, b, and C are defined as equation 4.9 and D_e is the diffusion coefficient.

4.4.1 Effect of temperature

Figure 4.11 illustrates the effect of temperature on vanadium extraction. It shows that by increasing the temperature, the rate of the reaction also increases.



Figure 4.11. The effect of temperature on vanadium reductive leaching (at 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, 90 μ m, pH 1, and 600 rpm)

Figure 4.12 was obtained for experiments with constant pH and sodium sulfite concentration using equations 4.8 and 4.9. The model showed a suitable fit based on chemical control compared to diffusion control. The data fit the required linear relationship with extrapolation through the origin. Therefore, it can be concluded that the reductive leaching of vanadium using sulfite is controlled by the reaction at the surface of the particle.

Using the data obtained at the various temperatures, the apparent activation energy of the reaction using an Arrhenius relationship has been obtained. Using the slope of the Arrhenius curve in Figure 4.13, an activation energy of 33 kJ/mol is calculated.



Figure 4.12. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various temperature test; (b) Plot of $(1-(1-X)^{\frac{2}{3}})$ versus time for various temperature test (at 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, 90 µm, pH 1, and 600 rpm)



Figure 4.13. Arrhenius plot for activation energy calculation for reductive leaching

The particles were studied during leaching by taking intermediate samples and observing using SEM (Hitachi model S-3000N). Figure 4.14 shows SEM pictures for particle shape after 20 minutes of leaching at pH 1 at temperatures of 30 and 90°C. It was shown that the particles are roughly round. As the leaching rate increases with temperature, the particles shrink and the porosity on the surface increases.



Figure 4.14. SEM image for (a) the initial particle; (b) after 20 minutes of leaching at 30°C; (c) after 20 minutes of leaching at 90°C (at 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, 90 μ m, pH 1, and 600

rpm; white right corner rectangle shows the scale bar for 50 μ m)

4.4.2 Effect of particle size

The fraction reacted versus time plots are shown in Figure 4.15 in different particles sizes. As shown, the kinetics of the leaching reaction increased with decreasing particle size. A shrinking sphere model was used to analyze the experimental data.

Figure 4.16 shows the linear relation between the reaction rate and 1/d and confirms the reaction control mechanism for reductive leaching (equation 4.8).



Figure 4.15. The effect of particle size on vanadium reductive leaching (at 70°C, 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, pH 1, and 600 rpm)

4.4.3 Effect of stirring speed

In order to rule out mass transfer as a possible rate control mechanism, the effect of stirring speed variation on vanadium reductive leaching was investigated at 500, 600, and 700 rpm. Figure 4.17 represents that stirring speed has no significant effect on the kinetics of leaching. Therefore, considering the obtained results for activation energy, particle size, and stirring speed, it can be positively claimed that the kinetics of leaching is controlled by chemical reaction rate, not mass transfer.



Figure 4.16. (a) Plot of $(1-(1-X)^{\frac{1}{3}})$ versus time for various particle sizes (b) The effect of particle size on the rate of dissolution of vanadium (at 70°C, 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, pH 1, and 600 rpm)



Figure 4.17. The effect of stirring speed on vanadium reductive leaching (at 10 g/L V₂O₅, 10.39 g/L Na₂SO₃, 90 μm, pH 1)

4.4.4 Effect of sodium sulfite concentration

To investigate the effect that reductive additive concentration had on leaching efficiency, 10 g/L of V_2O_5 was leached using different amounts of sodium sulfite. The temperature was set at 70°C, pH 1, and the stirring speed was adjusted to 600 rpm. As shown in Figure 4.18, by increasing the amount of sulfite, the leaching rate also increased.



Figure 4.18. The effect of sulfite concentration on vanadium reductive leaching (at 70°C, 10 g/L V₂O₅, 90 μm, pH 1, and 600 rpm)

The concentration of sodium sulfite has been changed significantly through the leaching processes due to its consumption. It can be concluded that sodium sulfite concentration dropped specifically in the low concentration tests and the reductive leaching rate was then decreased after 45 minutes because of the lack of sodium sulfite in the tank. Therefore, the order of dependence of rate on the initial sodium sulfite concentration has been investigated by plotting Log k (Figure 4.19) versus Log [SO₂]_{initial} in the first 45 minutes. As shown in Figure 4.20, the slope obtained was 0.57, which shows the approximate order of dependence of reductive agent on the kinetics of the reaction.



Figure 4.19. Plot of $(1 - (1 - x)^{\frac{1}{3}})$ versus time for various initial sulfite concentration tests

(at 70°C, 10 g/L V₂O₅, 90 $\mu m,$ pH 1, and 600 rpm)



Figure 4.20. The effect of initial sulfite concentration on the rate of dissolution of vanadium (at 70° C, 10 g/L V₂O₅, 90 μ m, pH 1, and 600 rpm)

4.4.5 Effect of pH

The effect of pH on leaching is seen in Figure 4.21 which indicates that pH has a significant effect on vanadium reductive leaching rates. The leaching process was completed in less than 30 minutes at pH 0.5 and about 1 hour at pH 1; however, less than 70% of vanadium was dissolved at pH 1.5 after one hour.



Figure 4.21. The effect of pH on vanadium reductive leaching

(at 70°C, 10 g/L V₂O₅, 10.39 g/L Na₂SO₃,90 µm, and 600 rpm)

Since pH can affect the leaching reaction and can change sulfite species as a reductive additive in the solution, it can be considered as an independent parameter. Therefore, to investigate the effect pH has on the kinetics of vanadium leaching, both chemistry and electrochemistry have been considered for vanadium reductive leaching.

4.4.6 Chemistry and electrochemistry of the reaction

The reduction of V_2O_5 by sodium sulfite in aqueous solutions can be considered as an electrochemical reaction. Sodium sulfite can form sulfur dioxide (SO_{2aq}) and bisulfite in solution (HSO₃⁻). These species are oxidized to sulfate (SO₄⁻²) and bisulfate (HSO₄⁻) by vanadium. The overall reaction can be represented by two half-cell reactions. The cathodic half-cell would be the dissolution of V₂O₅:

$$V_2O_5 + 6H^+ + 2e^- = 2VO^{+2} + 3H_2O$$
(4.10)

While the anodic half-cell may be presented as sodium sulfite oxidation in solution as per any of the following four reactions:

$$SO_2(aq) + 2H_2O = SO_4^{-2} + 4H^+ + 2e^-$$
 (4.11)

$$SO_2(aq) + 2H_2O = HSO_4^{-} + 3H^{+} + 2e^{-}$$
 (4.12)

$$HSO_{3}(aq) + H_{2}O = SO_{4}^{-2} + 3H^{+} + 2e^{-}$$
(4.13)

$$HSO_{3}(aq) + H_{2}O = HSO_{4} + 2H^{+} + 2e^{-}$$
 (4.14)

In the simplest form, the overall reaction at low pH can be presented by:

$$V_2O_5 + SO_{2(aq)} + 3H^+ = 2VO^{+2} + HSO_4^- + H_2O$$
 $K_{eq@25^{\circ}C} = 9.47 \times 10^{28}$ (4.15)

The Butler-Volmer equation (Bard and Faulkner, 2000) for reactions 4.10 and 4.12 can be written in the following form:

$$i_c = n_c F \vec{k_c} [VO^{+2}] \exp(\frac{\alpha_c Z_c F E}{RT}) - n_c F \vec{k_c} [H^+] \exp\left(\frac{-(1-\alpha_c) Z_c F E}{RT}\right)$$
(4.16)

$$i_a = n_a F \vec{k_a} [SO_2]_{aq} \exp(\frac{\alpha_a Z_a F E}{RT}) - n_a F \vec{k_a} [HSO_4^-] \exp\left(\frac{-(1-\alpha_a) Z_a F E}{RT}\right)$$
(4.17)

where n_c , n_a are total charge transfer, $\vec{k_c}$, $\vec{k_c}$, $\vec{k_a}$, and $\vec{k_a}$ are the rate constant for forward and reverse reactions for the cathodic and anodic, respectively. Z_c and Z_a are the number of electrons transferred in the charge transfer process. It was assumed that Z_c and Z_a are one. α_c and α_a are the transfer coefficients for equations 4.16 and 4.17 that represent the symmetry of the activation barrier for the cathodic and anodic charge-transfer reaction.

It was assumed that the potential difference is large enough that backward reactions kinetics are slow and can be neglected. Therefore, cathodic and anodic reactions can be rewritten as below:

$$i_c = -2F\dot{k}_c [H^+] \exp\left(\frac{-(1-\alpha_c)Z_c FE}{RT}\right)$$
(4.18)

$$i_a = 2F\vec{k_a}[SO_2]_{aq}\exp(\frac{\alpha_a Z_a FE}{RT})$$
(4.19)

The net current density is zero at the mixed potential:

$$i(E_m) = 0 \xrightarrow{\text{yields}} -i_c(E_m) = i_a(E_m) \tag{4.20}$$

Then, the exchange current density can be derived by the following relationship:

$$i_{\circ} = 2F \overleftarrow{k_c} [H^+] \exp\left(\frac{-(1-\alpha_c)Z_c F E_m}{RT}\right) = 2F \overrightarrow{k_a} [SO_2]_{aq} \exp\left(\frac{\alpha_a Z_a F E_m}{RT}\right)$$
(4.21)

$$\frac{k_a[SO_2]_{aq}}{\overleftarrow{k_c}[H^+]} = \exp\left(\frac{(\alpha_c - \alpha_a - 1)FE_m}{RT}\right)$$
(4.22)

It is common to assume symmetric electron transfer in the Butler Volmer equation and this often agrees well with experimental Tafel plots. This assumption is also mathematically convenient. Therefore, by assuming $\alpha_c = \alpha_a = 0.5$:

$$\frac{\overline{k_{a}}[SO_{2}]_{aq}}{\overline{k_{c}}[H^{+}]} = \exp\left(\frac{-FE_{m}}{RT}\right)$$
(4.23)

Considering Faraday's law, the rate of the overall electrochemical reaction can be obtained as:

$$-\frac{dn_{V_2O_5}}{dt} = \frac{dn_{SO_{2aq}}}{dt} = \frac{A_c i_c}{n_c F}$$
(4.24)

$$-\frac{dn_{V_2O_5}}{dt} = A_c \overleftarrow{k_c} [H^+] \exp(\frac{-FE_m}{2RT}) = A_c \overleftarrow{k_c} [H^+] \left(\frac{\overrightarrow{k_a} [SO_2]_{aq}}{\overleftarrow{k_c} [H^+]}\right)^{0.5} = k^* [H^+]^{0.5} [SO_2]_{aq}^{0.5}$$
(4.25)

On the other hand, SO_2 can be considered as a weak acid in the solution that dissociates as follows:

$$SO_{2(aq)} + H_2O = H^+ + HSO_3^-$$
, $K_e = \frac{[H^+][HSO_3^-]}{[SO_2]_{aq}^{0.5}}$ (4.26)

And the total concentration of SO₂ would be:

$$[SO_2]_{total} = [HSO_3^-] + [SO_2]_{aq}$$
(4.27)

Combining equations (4.26) and (4.27):

$$[SO_{2}]_{aq} = \frac{[SO_{2}]_{total}}{1 + \frac{K_{e}}{[H^{+}]}}$$
(4.28)

Considering equations (4.24) and (4.28), the rate of vanadium pentoxide dissolution would be:

$$-\frac{dn_{V_2O_5}}{dt} = k^* [H^+]^{0.5} \left(\frac{[SO_2]_{total}}{1 + \frac{K_e}{[H^+]}} \right)^{0.5} = k^* \frac{[H^+]}{(K_e + [H^+])^{0.5}} [SO_2]_{total}^{0.5}$$
(4.29)

The above equation predicts the rate of the overall reaction in terms of concentration of total SO_2 and H^+ in aqueous solution due to electrochemical analysis. It can be seen that the electrochemical analysis reports one-half-order dependence on SO_2 concentration which is consistent with the experimental results.

Based on the electrochemical analysis, the following equation shows the rate dependence of vanadium leaching on pH. This equation was used to compare experimental with predicted theoretical results considering the effect of pH.

Rate of the reaction =
$$f(\frac{[H^+]}{(K_e + [H^+])^{0.5}})$$
 (4.30)

The reaction constant for dissociation of SO₂, K_e , using thermodynamic data and the Criss-Cobble technique generated a value of 4.37×10^{-3} at 70°C. Then, the reaction rate ratio can be derived from the following equations:

$$\frac{R_{pH1}}{R_{pH0.5}} = \frac{\frac{10^{-1}}{(10^{-1} + 4.37 \times 10^{-3})^{0.5}}}{\frac{10^{-0.5}}{(10^{-0.5} + 4.37 \times 10^{-3})^{0.5}}} = 0.53$$
(4.31)

$$\frac{R_{pH1}}{R_{pH1.5}} = \frac{\frac{10^{-1}}{(10^{-1} + 4.37 \times 10^{-3})^{0.5}}}{\frac{10^{-1.5}}{(10^{-1.5} + 4.37 \times 10^{-3})^{0.5}}} = 2.44$$
(4.32)

Considering Figure 4.22, the rate of the reaction in different pH tests was obtained. $R_{pH1}/R_{pH0.5}$ and $R_{pH1}/R_{pH1.5}$ are found to be 0.51 and 2.57, respectively. The predicted ratios in electrochemical analysis are consistent with the experimental results.



Figure 4.22. Plot of $(1 - (1 - x)^{\frac{1}{3}})$ versus time for various pH (at 70°C, 10 g/L V₂O₅, 10.39 g/L Na₂SO₃,90 µm, and 600 rpm)

5 Vanadium (III) leaching

5.1 V₂O₃ leaching using oxygen

In this section, a model for the kinetics of vanadium leaching with oxygen is developed. The effects of varying parameters on the leaching rate are also studied. The leaching of vanadium trioxide using oxygen is thermodynamically favorable and exothermic as summarized in Table 5.1.

$$2V_2O_3 + O_{2(g)} + 8H^+ = 4VO^{+2} + 4H_2O$$
(5.1)

Temperature (°C)	ΔH° (kJ/mol)	ΔS° (kJ/mol.k)	ΔG° (kJ/mol)	Log K
30	-653.20	-640.18	-459.13	79.12
50	-642.52	-606.03	-446.68	72.21
70	-633.22	-578.08	-434.85	66.20
90	-625.18	-555.31	-423.52	60.92

Table 5.1. Thermodynamic data for reaction 5.1 (HSC)

Figure 5.1 illustrates the effect of temperature on vanadium extraction. Note that by increasing temperature from 50°C to 70°C, the rate of the reaction increases dramatically.



Figure 5.1. The effect of temperature on vanadium leaching (at 1 g/L V₂O₃, 480 mL O₂/min, 90 μ m, pH 0, and 600 rpm)

Temperature has an effect on the solubility of oxygen, the diffusion of oxygen in the solution, and the chemical reaction rate. The solubility of oxygen in a solution at different temperatures can be expressed by equations 5.2 (Tromans, 1998; Tromans, 2001):

$$(C_{aq})_{I} = \left[\frac{1}{1+k(C_{I})^{y}}\right]^{\eta} P_{O_{2}}f(T)$$
(5.2)

Where

$$f(T) = \exp\left[\frac{0.046T^2 + 203.35T\ln(\frac{T}{298}) - (299.378 + 0.092T)(T - 298) - 20.591 \times 10^3}{8.314T}\right]$$

Where $(C_{aq})_1$ is the molal solubility of oxygen and the coefficient k and the exponents y and η are solute-specific parameters (2.02, 1.25, and 0.17, respectively for sulfuric acid solution). As shown in equation 5.2, the solubility of oxygen is a temperature function which has a minimum of around 95°C. This means that oxygen solubility decreases by increasing temperature in the range of 30°C $\leq T \leq 90$ °C. Moreover, it can be seen from equation 5.2 that increasing acid concentration as well as decreasing the partial pressure of oxygen has a negative effect on the concentration of dissolved oxygen in the solution. However, by increasing temperature from 30°C to 90°C, water steam pressure increases significantly from around 0.041 to 0.69 atm (Hammett and Chapman, 1934; Romanov, 2009; Wexler, 1976). Thus, since total pressure above the solution is 1 atm at sea level in Vancouver, increasing temperature will lead to decreased partial pressure of oxygen in the solubility of oxygen in the solubility of the solution.

Therefore, for a solution of 0.85m H₂SO₄, the dissolved oxygen concentration was calculated at about 9.75×10^{-5} , 7.08×10^{-5} , 4.09×10^{-5} , and 2.1×10^{-5} m for temperatures of 30, 50, 70, and 90°C, respectively.

Likewise, it should be considered that by increasing temperature, the diffusion coefficient of oxygen in the solution increases about three times from 30°C to 90°C (Tromans, 2001). However, since the solubility of dissolved oxygen decreases by a factor of nearly five when increasing temperature from 30°C to 90°C, it can be assumed that the mass transfer rate for oxygen is not increasing fast enough to produce the rapid increase in vanadium leaching kinetics, shown in Figure 5.1. On the other hand, temperature also plays a significant role in the kinetics of the oxidative reaction on the surface. It is obvious that increasing temperature has led to increased kinetics of vanadium oxidative leaching.
Since pure vanadium trioxide has been used in this study, particles have decreased in size through the leaching process. There is no ash layer formed during leaching and all of the particles are fully depleted at the end of the process. Similar to acid leaching of vanadium pentoxide, the shrinking sphere model for small particles has then been chosen as a possible model for describing the kinetics of oxidative vanadium trioxide leaching.

As shown in Figure 5.2, comparing diffusion and reaction control models, there is an appropriate conformity of the derived reaction control model and experimental results. Therefore, the chemical control model based on shrinking spheres can be applied for the leaching kinetics.

Using equation 4.8, the rate constant for the surface oxidation reaction was obtained by factoring out the changing dissolved oxygen concentration with temperature (from equation 5.2). The activation energy of the reaction using an Arrhenius relationship has been then calculated to be 69 kJ/mol for the reaction as shown in Figure 5.3. This high value of activation energy supports the postulate that the kinetic of the leaching is reaction controlled (Levenspiel, 1999).



Figure 5.2. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various temperature test; (b) Plot of $(1 - (1 - X)^{\frac{2}{3}})$ versus time for various temperature test (at 1 g/L V₂O₃, 480 mL/min, 90 μ m, pH 0, and 600 rpm)



Figure 5.3. Arrhenius plot for activation energy calculation for oxidative leaching using oxygen

5.1.1 Effect of particle size

The fraction reacted versus time plot is shown in Figure 5.4 for different initial particles sizes. As shown, the kinetics of the leaching reaction increased with decreasing particle size. Considering equation 4.8, the rate constant of the reaction versus 1/d was investigated. Figure 5.4 shows the linear relation between the reaction rate and 1/d, which this confirms the reaction control mechanism for oxidative leaching.



Figure 5.4. The effect of particle size on the rate of vanadium oxidative leaching (at 70°C, 1 g/L V₂O₃, 480 mL/min oxygen, pH 0, and 600 rpm)

5.1.2 Effect of stirring speed

In order to rule out mass transfer as a possible rate control mechanism, the effect of stirring speed variation on vanadium oxidative leaching was investigated at 500, 600 and 700 rpm. Figure 5.6 represents that stirring speed has no significant effect on the kinetics of leaching. This data further confirms that the kinetics of leaching is controlled by the chemical reaction rate, not mass transfer.



Figure 5.5. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various particle sizes (b) The effect of particle size on the rate of dissolution of vanadium (at 70°C, 1 g/L V₂O₃, 480 mL/min oxygen,

pH 0, and 600 rpm)



Figure 5.6. The effect of stirring speed on vanadium oxidative leaching (at 70°C, 1 g/L V₂O₃, 480 mL/min oxygen, 90 μ m, and pH 0)

5.1.3 Effect of sulfuric acid concentration

Vanadium trioxide has been leached at different pHs. Temperature, stirring speed, and average particle size were constant at 70°C, 600 rpm, and 90 μ m, respectively. The results are given in Figure 5.7, which illustrates that sulfuric acid concentration does not have a significant influence on vanadium leaching. Figure 5.8 shows the order of the reaction which is 0.14 for the sulfuric acid concentration. To investigate the effect of pH in more detail, direct leaching of vanadium trioxide in the presence of nitrogen in the same conditions was also studied. As shown in Figure 5.7, the kinetics of direct vanadium trioxide in non-oxidative conditions is slow and decreasing the pH promoted the leaching rate slightly. Therefore, it is possible, based on these

results, that the non-oxidative leaching of V (III) followed by homogeneous oxidation of V (III) with oxygen may make a small contribution to the overall reaction rate.



Figure 5.7. The effect of sulfuric acid concentration on vanadium oxidative and non oxidative leaching (at 70°C, 1 g/L V₂O₃, 480 mL/min oxygen, 90 μm, and 600 rpm)



Figure 5.8. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various particle sizes; (b) The effect of particle size on the rate of dissolution of vanadium (at 70°C, 1 g/L V₂O₃, 480 mL/min oxygen,

pH 0, and 600 rpm)

5.2 V₂O₃ leaching using oxygen and ferric

It was found that leaching of vanadium trioxide using oxygen is slow; therefore, a mixture of oxygen and ferric has been studied for vanadium leaching. Table 5.2 shows the thermodynamic data for vanadium trioxide leaching using ferric. It can be seen that the oxidative vanadium (III) leaching using ferric is thermodynamically favorable.

$$V_2O_3 + 2Fe^{+3} + 2H^+ = 2VO^{+2} + H_2O + 2Fe^{+2}$$
(5.3)

Temperature (°C)	ΔH° (kJ/mol)	ΔS° (kJ/mol.k)	ΔG° (kJ/mol)	Log K
30	-125.99	56.06	-142.99	24.64
50	-120.16	74.70	-144.30	23.33
70	-114.94	90.37	-145.95	22.22
90	-110.15	103.96	-147.90	21.28

Table 5.2. Thermodynamic data for reaction 5.3 (HSC)

In addition, oxygen can oxidize ferrous in the solution:

$$4Fe^{+2} + O_{2(g)} + 4H^{+} = 4Fe^{+3} + 2H_{2}O$$
(5.4)

This means that at least five different oxidation reactions can occur in the system concurrently, that of oxidation of V_2O_3 , Fe (II), and V (III) by oxygen, and the oxidation of V_2O_3 and V (III) by Fe (III). All these oxidation reactions are thermodynamically `favorable (HSC). However, the relative kinetics of these reactions will control the overall rate process.

5.2.1 Effect of initial ferric concentration

The effect of the initial concentration of ferric has been studied. It can be seen in Figure 5.9 that by increasing the initial ferric concentration, the kinetics of leaching is also increased. Compared to the results for the oxidation of vanadium (III) using oxygen, oxidation of vanadium (III) in the presence of ferric is very rapid. This means that ferric plays a key role in the system for the oxidation of vanadium (III).



Figure 5.9. The effect of initial ferric concentration on the kinetics of vanadium oxidative leaching (at 70°C, 1 g/L V₂O₃, 180 mL/min oxygen, 90 μm, pH 0, and 600 rpm)

5.2.2 Effect of temperature

Figure 5.10 illustrates the effect of temperature on vanadium leaching in the presence of ferric and oxygen and it can be seen that vanadium leaching is strongly dependent on temperature. It

was shown that the leaching would be finished in about 20 minutes at 90°C, while less than 80% of vanadium has been leached in an hour at 30°C.



Figure 5.10. The effect of temperature on vanadium oxidative leaching (at 1 g/L V₂O₃, 1.5 g/L ferric, 180 mL/min oxygen, 90 μm, pH 0, and 600 rpm)

5.2.3 Effect of pH

The effect of pH on vanadium leaching has been investigated through the leaching of 1 g/L of vanadium trioxide with 1.5 g/L of ferric and 180 mL/min of oxygen at temperature 70°C and 600 rpm at pHs of 0, 0.3, 0.6, and 0.9. Leaching of vanadium using ferric was not studied beyond pH 0.9 because precipitation was observed in the solution in higher pHs. The results showed that pH does not have any significant effect on vanadium leaching. Morgan and Lahav (2007) claimed that the oxidation of ferrous by oxygen in aqueous solution is independent of pH in the acidic range of pH (below pH 4). Therefore, since the leaching has been controlled by the oxidation of ferrous to ferric and oxidation of ferrous is independent of pH, it could be expected that

vanadium leaching using ferric and oxygen is not affected by changing pH. Moreover, it was shown in non-oxidative leaching of vanadium trioxide that decreasing pH can promote direct leaching of vanadium; however, since kinetics of direct leaching is so slow compared to leaching using mixture of ferric and oxygen, the direct leaching process can be assumed to have minimal contribution to the overall leach kinetics.

5.3 Vanadium trioxide leaching using ferric-ferrous solutions

The kinetics of the oxidative leaching of V_2O_3 by ferric-ferrous was studied using constant ferric/ferrous ratio. In this technique, it was tried to keep the potential constant through the leaching process. The effects of ferric-ferrous ratio, temperature, pH, and stirring speed were all studied. The leaching was then modeled using the shrinking sphere model.

The oxidative leaching of vanadium trioxide can be considered as an electrochemical reaction. This electrochemical reaction can be represented by two half-cell reactions:

$$V_2O_3 + 2H^+ = 2VO^{+2} + H_2O + 2e^-$$
(5.5)

$$Fe^{+3} + e^{-} = Fe^{+2}$$
 (5.6)

And the overall reaction is represented as reaction 5.3.

Considering the kinetics of half-cell electrochemical reactions, oxidative leaching using ferricferrous can be considered as having three different types of reaction rate control. In Type I, ferric reduction is slow and, therefore, far from equilibrium. In this type, the reverse cathodic reaction may be neglected. The exchange current densities of the two half-cell reactions (ferric reduction and mineral oxidation) are similar in magnitude, and the rate is proportional to the square root of the ferric concentration and independent of ferrous concentration. (Type I: $j_a \propto (C_{Fe(III}))^{0.5}$). In Type II, ferric reduction is fast and, therefore, essentially at equilibrium. In this case, the exchange current density of the oxidizing couple is higher than that of the dissolution reaction by several orders of magnitude and the mixed potential thus corresponds to the reversible potential of the oxidizing (potential determining) couple. In this type, the leaching rate is proportional to

the square root of the Fe(III)/Fe(II) ratio (Type II:
$$j_a \propto (\frac{C_{Fe(III})}{C_{Fe(II)}})^{0.5}$$
).

In some systems, there is a third type where the leaching reaction is particularly fast and the leaching rate is limited by mass transfer of the oxidant to the mineral surface. In this situation, the leaching reaction will proceed at the limiting current density of the oxidant and the leaching rate is proportional to the oxidant concentration (Type III: $j_a \propto (C_{Fe(III)})$.

5.3.1 Effect of temperature

The effect of temperature on vanadium (III) leaching was investigated by the leaching of 1 g/L of V_2O_3 in sulfuric acid at pH 0 and temperatures of 30, 50, 70, and 90°C. In all experiments, the initial ferric concentration was 0.1 molar and the ferric-ferrous ratio was kept constant at 10 by using potassium permanganate. ORP was reported 496, 532, 563 and 611 mV for 30, 50, 70, and 90°C respectively. Figure 5.11 shows the effect of temperature on vanadium leaching. It can be seen that by increasing temperature, the rate of leaching increases. It was shown that at the higher temperature, vanadium was completely leached in about 20 minutes, however, it took about 3 hours to leach around 90% of vanadium in the lowest temperature.



Figure 5.11. The effect of temperature on vanadium oxidative leaching (at 1 g/L V₂O₃, $[Fe^{+3}]/[Fe^{+2}]=10$, 90 µm, pH 0, and 600 rpm)

The shrinking sphere model was applied to formulate the kinetics of leaching. Similar to oxygen leaching (section 5.1), the kinetics model using equations 4.8 and 4.9 was investigated. As can be seen in Figure 5.12, the shrinking sphere model based on chemical reaction control showed a suitable agreement with the experimental data. Activation energy of the reaction was then calculated as 38 kJ/mol using the Arrhenius equation in Figure 5.13.



Figure 5.12. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various temperature tests; (b) Plot of $(1 - (1 - X)^{\frac{2}{3}})$ versus time for various temperature test (at 70°C, 1 g/L V₂O₃, [Fe⁺³]/[Fe⁺²]=10, 90 µm, pH 0, and 600 rpm)



Figure 5.13. Arrhenius plot for activation energy calculation for oxidative leaching using a constant ferric-ferrous ratio

5.3.2 Effect of particle size

The effect of particle size on the vanadium trioxide oxidative leaching kinetics was studied using different initial particle sizes (Figure 5.14). Figure 5.15 represents the linear relation between the reaction rate and 1/d and provides support for the reaction control mechanism for the leaching.



Figure 5.14. The effect of particle size on the rate of vanadium oxidative leaching (at 1 g/L V₂O₃, [Fe⁺³]/[Fe⁺²]=10, 90 μm, pH 0, and 600 rpm)

5.3.3 Effect of ferric-ferrous ratio

To study the effect of the ferric-ferrous ratio on the kinetics of leaching, 1 g/L of V_2O_3 in sulfuric acid at pH 0 and 70°C was leached by ratio of Fe(III)/Fe(II) of 1, 10, 50, 100 and 300. About 0.1 g/L of ferric was added to the leaching tank and the target ferric/ferrous ratio was adjusted by adding the required ferrous using ferrous sulfate heptahydrate. The potential was recorded at values of 495, 563, 608, 631 and 669 mV versus Ag/AgCl electrode for ratio of 1, 10, 50, 100 and 300 ferric/ferrous respectively. The potential for each test was then controlled using an ORP electrode connected to the computer. Figure 5.15 represents the effect of the ferric-ferrous ratio on vanadium trioxide leaching. It was shown that by increasing the Fe(III)/Fe(II) ratio, the leaching kinetics increases significantly.



Figure 5.15. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various particle sizes; (b) The effect of particle size on the rate of dissolution of vanadium (at at 1 g/L V₂O₃, [Fe⁺³]/[Fe⁺²]=10, 90 µm, pH 0, and 600 rpm)



Figure 5.16. The effect of ferric/ferrous ratio on vanadium oxidative leaching (at 70°C, 1 g/L V₂O₃, 90 μ m, pH 0, and 600 rpm)

The shrinking rate of vanadium trioxide particles versus the ferric-ferrous ratio is depicted in Figure 5.17. The slope was regression fitted to a value of 0.47. This means that the oxidative leaching is of Type II, in which the shrinking rate is proportional to the square root of the Fe(III)/Fe(II) ratio in the solution.



Figure 5.17. (a) Plot of $(1 - (1 - X)^{\frac{1}{3}})$ versus time for various particle; (b) The vanadium dissolution rate dependence of ferric/ferrous ratio (at 70°C, 1 g/L V₂O₃, 90 µm, pH 0, and 600 rpm)

In addition, as shown in Figure 5.18, the effect of stirring speed on vanadium leaching was studied using 1 g/L of V₂O₃ in sulfuric acid at pH 0, 70°C, $[Fe^{+3}]/[Fe^{+2}]=10$ and a stirring speed of 500 to 700 rpm. Moreover, the effect of pH was investigated in Figure 5.19 by changing the pH from 0 to 1 at 70°C, $[Fe^{+3}]/[Fe^{+2}]=10$, 600 rpm and the same solid to liquid ratio. The leaching kinetics was shown to be independent of both stirring speed and the pH of the solution. This confirms that the oxidative leaching is under the chemical reaction rate control with an activation energy of about 38 kJ/mol. The oxidation of vanadium trioxide using ferric ions conforms to a Type II mechanism.



Figure 5.18. The effect of stirring speed on vanadium oxidative leaching (at 70°C, 1 g/L V_2O_3 , 90 μ m, and pH 0)



Figure 5.19. Effect of pH on vanadium oxidative leaching (at 70°C, 1 g/L V₂O₃, 90 μ m, and 600 rpm)

Therefore, based on the obtained data, the rate constant for the reaction can be calculated as below:

$$\frac{\partial d}{\partial t} = 12088 \times \exp(-\frac{4571}{T}) (\frac{C_{Fe(III)}}{C_{Fe(II)}})^{0.47}$$
(5.7)

Finally, the following kinetic equation was obtained for oxidative leaching of vanadium trioxide using the ferric-ferrous couple:

$$1 - X(t, d_{\circ}) = \left[1 - \frac{12088t}{d_{\circ}} \exp\left(-\frac{4571}{T}\right) \left(\frac{C_{Fe(II)}}{C_{Fe(II)}}\right)^{0.47}\right]^{3}$$
(5.8)

6 Solvent extraction

6.1 Extraction of vanadium (V) in the presence of iron (III)

6.1.1 Effect of pH value on selectivity

The extraction yield of vanadium (V) and iron (III) from the solution with phosphoric acid (D2EHPA), phosphonic acid (IONQUEST 801), phosphinic acid (CYANEX 272) and phosphine oxide extractant (CYANEX 923) (5% extractant (v/v) in SX-ORFOM 12) are shown in Figure 6.1 to Figure 6.2 respectively. All loading results were obtained after mixing aqueous and organic solution using a mechanical stirrer for 20 minute.



Figure 6.1. Extraction of V (V) and Fe (III) from sulfate solution as a function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-ORFOM12



Figure 6.2. Percentage of extraction of V (V) and Fe (III) from sulfate solution as a function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-ORFOM12

It can be seen that acidic phosphorus extractants had poor selectivity for V (V) over Fe (III). However, as was shown in Figure 6.2, CYANEX 923 may be a suitable extractant candidate for separation of vanadium from iron because CYANEX 923 cannot extract iron (III) from a sulfate solution. Since the extraction of Fe (III) by CYANEX 923 was very low based on aqueous solution analysis as a check, the loaded organic solution was also analyzed for mass balance confirmation.

6.1.2 Effect of contact time

The kinetics of vanadium extraction with CYANEX 923 was investigated by studying vanadium extraction versus time (Figure 6.3). The organic phase (40%, v/v) was made using CYANEX 923 and SX-ORFOM 12. The extraction was complete in approximately 10 minutes.



Figure 6.3. Effect of mixing time on the extraction yield of vanadium with 40% CYANEX 923 in SX-ORFOM 12 at pH 2

6.1.3 Vanadium (V) extraction mechanism using CYANEX 923

Considering the selectivity of CYANEX 923 compared with acidic phosphorus extractants, the effect of CYANEX 923 concentration on vanadium (V) extraction using 5%, 10%, 20%, and 40% of CYANEX 923 in SX-ORFOM12 was investigated. By assuming the average molecular weight of CYANEX 923 is 348 g/mol and the density is 880 kg/m³, the graph of log D versus log (TRPO¹) is depicted in Figure 6.4. The results show a linear slope and indicate the ratio of the extractant to the metal species at this pH value. At pH 0-2, one molecule of vanadium is extracted by approximately one molecule of CYANEX 923.

¹ [trialkylphosphine oxide (TRPO)] is used to represent the CYANEX 923 concentration. This is a simplification but is appropriate to test the mechanism of extraction.



Figure 6.4. Effect of CYANEX 923 concentration on vanadium extraction

In non-complexing acidic media (less than pH 2), the major species in aqueous solution of vanadium (V) is VO_2^+ (Olazabal et al., 1992; Pourbaix, 1949). Moreover, vanadium (concentration $\geq 10^{-5}$ molar) can form a complex (VO₂SO₄⁻) in sulfate media in the low pH range (Ivakin, 1966; Puigdomenech, 2004; Rakib and Durand, 1996). It was shown that vanadium can form VO₂SO₄⁻ and VO₂HSO₄ thermodynamically (Ivakin, 1966; Puigdomenech, 2004; Rakib and Durand, 1996). The equilibrium constant (Log β_1) for VO₂SO₄⁻ has been reported to be 0.97 (Ivakin, 1966) , 1.3 (Rakib and Durand, 1996), and 1.72 (Puigdomenech, 2004) in different reports and the equilibrium constant (Log β_1) of -0.136 was obtained for reaction VO₂HSO₄ in the solution. In addition, Rakib and Durand (Rakib and Durand, 1996) claimed that the assumed

species VO₂HSO₄ is totally dissociated behaving as a strong acid. Therefore, in a solution containing sulfate/bisulfate anions, a mono sulfate complex VO₂SO₄⁻ is a dominant complex in the approximate range of $1 \le pH \le 3$. Moreover, the peak position of this complex in Raman spectroscopy was specified in the solubility test (Figure 4.8). Therefore, considering the results in Figure 6.4 and the vanadium species, the extraction equilibrium of vanadium (V) with CYANEX 923 (TRPO: [trialkylphosphine oxide]) which is used as a candidate for CYANEX 923) is given by the following expressions, which may occur separately or simultaneously:

$$2VO_2^+ + SO_4^{-2} + 2\overline{TRPO} \to \overline{(VO_2)_2 SO_4(TRPO)_2}$$
(6.1)

Or

$$VO_2^+ + HSO_4^- + \overline{TRPO} \rightarrow \overline{(VO_2)HSO_4(TRPO)}$$
(6.2)

Or

$$VO_2SO_4^- + H^+ + TRPO \to VO_2HSO_4(TRPO)$$
(6.3)

Or

$$2VO_2SO_4^- + 2\overline{TRPO} \rightarrow \overline{(VO_2)_2SO_4(TRPO)_2} + SO_4^{-2}$$
(6.4)

The extraction equilibrium constant Kext is expressed respectively as follows:

$$K_{ext} = \frac{[(VO_2)_2 SO_4 (TRPO)_2]}{[VO_2^+]^2 [SO_4^{-2}] [\overline{TRPO}]^2}$$
(6.5)

Or

$$K_{ext} = \frac{[\overline{VO_2 HSO_4 TRPO}]}{[VO_2^+][HSO_4^-][\overline{TRPO}]}$$
(6.6)

Or

$$K_{ext} = \frac{[\overline{VO_2HSO_4TRPO}]}{[VO_2SO_4^-][H^+][\overline{TRPO}]}$$
(6.7)

Or

$$K_{ext} = \frac{\left[\overline{VO_2SO_4(TRPO)_2}\right]\left[SO_4^-\right]}{\left[VO_2SO_4^-\right]^2\left[\overline{TRPO}\right]^2}$$
(6.8)

To investigate the extraction mechanism, the effect of adding sodium sulfate on the extraction of vanadium with 5% CYANEX 923 was studied. Different solutions contained 1 g/L vanadium and 0.5, 1, and 2 molar sulfate concentrations at pH 1.5 were prepared. Vanadium extractions of 19.12, 8.35, and 1.78% were obtained respectively for 0.5, 1, and 2 molar sulfate in the solution. It is obvious that the extraction of vanadium decreases significantly by adding sodium sulfate in the solution.

It was shown that the extraction efficiency of vanadium using CYANEX 923 increases by increasing the pH while at the same time the amount of bisulfate in the solution decreases. It can then be concluded that reaction 6.2 cannot be correct for the system. Furthermore, it was revealed that by increasing the sulfate concentration, vanadium extraction decreases. Therefore, reaction 6.3 can also be excluded based on this observation. Hence, considering the suggested mechanisms, only reactions 6.1 and 6.4 can be considered. However, since the dominant species at pH 1.5 or 2 is a vanadium mono sulfate complex, as it was explained above, it can be said that reaction 6.4 is the most likely reaction in the system. Moreover, it can be seen from the reaction

6.4 that since sulfate is in the right side of the reaction, adding the sulfate in the system can shift the reaction to the left, which means the vanadium extraction should be decreased, consistent with the experimental results.

In order to confirm the extracted species, the ratio of vanadium to sulfur in the organic solution was analyzed after extraction. However, since CYANEX 923 tends to extract sulfuric acid in the solution as well (Wiśniewski et al., 1996), a blank test with only sulfuric acid extraction at pH 1.5 by CYANEX 923 was first performed. Vanadium solution was then extracted in a second test by CYANEX 923 at pH 1.5. Both organic solutions were then stripped with 2M sodium hydroxide. Vanadium and sulfur concentration in the strip solution was analyzed by ICP and the ratio of vanadium to sulfur after correction for the blank was calculated at 2.38. Although this value is a little above the ideal value of 2, this analysis can be taken as evidence to confirm that vanadium is extracted by reaction 6.4.

6.1.4 Stripping vanadium from CYANEX 923

The degree to which vanadium can be stripped from CYANEX 923 was studied using distilled water and sodium hydroxide solution. After the loading of vanadium by CYANEX 923 at pH 2, organic and aqueous solutions (A/O ratio of 1/1) have been shaken with a mechanical shaker for 20 minutes. This was found to be sufficient for equilibrium to be achieved. The aqueous phase was filtered for ICP analysis and the organic phase was filtered using the 1PS phase separation filter paper and advanced to the next batch stripping stage. The organic phase was stripped 5 times using fresh deionized water, 0.1 and 1N NaOH solution to make sure that all of the vanadium has been removed from the organic (Table 6.1). The results confirm that a range of dilute to concentrated solution of sodium hydroxide can be used effectively for the stripping of vanadium from CYANEX 923. Iron will form Fe(OH)₃ as a solid precipitate under high pH

conditions. In addition, VO_2^+ has low solubility in the mildly acidic pH region. However, mildly basic or highly basic strip solutions can change the cation to an anion such as decavandate $(V_{10}O_{28}^{-6}OH^-)$, metavanadate $(V_3O_9^{-3})$, and $(VO_3OH_2^-)$ at pH 5, 8, and more than 11, respectively. These anions have high solubility. As the following reactions illustrate, changing the pentavanadyl cation (VO_2^+) to anion species in the solution will release protons in the solution and hence decrease pH (Pourbaix, 1949; Puigdomenech, 2004):

$$10 \text{ VO}_2^+ + 8\text{H}_2\text{O} \rightarrow \text{V}_{10}\text{O}_{27}\text{OH}^- + 15\text{H}^+$$
 (6.9)

$$3 \text{ VO}_2^+ + 3 \text{H}_2 \text{O} \rightarrow \text{V}_3 \text{O}_9^{-3} + 6 \text{H}^+$$
 (6.10)

$$VO_2^+ 2H_2O \rightarrow VO_3OH_2^- 2H^+$$
 (6.11)

CYANEX 923 can extract sulfuric acid as well and sulfuric acid can also be stripped with sodium hydroxide solution (Wiśniewski et al., 1996). Therefore, the pH of the solution after water stripping decreases because of the changing vanadium species and sulfuric acid stripping. As shown in Table 6.1, water can also be applied to remove vanadium (V) from CYANEX 923 with less efficiency than sodium hydroxide solution. For water stripping, the pH was 2.85, 3.27, 3.68, 3.93, and 4.07, respectively for each stage of stripping at room temperature. It should be mentioned that for each stage of stripping, fresh water or sodium hydroxide solution was used.

Strip solution/Stripping Stage	1	2	3	4	5	Total (%)
Water	59.62	25.08	7.86	4.66	3.14	100.36
NaOH (0.1N)	79.65	10.11	6.52	2.35	2.11	100.74
NaOH (1N)	82.35	12.43	4.23	1.25	0.23	100.49

Table 6.1. Strip of vanadium (V) from the loaded solvent^a

^a The organic solvent was 40% CYANEX 923 in SX-ORFOM 12 at pH 2

6.1.5 Role of sulfate on vanadium (V) solvent extraction

As shown, sulfate has a significant effect on the extraction of vanadium (V) using CYANEX 923. It was shown that increasing sulfate increases the concentration of vanadium mono sulfate complex in the system which leads to increases in the vanadium species that tend to extract by CYANEX 923. However, since extraction of vanadium (V) using CYANEX 923 releases sulfate on the right side of the reaction, the extraction of vanadium (V) by the organic solvent is reduced by the increasing sulfate concentration due to Le Chatelier's principle. This means that sulfate concentration, on one hand, can increase loading because of promoting vanadium mono sulfate complex in the system; however, on the other hand, it can suppress the loading reaction due to the presence of sulfate on the right side of the reaction.

In addition, the effect of adding sulfate on vanadium (V) extraction using D2EHPA was studied as well. Different solutions contained 1 g/L vanadium and 0.5, 1, and 2 molar sulfate concentrations at pH 1.5 were prepared. Vanadium extraction was reported 79.45, 65.56 and 27.18%, respectively for 0.5, 1, and 2 molar sulfate in the solution. In fact, D2EHPA tends to extract VO_2^+ from the solution; however, adding sulfate decreases the free cation concentration in the solution and increases the $VO_2SO_4^-$ complex that leads to a decrease of the vanadium (V) extraction in the solution.

6.2 Extraction of vanadium (IV) in the presence of iron (III)

6.2.1 Effect of pH on selectivity

The effect of pH on selectivity of V (IV) over Fe (III) is illustrated in Figure 6.5 and Figure 6.6. As can be seen, none of the chosen extractants are selective for the extraction of V (IV) in the presence of Fe (III). CYANEX 923 is not able to extract V (IV) from a weakly-acidic sulfate solution.

6.3 Extraction of vanadium (IV) in the presence of iron (II)

6.3.1 Effect of pH on selectivity

Figure 6.7. Percentage of extraction of V (IV) and Fe (II) from sulfate solution as a function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-ORFOM12

and Figure 6.8 illustrate selectivity of V (IV) over Fe (II) using different extractants. It can be seen that CYANEX 272 and D2EHPA can extract vanadium (IV) over ferrous reliably. Moreover, it was shown that the distribution ratio (D) for D2EHPA is around 10.59 at pH 1.5 and 89.4% of vanadium was extracted by the solvent, while D was reported around 5.7 at pH 2 for CYANEX 272 where 78.9% of vanadium was extracted.



Figure 6.5. Percentage of extraction of V (IV) and Fe (III) from sulfate solution as a function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-ORFOM12



Figure 6.6. Percentage of extraction of V (IV) and Fe (III) from sulfate solution as a function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-ORFOM12



Figure 6.7. Percentage of extraction of V (IV) and Fe (II) from sulfate solution as a function of equilibrium pH with 5% D2EHPA & IONQUEST 801 dissolved in SX-ORFOM12



Figure 6.8. Percentage of extraction of V (IV) and Fe (II) from sulfate solution as a function of equilibrium pH with 5% CYANEX 272 & CYANEX 923 dissolved in SX-ORFOM12

6.3.2 Vanadium (IV) extraction mechanism using D2EHPA

Considering the selectivity of D2EHPA compared to other extractants, the stoichiometry of the extraction of vanadium (IV) using D2EHPA was studied. Generally, VO_2^+ is extracted by an organic acid HR according to a cationic exchange:

$$M^{+n} + (m+n)\overline{H_2R_2} \to \overline{MR_{2n}(HR)_{2m}} + 2nH^+$$
(6.12)

$$K_{ext} = \frac{[\overline{MR_{2n}(HR)_{2m}}][H^+]^{2n}}{[M^{+n}][\overline{H_2R_2}]^{m+n}}$$
(6.13)

in which the upper lined species are organic species.

Writing the apparent equilibrium constant K_{eq} under the logarithmic form and introducing the distribution coefficient D defined as:

$$D = \frac{[\overline{V}]}{[V]} = \frac{[\overline{VOR_{2n}(HR)_{2m}}]}{[VO^{+2}]}$$
(6.14)

Then:

$$Log D = Log K_{eq} + (n + m) Log [H_2R_2] + 2n pH$$
(6.15)

where m and n are constant and can be determined by slope analysis.

As shown in Figure 6.9, a straight line with a slope of 2 for Log D versus pH confirms the extraction of VO_2^+ in acidic media. The effect of D2EHPA concentration on vanadium (IV) extraction using 5%, 10%, 20% and 40% of D2EHPA in SX-ORFOM12 was also investigated. The molecular weight of D2EHPA is 322.48 g/mol, the density is 970 kg/m³ and the purity of
D2EHPA has been reported to be more than 96%. The graph of log D versus Log [D2EHPA] is demonstrated in Figure 6.10. The slope is 2 in equation 4.54 indicating m+n is 2 (Biswas and Mondal, 2003; Grosber-Manon, 2011).

Therefore, the equation 6.15 can be written as below:

$$VO^{+2} + 2\overline{H_2R_2} \to \overline{VOR_2(HR)_2} + 2H^+ \tag{6.16}$$

and the extraction equilibrium constant Kext is expressed as:

$$K_{ext} = \frac{[\overline{VOR_2(HR)_2}][H^+]^2}{[VO^{+2}]^2[\overline{H_2R_2}]^2}$$
(6.17)



Figure 6.9. Effect of pH on distribution coefficient (D2EHPA and vanadium (IV))



Figure 6.10. Effect of D2EHPA concentration on vanadium (IV) extraction

Moreover, the stripping of vanadium (IV) from D2EHPA using sulfuric acid was investigated. The procedure was the same as that used for the stripping from CYANEX 923. A fresh sulfuric acid strip solution was used for each contact stage. As Table 6.2 shows, sulfuric acid can strip vanadium (IV) effectively from D2EHPA.

Strip Solution/ Stripping Stage	1	2	3	Total (%)
H_2SO_4 (0.5M)	72.35	24.99	1.86	99.2
H ₂ SO ₄ (1M)	92.12	6.53	1.53	100.18
H ₂ SO ₄ (2M)	95.63	3.34	0.84	99.81

Table 6.2. Strip of Vanadium (IV) from the loaded solvent^a

^a The organic solvent was 40% D2EHPA in SX-ORFOM 12 at pH 1.5

7 Conclusions

and

recommendations for future work

7.1 Conclusions

As explained carefully, this research has been done to develop an understanding of vanadium behavior in leaching and solvent extractions. To cover that interest, this study has been completed in three different but relevant sections which are vanadium (V) and (III) leaching and vanadium (V) and (IV) solvent extraction:

1. <u>Vanadium (V) leaching</u>: This study has been done in three steps. First, it was found that V_2O_5 can be leached quickly in sulfuric acid. However, the pentavanadyl cation (VO_2^+) suffers from low solubility in solution. On the other hand, it was reported that the solubility can be raised by increasing the sulfate concentration in the solution.

Secondly, it was shown that V_2O_5 can be leached in water and mild sodium hydroxide solutions at a constant pH. At 90°C and pH 5, approximately all of V_2O_5 can be leached in less than 2 hours as a decavanadate. Whereas for pH 8 and maintained at the same temperature, 90°C, vanadium can be leached completely as a metavanadate after about an hour. It was found that temperature can significantly affect both the water and mild basic leaching.

Thirdly, it was observed that using reductive agents in an acidic pH range can increase leaching efficiency significantly. The kinetics of reductive leaching of vanadium pentoxide using sodium sulfite was then studied using a shrinking sphere model. It was shown that the reductive leaching is in a chemically-controlled regime with an activation energy of 33 kJ/mol. Finally, the following rate equation has been offered to predict the rate of vanadium reductive leaching:

$$\frac{dn_{V_2O_5}}{dt} = k^* [H^+]^{0.5} \left(\frac{[SO_2]_{total}}{1 + \frac{K_e}{[H^+]}} \right)^{0.5} = k^* \frac{[H^+]}{(K_e + [H^+])^{0.5}} [SO_2]_{total}^{0.57}$$

2. <u>Vanadium (III) leaching</u>: In this section, the kinetics of atmospheric oxidative leaching of vanadium trioxide were investigated in three steps. It was reported that leaching of V_2O_3 using oxygen is very slow and more than 90% of the vanadium was dissolved at pH 0, 90°C, and 10 hours by pumping 480 mL/min through the leaching process. It was claimed that the kinetics of vanadium (III) oxidative leaching using oxygen is chemically-controlled by the activation reaction of 69 kJ/mol. The effect of adding ferric on the leaching in the presence of oxygen was then studied. It was revealed that ferric can increase the rate of the leaching significantly so much so that vanadium is almost leached in 20 minutes at pH 0, 90°C, and 1.5 g/L ferric.

Finally, the kinetics of vanadium (III) leaching using constant ferric/ferrous ratio was investigated. It was observed that both temperature and ferric-ferrous ratio has a considerable effect on vanadium leaching. The kinetics study using mixed model revealed that the leaching rate is controlled by the reaction on the surface. An activation energy of 38 kJ/mol was reported for the reaction. The exponent of the Fe(III)/Fe(II) ratio was reported as 0.47 which is slightly less than the 0.5 that confirms Type II for the leaching.

3. <u>Vanadium solvent extraction</u>: In this part, it was shown that the phosphorus based extractants can be used to separate vanadium over iron selectively. The best separation of vanadium and iron using selected extractants were achieved when vanadium and iron species were either both reduced (vanadium (IV) and iron (II)) or both oxidized (vanadium (V) and iron (III)).

For vanadium (V), it was shown that acid extractants had poor selectivity for vanadium (V) over iron (III), however, CYANEX 923 as a solvating extractant showed an acceptable selectivity for vanadium (V) over iron (III). The molar ratio of CYANEX 923 and vanadium (V) in the extracted species was found to be approximately 1, which indicates the participation of one molecule of CYANEX 923 per molecule of vanadium (V) in the extracted species. In addition, it was shown that the stripping of vanadium (V) from CYANEX 923 can be accomplished by water, dilute or concentrate sodium hydroxide. Using sodium hydroxide as a stripping solution not only can increase selectivity of vanadium over iron but can also increase vanadium solubility in strip liquor.

For vanadium (IV), it was found that among selected organophosphorus reagents, D2EHPA showed a better selectivity for vanadium (IV) over iron (II). Stripping with sulfuric acid was effective. It was also found that two moles of D2EHPA were required per mole of the extracted vanadium (IV) species.

7.2 **Recommendations for future work**

This work formed a fundamental understanding for hydrometallurgy of vanadium. However, more studies have to be considered as a future research to complete this understanding and make it adopted into now progressing recovery of vanadium from various resources. To this end, the following investigations are recommended:

- ➤ Leaching:
- The experiment can be extended to study vanadium leaching from different resources contained in non-oxide vanadium materials. However, most of the resources can be fairly divided to vanadium (V) and vanadium (III) materials. Therefore, similar techniques from this study can be applied to investigate for a leaching study.
- This work may be extended to study the kinetics of atmospheric leaching of vanadium trioxide in basic pHs
- Oxidative leaching of vanadium (III) to form vanadium (V) species in the solution in different pHs can be considered as a potential future work
- This report may be completed by a kinetics study of vanadium (IV) oxidation to vanadium (V) using oxygen in an aqueous phase. This study not only can be used as a supportive research for direct leaching of vanadium (III) to get vanadium (V) species in the solution, but also may be applicable for a vanadium purification step when only vanadium (V) species are needed in the solution. Oxidation using other oxidizers such as H₂O₂ can also be investigated for the purification step

- Solvent Extraction:
- Using a mixture of different extractants as a synergic study can be considered for solvent extraction of vanadium by aiming to obtain higher selectivity of vanadium over some elements such as iron in acidic pHs
- Ion exchange technique can also be investigated as a potential future work for vanadium (IV) and vanadium (V). The extraction of different vanadium species using this technique is poorly studied. Therefore, this research may show other possible options for vanadium purification

This research has been focused on leaching and solvent extraction of vanadium and suggestions are then proposed around these two steps of the process. However, other parts of the process such as vanadium pentoxide precipitation or vanadium electrolyte production can be potentially considered as a future work. Deep understanding about each part of the vanadium process can help us to bring a more practical and feasible procedure to get the aimed vanadium product for any resource.

References

- Aarabi, M., Rashchi, F., Mostoufi, N. and Vahidi, E., 2010. Leaching of vanadium from LD converter slag using sulfuric acid. Hydrometallurgy, 102(1-4): 14-21.
- Abdel-latif, M.A., 2002. Recovery of vanadium and nickel from petroleum flyash. Minerals Engineering, 15 (11, Supplement 1): 953-961.
- Akita, S., Maeda, T. and Takeuchi, H., 1995. Recovery of vanadium and nickel in fly ash from heavy oil. John Wiley & Sons, 345-350.
- Akita, S., Maeda, T. and Takeuchi, H., 1995. Recovery of vanadium and nickel in fly ash from heavy oil. Journal of Chemical Technology & Biotechnology, 62(4): 345-350.
- Al-Ghouti, M.A., Al-Degs, Y.S., Ghrair, A., Khoury, H. and Ziedan, M., 2011. Extraction and separation of vanadium and nickel from fly ash produced in heavy fuel power plants. Chemical Engineering Journal, 173(1): 191-197.
- Alexander, J., 1929. Vanadium and some of its industrial applications. Harrison and sons.
- Amer, A.M., 1994. Hydrometallurgical processing of Egyptian black shale of the Quseir-Safaga region. Hydrometallurgy, 36(1): 95-107.
- Amer, A.M., 2002. Processing of Egyptian boiler-ash for extraction of vanadium and nickel.Waste Management, 22(5): 515-520.
- Bal, Y., Bal, K.E., Cote, G. and Lallam, A., 2004. Characterization of the solid third phases that precipitate from the organic solutions of Aliquat 336 after extraction of molybdenum(VI) and vanadium(V). Hydrometallurgy, 75(1-4): 123-134.
- Bard, A.J. and Faulkner, L.R., 2000. Electrochemical Methods: Fundamentals and Applications. Wiley, USA.

Barner, H.E. and Scheueman, R.V., 1978. Handbook of thermochemical data for compounds and aqueous species. John Wiley & Sons, USA.

Bibler, J.P., 1990. Ion exchange in the nuclear industry. Springer science.

- Biswas, R.K. and Mondal, M.G.K., 2003. Kinetics of VO²⁺ extraction by D2EHPA. Hydrometallurgy, 69(1-3): 117-133.
- Biswas, R.K., Wakihara, M. and Taniguchi, M., 1985. Recovery of vanadium and molybdenum from heavy oil desulphurization waste catalyst. Hydrometallurgy, 14(2): 219-230.
- Blizanac, B.B., Ross, P.N. and Markovic, N.M., 2007. Oxygen electroreduction on Ag: The pH effect. Electrochimica Acta, 52(6): 2264-2271.
- Bouffard, S.C., Rivera-Vasquez, B.F. and Dixon, D.G., 2006. Leaching kinetics and stoichiometry of pyrite oxidation from a pyrite–marcasite concentrate in acid ferric sulfate media. Hydrometallurgy, 84(3–4): 225-238.
- Butler, J.N., 1998. Ionic Equilibrium: Solubility and pH Calculations. A Wiley-Interscience publication, Canada.
- Cenni, R., Frandsen, F., Gerhardt, T., Spliethoff, H. and Hein, K.R.G., 1998. Study on trace metal partitioning in pulverized combustion of bituminous coal and dry sewage sludge.
 Waste Management, 18(6–8): 433-444.
- Chagnes, A., Rager, M.-N., Courtaud, B., Thiry, J. and Cote, G., 2010. Speciation of vanadium(V) extracted from acidic sulfate media by trioctylamine in n-dodecane modified with 1tridecanol. Hydrometallurgy, 104(1): 20-24.
- Chen, X., Lan, X., Zhang, Q., Ma, H. and Zhou, J., 2010. Leaching vanadium by high concentration sulfuric acid from stone coal. Transactions of Nonferrous Metals Society of China, 20(Supplement 1): s123-s126.

- Chen, Y., Feng, Q., Shao, Y., Zhang, G, Ou, L. and Lu, Y., 2006. Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst. International Journal of Mineral Processing, 79(1): 42-48.
- Choi, S.K., Lee, S., Song, Y.K. and Moon, H.S., 2002. Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound. Fuel, 81(8): 1083-1090.

Crouse, D.J., Brown, K.B., 1959. Solvent extraction recovery of vanadium and uranium nfrom acid liquors with DI(2-Ethylhexyl) phosphoric acid. Report by United States Atomic Energy Department.

- Das, B., Prakash, S., Reddy, P.S.R. and Misra, V.N., 2007. An overview of utilization of slag and sludge from steel industries. Resources, Conservation and Recycling, 50(1): 40-57.
- Deng, Z., Wei, C., Fan, G., Li. M., Li, C. and Li, X., 2010. Extracting vanadium from stone-coal by oxygen pressure acid leaching and solvent extraction. Transactions of Nonferrous Metals Society of China, 20(Supplement 1): s118-s122.
- El-Enein, S.A., Aassy. I.E., Rezk, A.A., Manaa, E.A. and Kassab, W.A., 2014. Uranium/vanadium separation from El-Shahu carnotite-bearing kaolin, south western Sinai Egypt. International Journal of Science Basic and Applied Research, ISSN 2307-4531.
- El-Nadi, Y.A., Awwad, N.S. and Nayl, A.A., 2009. A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst. International Journal of Mineral Processing, 92(3-4): 115-120.

- Evans J., H.T. and Garrels, R.M., 1958. Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. Geochimica et Cosmochimica Acta, 15(1–2): 131-149.
- Fernandez, A., Wendt, J., Wolski, N., Hein, K., Wang, S. and Witten, M., 2003. Inhalation health effects of fine particles from the co-combustion of coal and refuse derived fuel. Gemosphere, 51(10): 1129-1137.

Fischer, R., 1942. Vanadium deposits of Colorado and Utah. Report of United States Department of Strategic Minerals Investigation.

- Gavett, S.H., Madison, S., Dreher, K., Winsett, D., McGee, J. and Costa, D., 1997. Metal and sulfate composition of residual oil fly ash determines airway hyperreactivity and lung injury in rats. Environmental Research, 72(2): 162-172.
- Geyrhofer, W., Voglauer, B. and Joergl, H.P., 2003. Control of a roasting process for the recovery of vanadium, Control Applications, 2003. Proceedings of 2003 IEEE Conference, vol1, 614-617, Florida, USA.
- Giavarini, C., 1982. Recovery of vanadium from ash-leaching solutions by solvent extraction. Fuel, 61(6): 549-552.
- Gomez-Bueno, C., Spink, D. and Rempel, G., 1981. Extraction of vanadium from athabasca tar sands fly ash. Metallurgical and Materials Transactions B, 12(2): 341-352.
- Grosber-Manon, M., Stambouli, M., Gillet, J., Grossiord, J. and Pareau, D., 2011. Thermodynamic study of chloroquine extraction by organo-phosphorus and thiophosphorus acids, 19th International Solvent Extraction Conference, Santiago, Chile.

- Grzechowiak, J., Grysiewicz, W., Ostrowski, A., Radomyski, B. and Walendziewski, J., 1987.Recovery of aluminium, cobalt, iron and nickel from used catalysts containing metals of ferrous group and possibly molybdenum on alumina support. Polish Patent, No. 136713.
- Guibal, E., Guzman, J., Navarro, R. and Revilla, J., 2003. Vanadium extraction from fly ash: preliminary study of leaching, solvent Extraction, and sorption on Chitosan, Separation Science and Technology, 38, 2881-2899.
- Gupta, C. K. and Krishnamurphy, N., 1992. Extractive metallurgy of vanadium (Process Metallurgy). Elsevier Science, Netherland.
- Habashi, F., 1998. Handbook of extractive metallurgy. Wiley-VCH, Germany.
- Hammett, L.P. and Chapman, R.P., 1934. The solubilities of some organic oxygen compounds in sulfuric acid-water mixtures. Journal of the American Chemical Society, 56(6): 1282-1285.
- Holloway, P. and Etsell, T., 2004. Salt roasting of suncor oil sands fly ash. Metallurgical and Materials Transactions B, 35, 1051-1058.
- HSC, www.hsc-chemistry.net., Outokumpu.
- Hughes, M.A. and Biswas, R.K., 1991. The kinetics of vanadium (IV) extraction in the acidic sulphate-D2EHPA-n-hexane system using the rotating diffusion cell technique. Hydrometallurgy, 26(3): 281-297.
- Hukkanen, E. and Walden, H., 1985. The production of vanadium and steel from titanomagnetites. International Journal of Mineral Processing, 15(1–2): 89-102.
- Hurley, B., Qiu, S. and Buchheit, R.G., 2011. Raman spectroscopy characterization of aqueous vanadate species interaction with aluminum alloy 2024–T3 surfaces. Journal of the Electrochemical Society, 158, 125-131.

- Ipinmoroti, K.O. and Hughes, M.A., 1990. The mechanism of vanadium (IV) extraction in a chemical kinetic controlled regime. Hydrometallurgy, 24(2): 255-262.
- Ivakin, A.A., 1966. Complex ions quinquevalent vanadium with chloride and sulfate ions. Journal of applied chemistry 39(2): 252-258.
- Kametani, H. and Aoki, A., 1985. Effect of suspension potential on the oxidation rate of copper concentrate in a sulfuric acid solution. Metallurgical Transactions B, 16(4): 695-705.
- Kanamori, K., Sukurai, M., Kinoshita, T., Uyama, T., Ueki, T. and Michibata, H., 1999. Direct reduction from vanadium(V) to vanadium(IV) by NADPH in the presence of EDTA. A consideration of the reduction and accumulation of vanadium in the ascidian blood cells. Journal of Inorganic Biochemistry, 77(3–4): 157-161.
- Kar, B.B., 2005. Carbothermic reduction of hydro-refining spent catalyst to extract molybdenum. International Journal of Mineral Processing, 75(3–4): 249-253.
- Kar, B.B., Murthy, B.V.R. and Misra, V.N., 2005. Extraction of molybdenum from spent catalyst by salt-roasting. International Journal of Mineral Processing, 76(3): 143-147.
- Lan Yao-zhong, L.j., 2005. Review of vanadium processing in China. Engineer sciences, 3(3): 58-62.
- Lee, F.M., Knudsen, R.D. and Kidd, D.R., 1992. Reforming catalyst made from the metals recovered from spent atmospheric resid desulfurization catalyst. American Chemical Society, 31, 487-490.
- Levenspiel, O., 1999. Chemical reaction engineering. John wiley & Sons.
- Li, M., Wei, C., Fan, G., Li, C., Deng, Z. and Li. X.2009. Extraction of vanadium from black shale using pressure acid leaching. Hydrometallurgy, 98(3-4): 308-313.

- Li, M., Wei, C., Fan, G., Wu, H, Li, C. and Li., X. 2010a. Acid leaching of black shale for the extraction of vanadium. International Journal of Mineral Processing, 95(1-4): 62-67.
- Li, M., Fan, G., Li, C., Deng, Z. and Li. X.2010c. Pressure acid leaching of black shale for extraction of vanadium. Transactions of Nonferrous Metals Society of China, 20(Supplement 1): s112-s117.
- Li, M.T., Wei, C., Zhou, X., Deng, Z. and Li. X., 2012. Kinetics of vanadium leaching from black shale in non-oxidative conditions. Mineral Processing and Extractive Metallurgy, 121(1): 40-47.
- Li, X., Wei, C., Zhou, X., Deng, Z., Li, C., Li. X. and Fan, G., 2011. Selective solvent extraction of vanadium over iron from a stone coal/black shale acid leach solution by D2EHPA/TBP. Hydrometallurgy, 105(3-4): 359-363.
- Li, X.. and Xie, B., 2012. Extraction of vanadium from high calcium vanadium slag using direct roasting and soda leaching. International Journal of Minerals, Metallurgy, and Materials, 19(7): 595-601.
- Lozano, L.J. and Godínez, C., 2003. Comparative study of solvent extraction of vanadium from sulphate solutions by primene 81R and alamine 336. Minerals Engineering, 16(3): 291-294.
- Marafi, M. and Stanislaus, A., 2003. Options and processes for spent catalyst handling and utilization. Journal of Hazardous Materials, 101(2): 123-132.
- Meawad, A.S., Bojinova, D.Y. and Pelovski, Y.G., 2010. An overview of metals recovery from thermal power plant solid wastes. Waste Management, 30(12): 2548-2559.

- Mishra, D., Chaudhury, G.R., Kim, D.J. and Ahn, J.G., 2010. Recovery of metal values from spent petroleum catalyst using leaching-solvent extraction technique. Hydrometallurgy, 101(1-2): 35-40.
- Morgan, B. and Lahav, O., 2007. The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O₂ in aqueous solution basic principles and a simple heuristic description. Chemosphere, 68(11): 2080-2084.
- Moskalyk, R. R. and Alfantazi, A. M., 2003. Processing of vanadium: a review. Minerals Engineering, 16(9): 793-805.
- Navarro, R., Guzman, J., Saucedo, I., Revilla, J. and Guibal, E., 2007. Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. Waste Management, 27(3): 425-438.
- Nekovár, P. and Schrötterová, D., 2000. Extraction of V(V), Mo(VI) and W(VI) polynuclear species by primene JMT. Chemical Engineering Journal, 79(3): 229-233.
- Okuwaki, A., Kimura, A., Umetsu, Y., Tozawa, K. and Okabe, T., 1988. Extraction of vanadium from electrostatic precipitator ashes of oil power plants. American Chemical Society, 27(7), 1218-1222.
- Olazabal, M. A., Orive, M. M., Fernández, L.A. and Madariaga, J.M., 1992a. Selective extraction of vanadium (V) from solutions containing molybdenum (VI) by ammonium salts dissolved in toluene, Solvent Extraction and Ion Exchange, 10(4), 623-635.

Pourbaix, M., 1949. Thermodynamics of dilute aqueous solutions. E. Arnold, London.

Puigdomenech, I., 2004. Medusa software. KTH University, Sweden.

- Qiu, S., Wei, C., Li, M., Zhou, X., Li, C. and Deng Z., 2011. Dissolution kinetics of vanadium trioxide at high pressure in sodium hydroxide–oxygen systems. Hydrometallurgy, 105(3-4): 350-354.
- Querol, X., Fernandez, J. and Lopez, A., Trace elements in coal and their behavior during combustion in a large power station. Fuel, 74(3), 331-343.
- Querol, X., Moreno, N., Alastuey, A., Juan, R., Andrés, J. M., López-Soler, A., Ayora, C., Medinaceli, A. and Valero, A., Synthesis of high ion exchange zeolites from coal fly ash. Geologica Acta, 5(1): 49-57.
- Querol, X., Umana, J., Alastuey, A. 2001. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. Fuel, 80(6): 801-813.
- Radosevich, A.T., 2007. Application of rhenium and Vanadium-oxo complexes as catalysts in organic synthesis. Berkeley, USA.
- Rakib, M. and Durand, G., 1996. Study of complex formation of vanadium(V) with sulphate ions using a solvent extraction method. Hydrometallurgy, 43(1–3): 355-366.
- Robert J. Pritchard, A., James R. Lehmann, Darrell W. Winsett, Jeffrey S. Tepper, Patricia Park,
 M. Ian Gilmour, Kevin L. Dreher ,Daniel L. Costa, 1996. Oxidant generation and lung
 injury after particulate air pollutant exposure increase with the concentrations of
 associated metals. Inhalation Toxicology, 8(5): 457-477.
- Rohrmann, B., 1985. Vanadium in South Africa. Journal of the South African Institute of Mining and Metallurgy, 85, 141-150.
- Romanov, N.P., 2009. A new formula for saturated water steam pressure within the temperature range –25 to 220°C. Izvestiya, Atmospheric and Oceanic Physics, 45(6): 799-804.

- Rydberg, J., Cox, M., Musikas, C. and Choppin, G.R., 2004. Solvent extraction principles and practice, Revised and Expanded, 2 edition. CRC Press, USA.
- Shlewit, H. and Alibrahim, M., 2006. Extraction of sulfur and vanadium from petroleum coke by means of salt-roasting treatment. Fuel, 85(5-6): 878-880.
- Sun, D., Li, X., Brungs, M. and Trimm, D., 1998. Encapsulation of heavy metals on spent fluid catalytic cracking catalyst. Water Science and Technology, 38(4–5): 211-217.
- Sun, D.D., Tay, J.H., Cheong, H.K., Leung, D.L.K. and Qian, G., 2001. Recovery of heavy metals and stabilization of spent hydrotreating catalyst using a glass-ceramic matrix. Journal of Hazardous Materials, 87(1–3): 213-223.
- Tavakoli, M.R., Yoozbashizadeh, H. and Halali, M., 2010. The effect of leaching parameters on vanadium recovery from oil residue. Canadian institute of mining and metallurgy, 355-362, Vancouver, Canada.
- Tomikawa, K. and Kanno, H., 1998. Raman study of sulfuric acid at low temperatures. The Journal of Physical Chemistry A, 102(30): 6082-6088.
- Tracey, A.S. and Crans, D.C., 1998. Vanadium compounds: chemistry, biochemistry, and therapeutic applications. American Chemical Society, USA.
- Tracey, A.S., Willsky, G.R. and Takeuchi, E.S., 2007. Vanadium: chemistry, biochemistry, pharmacology and practical applications. CRC Press, USA.
- Tromans, D., 1998. Oxygen solubility modeling in inorganic solutions: concentration, temperature and pressure effects. Hydrometallurgy, 50(3): 279-296.
- Tromans, D., 2001. Modelling oxygen solubility in bleaching solutions. The Canadian Journal of Chemical Engineering, 79(1): 156-160.

- Tsai, S. and Tsai, M., 1998. A study of the extraction of vanadium and nickel in oil-fired fly ash. Resources, Conservation and Recycling, 22(3-4): 163-176.
- Veranth, J.M. et al., 2000. Coal fly ash and mineral dust for toxicology and particle characterization studies: equipment and methods for PM2.5 and PM1 enriched samples. Aerosol Science and Technology, 32(2): 127-141.
- Villarreal, M.S., Kharisov, B.I., Torres-Martínez, L.M. and Elizondo, V.N., 1999. Recovery of vanadium and molybdenum from spent petroleum catalyst of PEMEX. American Chemical Society, 38(12), 4624-4628.
- Vitolo, S., Seggiani, M. and Falaschi, F., 2001. Recovery of vanadium from a previously burned heavy oil fly ash. Hydrometallurgy, 62(3): 145-150.
- Vitolo, S., Seggiani, M., Filippi, S. and Brocchini, C., 2000. Recovery of vanadium from heavy oil and Orimulsion fly ashes. Hydrometallurgy, 57(2): 141-149.
- Wang-xing, L., Zhuo, Z., Zhao-hui, S.U., Xiao-bin, L. and Qing-jie, Z., 2010. Leaching kinetics of calcium vanadate by Na₂CO₃ solution. Journal of Process Engineering, 10(3): 548-553.
- Wexler, A., 1976. Vapor pressure formulation for water in range 0 to 100°C: a revision. Journal of Research of NIST, 80A: 775-785.
- Wiewiorowski, E.I., Tinnin, L.R. and Crnojevich, R., 1986. Cyclic process for recovering metal values and alumina from spent catalysts. US Patent. No.4670229.
- Wiśniewski, M., Bogacki, M.B. and Szymanowski, J., 1996. Extraction of sulphuric acid from technological solution of hydroxylamine sulphate. Journal of Radioanalytical and Nuclear Chemistry, 208(1): 195-206.

www.infomine.com.

www.minerals.usgs.gov.

- Xiao, Q., Chen, Y., Gao, Y., Xu, H. and Zhang, Y., 2010. Leaching of silica from vanadiumbearing steel slag in sodium hydroxide solution. Hydrometallurgy, 104(2): 216-221.
- Yang, Z. and Gould, E.S., 2003. Reactions of vanadium(iv) and (v) with s2 metal-ion reducing centers. Dalton Transactions, 20: 3963-3967.
- Yasuhara, H., 1982. Treatment of waste desulphurisation catalyst. Japanese Patent.
- Zeng, L. and 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.
- Zeng, L. and Cheng, C.Y., 2010. Recovery of molybdenum and vanadium from synthetic sulphuric acid leach solutions of spent hydrodesulphurisation catalysts using solvent extraction. Hydrometallurgy, 101(3-4): 141-147.
- Zeng, L. and Yong Cheng, C., 2009. A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts: Part II: Separation and purification. Hydrometallurgy, 98(1-2): 10-20.
- Zhang, P., Inoue, K. and Tsuyama, H., 1995. Recovery of metal values from spent hydrodesulfurization catalysts by liquid-liquid extraction. Energy & Fuels, 9(2): 231-239.
- Zhang, P., Inoue, K., Yoshizuka, K. and Tsuyama, H., 1996. Extraction and selective stripping of molybdenum (VI) and vanadium (IV) from sulfuric acid solution containing aluminum (III), cobalt (II), nickel (II) and iron (III) by LIX 63 in Exxsol D80. Hydrometallurgy, 41(1): 45-53.
- Zhang, Y., Hu, Y. and Bao, S., 2012. Vanadium emission during roasting of vanadium-bearing stone coal in chlorine. Minerals Engineering, 30: 95-98.

- Zheng, C.Q., Allen, C.C. and Bautista, R.G., 1986. Kinetic study of the oxidation of pyrite in aqueous ferric sulfate. Industrial & Engineering Chemistry Process Design and Development, 25(1): 308-317.
- Zhou, X., Wei, C., Xia, W., Li, M., Li, C., Deng, Z. and Xu, H. 2012. Dissolution kinetics and thermodynamic analysis of vanadium trioxide during pressure oxidation. Rare Metals, 31(3): 296-302.
- Zhu, Y., Zhang, G., Feng, Q., Lu, Y., Ou. L., Huang, S., 2010. Acid leaching of vanadium from roasted residue of stone coal. Transactions of Nonferrous Metals Society of China, 20, Supplement 1(0): s107-s111.