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Leaching of Vanadium from a Vanadium bearing slag using organic acids

by

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(201608977)

A Master’s Research dissertation submitted in fulfilment of the requirements for the degree of

MAGISTER TECHNOLOGIAE
in
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in the
Faculty of Engineering and the Built Environment
at the
UNIVERSITY OF JOHANNESBURG

Supervisor: Dr Willie Nheta
Co-Supervisor: Mr Petrus Van Staden
31 May 2018
Dedication

I dedicate this dissertation to my dear parents Armand Ntita and Clarisse Ntumba. I trust that this achievement will accomplish the dream you had for me all those numerous years when you gave me the best education you could.
Declaration

I Joelle Ntita K. hereby declare that this master’s research dissertation is wholly my own work and has not been submitted anywhere else for academic credit either by myself or another person. I understand what plagiarism implies and declare that this proposal is my own ideas, words, phrase, arguments, graphics, figures, results and organisation except where reference is explicitly made to another’s work. I understand further that any unethical academic behaviour, which includes plagiarism, is seen in a serious light by the University of Johannesburg and is punishable by disciplinary action.

Signed………………….. Date…………………..
Acknowledgement

I wish to acknowledge God the almighty, my heavenly father for the breath of life and his grace in all the domain.

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And finally, my mom and dad, my foundation, whom without unconditional support and love I could not stand where I am standing today. This dissertation is dedicated to them.
# List of papers

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Abstract

The bioleaching of Vanadium (V) from a V bearing slag with microorganisms such as *Pseudomonas putida* or *Aspergellius niger* was mimicked using commercial organic acids and a slag roasted in the presence of Na$_2$CO$_3$. A slag sample received from a steel making plant based in the North-West province of South Africa, was characterised using X-Ray Fluorescence (XRF), X-Ray diffraction (XRD) and Scanning Electron Microscope / Energy Dispersive X-Ray (SEM/EDX) in order to access the chemical composition, the mineralogy and surface morphology. The results revealed the presence of V in the form of indissoluble Vanadium oxide at a grade of 4.58% wt. To convert the Vanadium oxide into a soluble sodium vanadate, the slag sample was submitted to a sodium carbonate roasting process at various ratios and roasting temperatures in order to optimise the roasting process.

XRD analysis of the slag roasted at lower temperature (800ºC) revealed a slight change of V-oxide phase into sodium vanadate. The middle roasting temperature (900ºC) showed a high modification of V-oxide phase into soluble sodium vanadate with appearance of impurities soluble phase such as sodium aluminate. Roasting at higher temperature (1000ºC) revealed a higher formation of soluble sodium vanadate and soluble impurity phase (sodium aluminate). The ratio of sodium vanadate was important due to the fact that lower ratios of sodium carbonate did allow lower sodium vanadate formation compared to higher ratios.

The leaching tests were done on the slag roasted in different conditions of temperature (800, 900 and 1000ºC) and Na$_2$CO$_3$ ratio (10, 20, 30 and 40 % wt) using 50mM of commercial organic acids (Gluconic, Citric, Oxalic and Mixture of the three acids) to confirm the leachability of the roasted slag compared to the raw slag. Gluconic acid was the most effective in leaching of V followed by Citric, Oxalic and mixed acids. The optimum conditions for roasting the slag were found to be 900ºC and 20% wt. Na$_2$CO$_3$. These conditions were used to prepare all the roasted slag used in the succeeding leaching experiments. The SEM/EDX of the selected roasted slag revealed the presence of V and Na scattered throughout the slag matrix confirming the presence of the soluble sodium vanadate phase.

The roasted slag was leached using a mixture of Gluconic, Citric and Oxalic acid in the growing conditions of the microorganisms considered. Effect of different parameters such as acid concentration, solid-liquid ratio, particle size and temperature were investigated. It was found that the enhancement of the acid concentration has a positive effect on the V leaching
with the highest dissolution occurring at 200mM. High solid-liquid ratio gives a low V dissolution while the lower solid-liquid ratio used showed higher V dissolution. Smaller particle sizes gave good V dissolution while higher temperatures increased the dissolution. Leaching with the mixed organic acids in the optimum conditions gave a V dissolution of 78% with an Al co-leaching around 66%.

Kinetics of the leaching process was studied and it was found that the V leaching process was an intermediate between a diffusion and a chemically controlled reaction with an activation energy of 34 kJ/mol during the first ten minutes of the leaching process. After 10 minutes, the dissolution was a diffusion controlled reaction with an activation energy of 13kJ/mol.

The roasted slag was then leached with individual organic acids in order to assess the V dissolution for each acid. The findings showed that Gluconic acid gave the highest V dissolution under the optimum conditions of 150mM, 2% (S/L), -38µm (particle size) and 45ºC, followed by Citric acid and then Oxalic acid at a concentration of 100mM, 2% (S/L), -38µm (particle size) and 45ºC. Dissolution was found to be 90, 88 and 80% for Gluconic, Citric and Oxalic acid respectively.

The main impurity (Al) was considerably co-leached at an average of 60%, 72% and 73% for Gluconic, Citric and Oxalic acid respectively.
List of abbreviations

Al: Aluminium
Cit: Citric acid
EDX: Energy Dispersive X-Ray
ENDOR: Electron Nuclear Double Resonance
EPR: Electron Paramagnetic Resonance
ESEEM: Electron Spin Echo Envelope Modulation
Fe: Iron
FeV: Ferrovanadium
Gl: Gluconic acid
Na: Sodium
Ox: Oxalic acid
Pb: Lead
SCM: Shrinking Core Model
SCP: Shrinking Core Particle
SEM: Scanning Electron Microscope
Ti: Titanium
U: Uranium
V: Vanadium
XRD: X-Ray diffraction
XRF: X-Ray Fluorescence
Zn: Zinc
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Chapter 1: INTRODUCTION

Demand for metals never cease to increase. The valorisation of resources formerly considered not very useful is now of growing economic interest. These resources can be old mining waste deposits containing large quantities of residual metals or low-grade ores with a complex composition comprising different metals and/or including a high level of impurities. Moreover, these metals are often found in the form of sulphide compounds of which the treatment is technically complex and capital intensive (Anne-Gwénaëlle, et al., 2015)

One of the most frequently used methods to treat sulphide minerals after concentration by physicochemical treatment processes is pyrometallurgy. This process generally consists of thermal treatment of the sulphide concentrates using drying, oxidative roasting, smelting, converting and fire refining. These processes are not very effective for the treatment of ores containing a high level of carbonate and they involve the emission of gases which are hazardous to the environment. Apart from that, they are energy intensive (Kulczycka, et al., 2015). Compared to pyrometallurgy, the hydrometallurgical processes generally require a low investment and are particularly suitable for the treatment of metal resources having a complex composition and/or of low content in the metal of interest. Amongst the hydrometallurgical processes is biohydrometallurgy, which is generally very satisfactory from an environmental point of view. It involves extraction of the metals using microorganisms. This process makes the treatment of mining waste as well as low grade sulphide minerals possible (Bosecker, 1997).

The dissolution process of sulphide minerals using microorganisms forms the basis of the bioleaching process used in biohydrometallurgy. These microorganisms draw necessary energy for their metabolism from the oxidation reactions of iron and sulphur in a very acidic medium. These are the major components of sulphide ores that contain large quantities of metals of great economic value. Therefore, bioleaching allows to use the metabolic capacity of certain microorganisms. These microorganisms include various species such as bacteria and fungi are used to leach and mobilize metals from solid materials. Renowned species are the *Thiobacilli* genus, and acidophilic species such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* are used more for the leaching of sulphide minerals. More species such as *Aspergillus* and *Penicillium* have also been used successfully to recover metals from solid waste (Ewart & Hughes, 1991).
Bioleaching of oxide minerals occurs mostly with the use of fungal species. The process happens through the four known mechanisms which are acidolysis, complexolysis, redoxolysis and bioaccumulation. Acidolysis (known as the most significant mechanism) is a mechanism in which metals are dissolved by organic acids produced by the microorganisms. Formation of metal complexes of excreted organic acids and amino acids occurs during the complexolysis. Redoxolysis is mostly known as the mechanism where the metal is reduced by the mediation of organic acids while in the bioaccumulation, the metal is sunk in the microorganism mycelium (Rasoulnia, et al., 2016).

Due to its excellent properties such as fatigue resistance, high tensile strength and hardness, Vanadium (V) is a strategic metal widely used to produce alloy in many industrial applications. These include production of special tubes and pipes for the chemical industry, airframes in the aerospace industry and reinforcement steel in the construction industry.

Reinforcement of environmental regulations has urged mines to utilize waste material as another source of V. This decreases hazards caused by waste material disposal and simultaneously generate revenue. Steelmaking operations produce various types of waste materials of which V-bearing slag is one of them. Extensive studies have been devoted to the recovery of V from V-bearing slags. Potential promising methods include roasting with Na₂CO₃ followed by leaching (Li & Xie, 2012), oxidation of a molten V slag with pure oxygen in the presence of Lime (Song, et al., 2014) and high pressure oxidative acid leaching (Zhang, et al., 2015). However, the high operational temperatures coupled with release of hazardous gases in the atmosphere have hindered the application of these processes at a larger scale.

In recent works, bioleaching has proven to be efficient in the recovery of V from V-bearing slags. Since vanadium oxide in slag is not easily leachable, roasting in the presence of a sodium salt is the usual process used to covert the vanadium oxide phase into a soluble sodium vanadate prior to leaching. The roasting process is generally carried out in a furnace in the presence of oxygen or air in temperature ranges of 800 to 1000°C depending on the composition of the slag (Lui, et al., 2016).

Microorganisms such as *Pseudomonas putida* (heterotrophic bacteria) and *Aspergillus niger* (fungi) have also been used to recover V from V-bearing slags. These microorganisms produce organic acids such as Gluconic, Citric and Oxalic which act as leaching agents for the metal. These acids concentration can range from 50 to 500mM as demonstrated by many researchers such as (Mirazimi, et al., 2015) who were therefore able to reach vanadium recoveries of around 90%. The process is however prolonged because of the need of adaptation of the microorganisms to dilute the toxicity of the metals on them.
1.1 Research problem statement

Pyrometallurgical processing of ore produces slag as a waste product. Millions tonnes of slag are produced each year all over the world (Piatak & Seal, 2015), thereby driving the attention of many researchers due to the fast increase in their volumes. The characteristics and chemical composition of the slag depends on the ore, fluxes and metallurgical procedure from which it was generated. Depending on the slag composition, heavy elements are released into the environment and are found in water bodies and the soil. Every type of slag contains a component that might be environmentally hazardous although ferrous slags are generally less hazardous than the non-ferrous slags. Nevertheless, the chemical composition does not determine the amount of the elements released to the environment. Studies have proven that non-ferrous slag produces a metal-rich leachate which will eventually become acidic (due to sulphides oxidation) compared to ferrous slag which produce an alkaline leachate (Mohanty, et al., 2018).

Vanadium compounds are not considered as dangerous at lower concentrations but can cause bronchitis and pneumonia (when ingest from the air) at high concentrations. Exposure to vanadium pentoxide is more hazardous than to the elemental V. Effects such as irritation of lungs, throat, eyes and nasal cavities, cardiac and vascular disease, damage to the nervous system, bleeding of livers and kidneys are noticed while exposed to the vanadium pentoxide.

Huge quantities of V-bearing slags are produced in South Africa every year during the production of ferrovanadium (FeV) steel. Figure 1.1 shows a typical flowsheet of FeV production process.
The V production facilities at a steel making plant, North West province, South Africa, comprise conventional vanadium pentoxide ($V_2O_5$) and FeV plants. Run-of-mine ore is crushed and sent to a closed circuit of a grinding mill fitted with a pebble crusher running in circuit with cyclones. After separation of the magnetite from the non-magnetic material, regrinding occurs in a ball mill and a second stage of magnetic separation. The magnetic concentrate is then mixed with sodium carbonate before roasting in a coal-fired kiln. The obtained calcine is leached to obtain the vanadium bearing solution. After a solid-liquid separation, the vanadium bearing solution is submitted to a desilication process using aluminium sulphate followed by a filtration. Ammonium sulphate is then added to the pregnant solution to precipitate the ammonium metavanadate. The electric kilns are further used to drive off ammonia which will be melted from the $V_2O_5$ flakes. The ferrovanadium process is then fed using the previous $V_2O_5$ flakes which react with Al, Fe and lime and produce the FeV and an Al slag containing V. Currently this V-bearing slags are piled up and there is need to come up with a technology to recover the V that is environmentally friendly and cost effective.
1.2 Research aim and objectives

The main aim of this dissertation is to contribute to the ongoing studies on the recovery of V from V-bearing slags using organic acids.

The specific project objectives are to:

- Perform chemical, mineralogical and morphological analysis of a V-bearing slag and identify the chemical composition, mineral phases and morphology of the slag and ascertain the appropriate leaching method;
- Perform an alkaline roasting of the slag and convert the insoluble calcium vanadate phase into a soluble sodium vanadate phase and assess formation of any other new phases that might affect dissolution of V;
- Conduct leaching experiments using commercial organic acids (Gluconic, Citric and Oxalic) on roasted V-bearing slag using acid concentrations as those produced by microorganism and same leaching conditions as in bioleaching;
- Determine the kinetics of the leaching process while using the mixture of the three acids as in bioleaching.

1.3 Research questions

The research questions for this study were:

What is the impact of roasting on the dissolution process of V from a V-bearing slag?

Is it possible to leach the V from slag using commercial organic acids?

What is the kinetics and mechanism controlling the leaching process?

To what extent can each acid leach the vanadium?

1.4 Research Motivation

Vanadium, a silvery-grey metal which is used as an alloying element in most steels, in the manufacturing process of FeV (an alloy of V and Fe), and its compounds are used in catalysts and chemicals... South Africa is counted among the three biggest producers of V in the world with a V reserve of 3.5 million MT. The distribution of minable vanadium reserves worldwide is shown on the Figure 1.2.
China has the highest minable reserve of V (5100 kt) followed by Russian Federation (5000 kt) then South Africa (35000 kt) and other countries including Australia (376 kt). In 2016, about more than 168 kt of the metal in a form of $\text{V}_2\text{O}_5$ was estimated as the world resource (Mejia & Smith, 2016). These resources are not really considered as an indicative of available provision of the V because it is generally extracted as a by-product. The production of V worldwide is shown in Figure 1.3.
Figure 1.3: V production worldwide (Kelley, et al., 2017)

China is known as the highest producer of V and likewise a huge customer of the metal. Russian Federation is third on the list after South Africa and reached a V production of 16000 MT in 2016 (Luis & Mark, 2016). Steelmaking slags and mine ores are the main sources of world’s V supply. Materials such as spent catalysts or residues from the production of alumina are the other sources of V world supply.

Large Vanadium losses to the slag occur due to incomplete reaction of V oxidation. As a result of large amount of slags produced each year by the steel making industry, the motivation behind this study is to find a process that can recover the considerable amount of V lost in the slags. Bioleaching is a clean and environmentally friendly method used to recover metals from their occurrences. Parameters such as acid concentration, solid/liquid ratio, particle size and temperature have considerable impact on the efficiency of V leaching. A good understanding of the leaching kinetics and study of the leaching mechanisms is necessary to fully understand the leaching behaviour of V-bearing slags using microorganism.

1.5 Significance of the study

The dissertation presents the extraction of V from a V-bearing slag using organic acids mimicking a bioleaching process. The findings of this project added to the body of knowledge on the leaching behaviour of V from slag using microorganism. Apart from that, recovery of
V from slag has an advantage of reducing tailing dumps and environmental impact of waste. At the same time, job opportunities are created.

1.6 Research Methodology

The leaching behaviour of V from a V-bearing slag with micro-organisms such as Pseudomonas putida or Aspergillus niger in their growing temperature range (25ºC) and higher temperatures (35-45ºC) was investigated by using a mixture of commercial organic acids such as Gluconic, Citric and Oxalic acid in the concentration produced by the microorganisms.

The slag sample was collected from a steelmaking plant in the North West Province, South Africa. The facilities comprise of a conventional vanadium pentoxide (V₂O₅) and (FeV) plants. An alumina slag containing V is produced during the production of FeV.

After reception of the slag sample, the sample preparation was done in the Mineral Processing Laboratory while the slag characterisation, the leaching experiments and analysis of the leachate were done in the Analytical Laboratory at the University of Johannesburg.

The V-bearing slag was roasted in the presence of sodium carbonate and the calcine (roasted slag) was leached using Gluconic, Citric, Oxalic and a mixture of the three organic acids using concentrations similar to those produced by microorganisms. Study on the influence of parameters such as acid concentration, solid-liquid ratio, particle size and temperature was done to determine the impact of each parameter on the leaching process. The leaching data were fitted to the shrinking core model to study the leaching kinetics and understand the controlling mechanisms of the mixed acid leaching.

1.7 Delimitation

The limitations of bioleaching process being the long period of time required for the growth of microorganisms (up to 21 days) and their adaptation on the slag, this study was conducted using commercial organic acids in the microorganism’s growth conditions and concentrations. These microorganisms are mesophilic with a growing temperature ranging from 25 to 45°C. Gluconic, Citric and Oxalic acids in the concentrations ranging from 50mM to 200mM were used.

1.8 Dissertation layout

This dissertation comprises of 5 chapters. Chapter 1 presents the research problem statement, the research questions, the aim and objectives of the project, the research motivation,
the significance of the study, the methodology used, the delimitation of the research project and the dissertation layout. Chapter 2 provides the literature review on V production methods, V recovery from slags with more focus on the bioleaching process of V-bearing slags. The literature review also explores some previous work done by various authors on different V recovery routes. Chapter 3 describes the experimental methods used which include characterisation of the V-bearing slag, alkaline roasting of the slag and leaching of the slag using organic acids. Chapter 4 presents and discusses characterisation of the slag samples, roasting and leaching results, determination of the leaching kinetics and the dissolution behaviour of V in individual organic acid. Chapter 5 reflects on the conclusions drawn from the research and recommendations. References are on Section 6 and the Appendices is reflected on Section 7.
Chapter 2: LITERATURE REVIEW

2.0 Introduction

Parameters such as flux additions, tapping procedures, temperature control, raw material handlings influence the V recovery in the electro-aluminothermic process. Due to entrainment of considerable amount of V in the slag and reinforcement of environmental regulations, it is essential to recover the V from the slag using economic routes. Different species of microbial and bacterial systems have been used over the years for the recovery of metals in general and particularly V from its occurrences (ores, slags and spent catalysts) proving that bioleaching is an efficient technology for recovering of V from slag. The objectives of this chapter are to give an overview on the occurrence and production of V and ferrovanadium, losses of V in the slags, recovery of V from the slags using conventional methods, bioleaching method, leaching mechanisms and kinetics.

2.1 Occurrence of V

The major V ores are patronite (VS₄), vanadinite (Pb₂(VO₄)₂Cl), and carnotite (K₂(UO₂)₂(VO₄)·3H₂O) (Hammond, 2013). Magnetite ores also contain high percentages of V. V–Ti magnetite ore is one of the principal raw material for the extraction of V (Song, et al., 2014).

The main V minerals in South Africa are ulvospinel Fe(V)₂TiO₄ found in the Limpopo Mpumalanga and North-West Province and Ilmenite Fe(V)TiO₃ which is found in the Northern Cape Province (Rohrmann, 1985).

2.1.1 Physical properties of V

V metal is a grey soft and ductile metal that can change its properties to hard and brittle in the presence of impurities such as C, H, O, and N (Bradford, 1961). The main physical properties of V are given in Table 2.1.
Table 2.1: Physical properties of V (Tirado L, et al., 2007)

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
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<tr>
<td>Density</td>
<td>g/cm³</td>
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</tr>
<tr>
<td>Melting point</td>
<td>°C</td>
<td>1900 ± 25</td>
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<tr>
<td>Boiling point</td>
<td>°C</td>
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<td>Hardness</td>
<td>Mohr's scale</td>
<td>7.5</td>
</tr>
<tr>
<td>Refractive index</td>
<td>yellow light of λ = 5790</td>
<td>3.03</td>
</tr>
<tr>
<td>Coefficient of absorption</td>
<td>yellow light of λ = 5790</td>
<td>3.51</td>
</tr>
<tr>
<td>Reflexion capacity</td>
<td>yellow light of λ = 5790</td>
<td>57.5</td>
</tr>
</tbody>
</table>

2.1.2 Chemical properties of V

V is found in four valences (II, III, IV, and V) and forms different oxides such as V₂O₅ (red to orange and the most valuable commercially), V₂O₃ (blue-black), V₂O₅ (brownish black), VO (grey metallic powder) and the following series of vanadates: orthovanadates M₃VO₄, pyrovanadates M₃V₂O₇ and metavanadates MVO₃ (With M: Metal). The main chemical properties of V are given in Table 2.2.

Table 2.2: Chemical properties of V (Baranov & Fortunatov, 2012)

<table>
<thead>
<tr>
<th>Chemical Symbol</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>23</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>50.942</td>
</tr>
<tr>
<td>Chemical group</td>
<td>Vb</td>
</tr>
<tr>
<td>Electron in subsequent shell</td>
<td>2 8 11 2</td>
</tr>
</tbody>
</table>
2.2 Extraction metallurgy of V

V can be recovered as a vanadium pentoxide (V₂O₅) by leaching of the ore prior to an alkaline roasting or as a by-product (V contained in a slag: V-slag containing V₂O₅) from the iron or steel manufacture (Amirhossein, et al., 2012). V is not used in its elemental state in industry but as an alloying element to improve the quality of steel alloys. Most of the V ores exploited are nearly low grade (<2% V₂O₅) and are generally exploited for the recovery of V as a by-product of iron, uranium, lead or phosphorous industry or used in the preparation of steel (Beolchini, et al., 2009).

The magnetite ore bearing V minerals can undergo a concentration process after which V is recovered in the concentrate with a small amount of Ti. However, Ti is generally so intergrown with V in the magnetite ore that it is impossible to remove the Ti or to make any significant up-grading of the V by physical beneficiation methods. The only way to recover V is therefore, by smelting the ore and recovery of V as (V₂O₅) in the resulting slag to be fed to the conventional salt-roast and leach process to obtain high purity V pentoxide (Roschin & Roschin, 2007).

2.2.1 V extraction processes in South Africa

EVRAZ Highveld has innovated a method to recover V either as a vanadium pentoxide or a slag bearing vanadium depending on the occurrence of the ore. This method is well-known and the most applied in South Africa and is shown in Figures 2.1 and 2.2. The process in Figure 1.1 is a pyrometallurgy-based process extraction of V from titaniferous magnetite ore.
Titaniferous magnetite ores are processed as follows:

**Concentration processes**

Concentration processes consist of crushing, milling and an eventual magnetic separation or flotation of the ore to produce a concentrate product.

**Pre-reduction process**

The concentrate is then submitted to a pre-reduction process in the presence of coal, dolomite and quartz at 1140°C in a fluo-solid furnace. This heating process saves energy during smelting process.

**Smelting process**

The smelting process takes place in an arc furnace. Carbon is added as a combustible and reduction agent. Two products are formed: Molten pig iron and Slag. The molten pig iron is essentially composed of elements such as C, V, Si, Ti, S, P and the slag is constituted with titanium oxides.
Conversion

The molten pig iron is oxidized in a furnace under pressure and agitation. Two products are produced: a molten iron that remains in the sulphur phase and a V-rich slag. The iron is then sent to a basic oxygen furnace and the V slag to the V extraction process. The V is then extracted using hydrometallurgical processes as illustrated in Figure 2.2.

---

**Figure 2.2: Hydrometallurgy process of V production in South Africa (Moskalyk & Alfantazi, 2003)**

The well-known conventional salt-roasting leaching treatment of V can be summarized by the following steps:

- **Salt roasting**
  
The concentrate, milled ore or slag is blended with a carefully controlled quantity of sodium salt (sodium carbonate, sodium chloride or sodium sulphate) and then subject to an oxidizing roasting at temperatures up to 1000°C to form water soluble vanadate. This process can be summarized by the following equations:

\[
2\text{NaCl} + V_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{NaVO}_3 + 2\text{HCl}, \text{ salt roasting at } 800 – 900^\circ\text{C}
\]

*Equation 2.1*

\[
2\text{NaCl} + V_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{Cl}_2, \text{ salt roasting at } 800 – 900^\circ\text{C}
\]

*Equation 2.2*

\[
\text{Na}_2\text{SO}_4 + V_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{SO}_3, \text{ sulphate roasting at } 1200 – 1230^\circ\text{C}
\]

*Equation 2.3*
Na$_2$CO$_3$ + V$_2$O$_5$ → 2NaVO$_3$ + CO$_2$, soda ash roasting at 900 – 1200°C

Equation 2.4

✓ Acid leaching

The V salt is subjected to leaching in an acid environment in order to solubilise the vanadate.

✓ Precipitation

Vanadium is then precipitated in the form of ammonium metavanadate by adding ammonium sulphate to the vanadium-bearing leach liquor. The ammonium vanadate is calcined to drive out the ammonia.

After evacuation of the ammonia, remaining vanadate can be converted to diverse oxide forms like V$_2$O$_3$ and V$_2$O$_5$ by fusion of the residue of vanadium pentoxide in an electric furnace (Jena, et al., 1995).

Numerous different techniques in which V is produced as a by-product of other metal production processes are also used.

2.2.2 Production of ferrovanadium and coproduction of V-slags

Ferrovanadium comprise V compounds and alloys not necessarily containing iron. V in its pure state as a metal is difficult to produce since it is very reactive and absorbs gases such as carbon, oxygen, nitrogen with consequences of rendering the metal brittle. V-bearing materials such as vanadium oxides, fly ashes, slags and boiler residues are reduced using aluminium, carbon or silicon to produce ferrovanadium (Vermaak, 2000).

V in its oxide form can be found in a valence state of III (V$_2$O$_3$), IV (V$_2$O$_4$) or V (V$_2$O$_5$). The extend of the required external calorific energy to convert V oxide is determined by the concentration of each spices and the value of the valance. Conversion of V in ferrovanadium depends generally on the nature of the raw material and technique used.

Production of ferrovanadium can be summarised by the following processes:

a. Aluminium reduction

This method uses aluminium for the reduction of V-oxide. It is subdivided in two processes: the electro-aluminothermic and the aluminothermic processes (Kubaschewski, et al., 1993). The production route is controlled by the characteristics of the V-oxide used as the feed:
Reduction of V-oxide by aluminium is summarised by the following reactions:

\[
3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3 \quad \Delta H^0 = -4.28 \times 10^5 \text{ J/mol V} \quad \text{Equation 2. 5}
\]

\[
3V_2O_4 + 8Al \rightarrow 6V + 4Al_2O_3 \quad \Delta H^0 = -2.37 \times 10^5 \text{ J/mol V} \quad \text{Equation 2. 6}
\]

\[
V_2O_3 + 2Al \rightarrow 2V + Al_2O_3 \quad \Delta H^0 = -9.25 \times 10^5 \text{ J/mol V} \quad \text{Equation 2. 7}
\]

\[
3VO + 2Al \rightarrow 3V + Al_2O_3 \quad \Delta H^0 = -1.52 \times 10^5 \text{ J/mol V} \quad \text{Equation 2. 8}
\]

Prediction of the amount of energy required for melting the metal and slag can be done using the enthalpy of the exothermic reaction. Exothermicity of the reaction is determined by the ratio of the heat of the reaction and the molecular weight of the products. The reactions are classified as shown in Table 2.3 (Vermaak, 2000):

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 4500 J/gram</td>
<td>Violent reaction</td>
</tr>
<tr>
<td>&lt; 2250 J/gram</td>
<td>Necessity of external supply of heat</td>
</tr>
<tr>
<td>2250 J/gram &lt; Ratio &lt; 4500 J/gram</td>
<td>External energy not required</td>
</tr>
</tbody>
</table>

The reaction 2.5 which being very exothermic, allows the melting of the additional iron to form an alloy and even grants an efficient separation of the alloy and high aluminium slag (Gupta, 2004).

The feed to a reactor comprises generally a mixture of aluminium, scrap iron, V_2O_5 and lime (Vermaak, 2000). The smelting methods can be the ‘fedded reaction’ or the ‘reverse reaction’. In the first reaction, the charge is fed progressively into the reactor according the reaction velocity. In the reverse reaction, the entire charge is fed and ignited in the reactor. A coil is embedded in the mixture to start the reaction by passing a current through the coil and the reaction continues to completion.

The rate of the reaction can be controlled by the feed rate and the aluminium size. Slow and incomplete reaction happens if the aluminium particles are too big (small reaction interface). Increase in specific surface area leads to an increase in the rate of fusion of the initial charge.
Electro-aluminothermic production of ferrovanadium

The amount of aluminium needed to reduce the V depends on the V oxidation level in the feed. Less aluminium used for a lower V oxidation level material and the reaction is less exothermic. Additional external energy is then required to sustain the reduction process when using V₂O₃ and V₂O₄ as raw materials (Guisheng, et al., 2001). This process is more controllable and less violent than the aluminothermic process allowing a better control over the process. The V yield, the quality of the product, viscosity of the slag, the separability of the slag and the metal, and the dissolution of the refractory lining are very dependent and controlled by the temperature.

Production of ferrovanadium can be obtained by reducing V₂O₃ with Al in an electric arc furnace in presence of iron in the form of scrap and lime as a fluxing agent for the alumina (Al₂O₃) - a by-product from the reduction reaction. Typical composition of the produced metal and slag are given in Table 2.4.

Table 2.4: Typical metal and slag compositions (mass percentages) (Vermaak, 2000)

<table>
<thead>
<tr>
<th>Metal composition (%)</th>
<th>Slag composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>Al</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
</tr>
</tbody>
</table>

Silicon reduction

High grade ferrosilicon is used as a reductant. A two-stage process is compulsory as silicon is not a powerful reductant of V-oxides. Ferrovanadium containing 30% V and a significant quantity of residual Si is produced from the melting of technical grade V₂O₅. The slag composition is generally 0.5% V, 5-10% MgO, 28-30% SiO₂, and 50-55% CaO (Vermaak, 2000).

The general reaction can be established as:

\[ 2 \text{V}_2\text{O}_5 + 5 (\text{Fe}_{y/5}\text{Si})_{\text{alloy}} + 10 \text{CaO} = 4 (\text{Fe}_{y/4}\text{V})_{\text{alloy}} + 5 \text{Ca}_2\text{SiO}_4 \]  \hspace{1cm} \text{Equation 2.9}

V₂O₅ and lime are used to refine the primary metal in a second stage and the secondary slag is returned to the feed load for production of primary metal. Formation of V-silicates by the reaction of lower V-oxides such as VO and V₂O₃ with silicon makes the process difficult and perplexing. Consequently, some V is trapped into the slag and the recovery can go up to 75-82%.
c. Carbothermic reduction

Carbothermic reduction is carried out using carbon (coal, coke or charcoal) in a submerged-arc furnace. The charge (a mixture of V-oxide, carbon source, steel scrap and fluxing agents) is brought into the high temperature zone of the furnace. Therefore, two or three electrodes are arranged in line creating a high temperature reduction zone. The accumulated ferrovanadium and slag are then tapped at 4-12 hours’ time intervals. Ferrovanadium composition for this process is typically 3-5% Si, 3-3.5% C, 33-42% V and balanced with Fe. Difficulties in controlling the carbon content has made this method less attractive and limited to the production of high carbon graded ferrovanadium. Nevertheless, the method is principally used to produce high carbon-grade ferrovanadium alloys (Howard, et al., 1992).

2.3 Roasting of V-slags with sodium carbonate

Phosphates and other minerals such as Pb, Fe, Zn and U are usually combined with V-oxide. The common procedure in the separation of V-oxides from its ores comprises of changing it into a dissolvable salt by roasting with an alkali source in oxidising condition. Sodium carbonate is the widely-used salt for this purpose (KoltaI, et al., 1973).

During roasting of V ore with soda, the chemical behaviour follows an irregular pattern of converting elements into many compounds. The main problem is the selective character of the sodium carbonate and the side reactions that may occur with the associated elements in the slag.

The reaction of sodium carbonate with vanadium pentoxide ($V_2O_5$) occurs in five unique ways according to the following equations:

\[ \text{Na}_2\text{CO}_3 + 6\text{V}_2\text{O}_5 \rightarrow \text{Na}_2\text{V}_{12}\text{O}_{31} + \text{CO}_2, \text{ vanadium bronzes (I)} \]  \hspace{1cm} \text{Equation 2.10}

\[ \text{Na}_2\text{CO}_3 + 3\text{V}_2\text{O}_5 \rightarrow 2\text{NaV}_3\text{O}_3 + \text{CO}_2 + 5\text{O}_2, \text{ vanadium bronzes (II)} \]  \hspace{1cm} \text{Equation 2.11}

\[ \text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{CO}_2, \text{ metavanadate} \]  \hspace{1cm} \text{Equation 2.12}

\[ 2\text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow \text{Na}_4\text{V}_2\text{O}_7 + 2\text{CO}_2, \text{ pyrovanadate} \]  \hspace{1cm} \text{Equation 2.13}

\[ 3\text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{Na}_3\text{VO}_4 + 3\text{CO}_2, \text{ orthovanadate} \]  \hspace{1cm} \text{Equation 2.14}

At temperatures exceeding 550ºC, the reaction is fast and arrives at completion after brief time frames; which decrease with increase in $\text{Na}_2\text{CO}_3$ content. The Blend’s semi fusion or melting occurs at such high temperatures, quickening the dissemination procedure of ions and therefore an expansion in the interactions between $\text{Na}_2\text{CO}_3$ and $\text{V}_2\text{O}_5$. At temperatures less than 800ºC, sudden decrease of the rate of reaction of the blend of equations 2.10:2.12 is
noticed after few moments and Na$_4$V$_2$O$_7$ tends to limit the reaction. Therefore, remaining Na$_2$CO$_3$ reaction with Na$_4$V$_2$O$_7$ can be the rate-determining step for orthovanadate’s formation.

Differential thermal analysis has shown that reaction between V$_2$O$_5$ and Na$_2$CO$_3$ can occur at lower temperatures even in the solid phase. In the equation 2.10 for example, the formation of Na$_2$V$_{12}$O$_{31}$ (vanadium bronze I) begins at 320°C. V$_2$O$_5$ initiate the process of dissociation of Na$_2$CO$_3$, to Na$_2$O and CO$_2$. The heat from the self-generated reaction between V$_2$O$_5$ and the Na$_2$O formed makes this reaction incomplete (Tian, et al., 2015).

The two reactions’ succession extends with grow of temperature and is achieved at 500°C (semi fusion point), where the rate of Na$_2$CO$_3$ deterioration is moderately high and interactions between Na$_2$O and V$_2$O$_5$ are vigorous. 550°C is the temperature of completion of bronze I (Na$_2$V$_{12}$O$_{31}$). Chance of formation of another form of bronze I, having the structural formula NaV$_6$O$_{15}$ may occur near the melting point of bronze I.

At high temperature (550-600°C), this compound is effectively changed in to Na$_2$V$_{12}$O$_{31}$ an operation accompanied by oxygen consumption. This step is followed by the melting of Na$_2$V$_{12}$O$_{31}$ (600-650°C). During the cooling of the molten bronze I, solidification is displayed at 645°C. Dissociation of Na$_2$V$_{12}$O$_{31}$, to NaV$_6$O$_{15}$ with oxygen evolution per the following equation:

$$Na_2V_{12}O_{31} \rightarrow 2NaV_6O_{15} + \frac{1}{2}O_2 \quad Equation \ 2.15$$

Melting of this compound happens harmoniously with no solid point and production of heat. At 700°C, the patterns of unadulterated vanadate are noticed for the reaction products of the respective blends except that at the highest Na$_2$CO$_3$ concentration (3Na$_2$CO$_3$ + V$_2$O$_5$), where the reaction of the latter mixture is only accomplished at 800°C.

2.4 The chemistry of V in aqueous solution

V is naturally found as a trace metal in water and soil. The aqueous and no aqueous chemistry are differentiated by some self-condensation and hydrolytic reactions experienced by both vanadate and vanadyl oxoions in aqueous solution. These reactions are extremely sensible to the hydrogen potential of the solution (pH) and the presence of possible ligands which can react with the metal and form some complexes with various coordination geometries. The easy interconversion within different oxidation states brings some complications. Yield of an oxidized product can happen under some conditions where vanadate reacts as an oxidizing agent and is reduced to either vanadium IV or III. Unless the vanadyl is strongly complexed by effective stabilizing ligands, it is speedily oxidised by air in to vanadate
under neutral and basic pH ranges. It is only under acidic conditions that aqueous V (IV) in the form of vanadyl is stable (Drinčić, et al., 2017).

2.4.1 Aqueous chemistry

Dissolved vanadium III, IV and V can be submitted to reactions such as condensation, hydrolytic, acid/base and redox. Figure 2.3 represents the equilibrium Eh-pH diagram for the V-H$_2$O system.

![Figure 2.3: E-pH diagram of V in water](image)

Since V (III) and (IV) are cationic and V (V) species are anionic in aqueous solution, the chemistry difference within the three oxidations state drive to a further complex situation.

Vibrational and electronic spectroscopies, $^{51}$V NMR spectroscopy and other NMR spectroscopies (ligand nuclei) have been used to study the diamagnetic d° metal V (V). Paramagnetic d1 metal V is commodiously study using techniques such as Electron Spin Echo Envelope Modulation (ESEEM) and Electron Nuclear Double Resonance (ENDOR) and electronic and vibrational spectroscopies.

In contrary to V (IV) and (V), more restricted strategies used for structural characterization are accessible for the investigation of V (III). Generally, Electron Paramagnetic Resonance (EPR) and related methods don't give valuable structural probes making the investigation of the V(III) oxidation state.

The three oxidation states will be reported independently.
Vanadium (III)

The limited potential and pH range over which V (III) is stable is the major problem met throughout the study of its aqueous chemistry. The pKa values being around 2.6 and 4.2, the monomeric species \([V(H_2O)_6]^{3+}\) and \([V(OH)(H_2O)_5]^{2+}\) protonation happens promptly. \([V(OH)_2(H_2O)_4]\) is the major stable monomeric species in the neutral pH range.

A combination of electrochemistry and potentiometry is a requisite for the characterization of the speciation of solvated vanadium (III), of which interpreting is much tough. In aqueous solution, complexes of vanadium (III) with enough reducing ligands can occur (Crans, et al., 2004).

Vanadium (IV)

The hydrated vanadyl cation \((VO(H_2O)_5)^{2+}\) usually shorten as \(VO^{2+}\) is produced by dissolution of VOSO\(_4\) in acidic aqueous solutions. This species is air stable in acidic solutions. In the neutral pH range, regardless of the amounts of VOSO\(_4\) added to the solution, the concentration of hydrated monomeric \(VO^{2+}\) is restrained between 10\(^{-6}\) to 10\(^{-9}\) M by the aqueous equilibria limit. Nevertheless, formation of the polymeric can be prevented by complexation due to the high affinity of V(IV) for oxygen- nitrogen- and sulphur- containing ligands (Crans, et al., 2004).

Vanadium (V)

V is found generally in monomeric form as the \(H_2VO_4^-\) anion in solution having a concentration below 1mM. This applies as well when the stock solutions have been prepared using solids such as \(V_2O_5\), \(NH_4VO_3\), \(NaVO_3\), \(Na_3VO_4\) (Bolte, et al., 2007). The general formula \(HnVO_4^{(3-n)-}\) describe all the protonation states with “n” an integer number between 0 to 3. The neutral fully protonated species, \(H_3V_0_4\) is restricted to a pH value of 3 with a pKa value is estimated around 3.6.

2.4.2 Reactions of V (IV) with organic ligands.

Strong complexes are formed by the reaction of vanadyl cation and carboxylate functionalities and the carbonyl group can be good ligands for vanadyl cation. Vanadyl cation form strong complexes with many ligands of physiological interest containing more than one oxygen functionality. Hydroxycarboxylic acids such as citric, lactic, tartaric, glyceric, etc are of a particular interest (Crans, et al., 2004).

2.4.3 Reactions of vanadium (V) with organic ligands

Reactions between acids, hydroxylic compounds, or alcohols and the singly and doubly protonated vanadate ions produces complexes denoted as esters and acid anhydrides. These
aqueous complexes are generally considered as four coordinates. Complexes with the coordination number increasing to five or six are formed when vanadate reacts with carboxylic acids. The similar structure of vanadium-carboxylates and organic acid anhydrides have drove vanadium-carboxylates to be mentioned as vanadate anhydrides.

Complexes of Vanadium (IV) and (V) with a multidentate ligand are structurally quite alike but being different in some other cases. Lack of data make the establishment of guide lines too tough whilst some structural patterns may be rising (Crans & Tracey, 1998).

2.5 Leaching mechanisms

Leaching is a metallurgical process for extraction of metals from an ore that has come into contact with an aggressive solution. During the leaching process, movements of charges across the solid-solution phase boundary are indispensable for the dissolution process. The leaching mechanism can be described as pathway by which the reaction occurs or the rate controlling step (kinetic mechanism) of the reaction. (Lakshmanan, et al., 2016)

Parameters such as the temperature and the concentration of reagents in solution are the most controlling parameters of the rate of dissolution, thus the two kinetic parameters are the order of reaction and the activation energy.

Rate of reaction can be described by equation 2.16 (Crundwell, 2014)

\[
\text{RATE} = K [C]^n \exp(\frac{EA}{RT})
\]

where \([C]\) represents the concentration of a reagent, \(K\) the rate constant, \(n\) the order of reaction, \(EA\) the activation energy, \(R\) the gas constant and \(T\) the temperature.

The two parameters are the activation energy \(EA\) and the reaction order \(n\).

For diffusion-controlled reactions: \(EA < 20\) kJ/mol and for chemically-controlled reactions: \(EA > 40\) kJ/mol (Bamford, et al., 1985).

2.5.1 The kinetics of leaching reactions

Knowledge of the leaching kinetics allows the investigator to accelerate or retard the leaching rate. The rate expression will closely predict and describe the actual kinetics if the model corresponds closely to what is really taking place (Prajapati, et al., 2014). A good model requires to be the closest representation of reality which can be treated without too many mathematical complexities.

The important models that have been developed for leaching reactions are:
✓ Shrinking particle model (SCP): appropriate for non-porous particles where no product layer is left around the unreacted core;

✓ Shrinking core model (SCM): appropriate for non-porous particles where a reagent leaves a reacted layer around the unreacted core;

✓ Grain models: appropriate for solids containing individual dense grains compacted together;

Homogeneous model: appropriate for solids with a homogeneous distribution of pores (Gbor & Jia, 2004). The shrinking core model is generally the best fitting model for heterogeneous systems and it has been used to model many solids-fluids reactions.

The model assumes the formation of an ash layer around a shrinking core of unreacted solid reactant. The ash layer steadily grows inward towards the shrinking core with the progression of the reaction, up until the completion of the reaction.

The followings have been predicted as the major resistance to the reactions:

✓ The diffusion of the reactant gas A to the surface of the solid through the gas film surrounding the particle;

✓ The diffusion of the reactant gas through the solid ash layer to the reaction surface at the unreacted core;

✓ Reaction of the gaseous reaction A at the reaction surface of the unreacted core with solid B;

✓ Diffusion of the gaseous product from the surface of the unreacted core through the ash layer back to the outer part of the ash layer;

   Diffusion of the gaseous product through the gaseous film surrounding the particle (Nazemi, et al., 2011).

   One or an association of the resistances notified above can control the reaction depending on the occurring reaction, and therefore can be applied to develop a model that will help predict how the chemical process will proceed with time.

   The products formed in the leaching reaction of slags are liquid products, therefore the reaction occurring will be of the form:

   \[ aA_{(S)} + bB_{(l)} \rightarrow cC_{(S)} + dD_{(l)} \]  

   Equation 2.17

   Where a, b, c and d are the coefficient of the reagent and products

   If the diffusion through the liquid film is the controlling mechanism, the next equation is usually applicable assuming spherical shape of the ore particle (Crundwell, 1995):
\[ \alpha = k_1 \cdot t \]  \hspace{1cm} \textit{Equation 2.18}

where \( k_1 \) is the reaction constant and \( \alpha \) the leaching fraction of the metal.

If the chemical reaction is the controlling mechanism for small particles in the stokes regime, the process can be modelled as:

\[ 1 - (1 - \alpha)^{1/3} = k_1 \cdot t \]  \hspace{1cm} \textit{Equation 2.19}

If the diffusion through the solid film is the controlling mechanism for small particles in the stokes:

\[ 1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = k_2 \cdot t \]  \hspace{1cm} \textit{Equation 2.20}

where \( k_2 \) is the reaction constant and \( \alpha \) the leaching fraction of the metal.

The difference in the leaching rate at two stages suggest a different controlling step in each stage. When none of the above mechanisms is the rate controlling step, all three steps can be taken into account for describing the kinetics of the leaching by the SCM (Mirazimi, et al., 2015).

\subsection*{2.5.2 General notions on bioleaching processes}

In recent years, the combination of hydrometallurgy and biology (microbes) has allowed the development of a powerful metal’s extraction method called bioleaching allowing recovery of metals from occurrence that was previously considered as metallurgical waste. Bioleaching or bio-oxidation is a process that uses microorganisms to catalyse the reactions of some minerals. These microorganisms capture electrons from the minerals for their growth. The minerals are therefore used as a source of energy for the microorganisms. This microorganism can be isolated from the mining drainage (mesophiles) making the possibility of the process to occur naturally or from hydrothermal strain (thermophiles) (Kundu & Kumar, 2014).

Bioleaching expels the Sulphur in the form of sulphate (gypsum) while smelting produces \( \text{SO}_2 \) from which typically sulphuric acid is produced. This process offers the possibility to treat concentrate of metals and low-grade ores as well (less than 1\% Cu). It can be used to heat wet material skipping the drying process compulsory to the pyrometallurgy processes, therefore using less energy and occurs at lower temperatures and pressure. The
disadvantage of the method is slowness of the reactions and the production of diluted solutions (Sohn & Kim, 2002).

Microorganisms can be classified according to the source of carbon and energy they use for their metabolisms, then grouped according to their optimum temperature growth. There are autotrophic bacteria which assimilate carbon CO$_2$ from the air and HCO$_3^-$ ion in an aqueous medium while the heterotrophic bacteria require carbon organic substances. They can subsequently be classified according to their optimal growth temperature, into three groups: mesophiles (27-38°C), moderate (50°C) and extreme thermophiles microorganisms (70-80°C). Apart from strains working at elevated temperature (extreme thermophiles), the major microorganisms used in hydrometallurgy are autotrophic.

2.5.3 Bioleaching mechanisms

a. Leaching bioreactor

Bioleaching is made up of three phases which are solid phase, an aqueous phase and a gaseous phase (which is a mixture of oxygen and carbon dioxide) (Behera, et al., 2011). The three phases must rigorously be mixed for an effectual fixture of the micro-organisms and the solid particles. Microorganisms can mobilise metals by:

- Formation of organic acids: acidolysis
- Oxidation and reduction reaction: redoxolysis
- Extraction by complexing agents: complexolysis
- Chelate formation: bioaccumulation (Mirazimi, et al., 2015)

Unlike sulphides, conventional bioleaching methods with ferric ions as the main element may not be feasible for oxides, carbonates and silicates. Therefore, bioleaching processes occurs through the protonation of the mineral surface as well as the surface concentration of suitable complex forming leachants. The organic acids produced by the microorganisms can act as chelating agents and therefore, form complexes such as gluconate, oxalate or citrate complex of metals (Gadd, 2010).

An acid is a chemical substance able to give a proton in its reaction with a base. The acids are generally grouped in Lewis and Bronsted Lowry acids. Nevertheless, another specific type of acids is organic acids. Some organic compounds reveal acidic properties giving them a qualification of organic acids. Being organic, presence of a carbon atoms is indispensable. Carboxylic acid is the most common with the formula RCOOH. They are generally weak acids.
✓ **Gluconic acid**

Gluconic acid was discovered by Hlasiwetz and Habermann in 1870 and it is being produced since then. It is produced by microorganisms such as acetic acid bacteria and several fungal species. Gluconic acid, \( \text{CO}_2\text{H} (\text{CHOH})_4\text{CH}_2\text{OH} \), is a polyhydroxylated carboxylic acid with potentially labile hydroxyl protons that can be displaced during metal complexation at high pH.

Research has proved that specie *Aspergillus niger* produce high quantities of gluconic acid when being neutralise by calcium carbonate and pH is a very important factor influencing this production (Ramachandran, et al., 2006). Nevertheless, pH reliance is not as basic with *Penicillium species*. with respect to *Aspergillus niger*, suggesting that there is a relationship between the amount and time-dependent appearance of organic acids, such as gluconic acid, citric acid, oxalic acid, which are formed under different conditions. The Figure 2.4 describes the atomic structure of gluconic acid.

![Gluconic acid structure](image)

*Figure 2.4: Gluconic acid structure* (Ramachandran, et al., 2006)

The general characteristics of Gluconic acid are described in Table 2.5.
Table 2. 5 General characteristics of Gluconic acid (Ramachandran, et al., 2006)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative molecular mass</td>
<td>196.16 (g)</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₆H₁₂O₇</td>
</tr>
<tr>
<td>Synonym</td>
<td>2,3,4,5,6-pentahydroxyhexanoic acid</td>
</tr>
<tr>
<td>pKa</td>
<td>3.7</td>
</tr>
<tr>
<td>Melting point (50 % solution)</td>
<td>Lower than 12 °C</td>
</tr>
<tr>
<td>Boiling point (50 % solution)</td>
<td>Higher than 100 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.24 g/mL</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear to brown</td>
</tr>
<tr>
<td>Soursness</td>
<td>Mild, soft, refreshing taste</td>
</tr>
<tr>
<td>Degree of sourness (sourness of citric acid is regarded as 100)</td>
<td>29 – 35</td>
</tr>
</tbody>
</table>

Gluconic acid contains one carboxyl group and while dissociating it can form gluconate complex of V according to equations 2.21 and 2.22:

\[
HC_6H_{11}O_6 \leftrightarrow (C_6H_{11}O_7)^- + H^+ \quad pKa1 = 3.7 \quad \text{Equation 2.21}
\]

\[
5 (C_6H_{11}O_7)^- + V^{5+} \leftrightarrow V(C_6H_{11}O_7)_5 \quad \text{Equation 2.22}
\]

Citric acid

Citric acid is an organic acid with formula C₆H₈O₇. It is naturally found in citrus fruits and in physiological fluids, animal tissues and many plants. It was discovered for the first time by Islamic alchemist Jabir Ibn Hayyan (Geber) in the 8th century (Ciriminna, et al., 2017).

The Figure 2.5 describes the atomic structure of citric acid.

![Figure 2.5: Citric acid structure](Ciriminna, et al., 2017)

The general characteristics of Citric acid are reported in Table 2.6.
Table 2.6: General characteristics of Citric acid (Ciriminna, et al., 2017)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative molecular mass</td>
<td>192.12 g·mol⁻¹</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₆H₈O₇</td>
</tr>
<tr>
<td>Synonym</td>
<td>2-hydroxy-1,2,3-tricarboxylic acid</td>
</tr>
<tr>
<td>pKa</td>
<td>pKa₁ = 3.09, pKa₂ = 4.75, pKa₃ = 5.41</td>
</tr>
<tr>
<td>Melting point (50 % solution)</td>
<td>156 °C (313 °F; 429 K)</td>
</tr>
<tr>
<td>Boiling point (50 % solution)</td>
<td>310 °C (590 °F; 583 K) decomposes from 175 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.665 g/cm³ (anhydrous), 1.542 g/cm³ (18 °C, monohydrate)</td>
</tr>
<tr>
<td>Appearance</td>
<td>Crystalline white solid</td>
</tr>
<tr>
<td>Solubility</td>
<td>592 g/l</td>
</tr>
<tr>
<td>Sourness</td>
<td>Strong</td>
</tr>
<tr>
<td>Degree of sourness (sourness of citric acid is regarded as 100)</td>
<td>100</td>
</tr>
</tbody>
</table>

Citric acid can be produced by microorganism such as Fungi (*Aspergillus niger*, *Penicillium janthinellum*), Bacteria (*Bacillus licheniformis*, *Corynebacterium* sp.) and yeast *Saccharomycopsis lipolytica*, *Hansenula anamola* (Vandenberghe, et al., 1999).

Citric acid contains three carboxyl groups. When fully dissociated, the possible complexes of metal cation with citrate anion are expressed as shown in equations 2.23-2.27:

\[
H_3C_6H_5O_7 \leftrightarrow (H_2C_6H_6O_7)^{-} + H^+ \quad pK_a1 = 3.09 \quad \text{Equation 2.23}
\]

\[
H_2C_6H_5O_7^{-} \leftrightarrow HC_6H_5O_7^{2-} + H^+ \quad pK_a2 = 4.75 \quad \text{Equation 2.24}
\]

\[
HC_6H_5O_7^{2-} \leftrightarrow C_6H_5O_7^{3-} + H^+ \quad pK_a3 = 5.41 \quad \text{Equation 2.25}
\]

\[
C_6H_9O_7 \leftrightarrow (C_6H_5O_7)^{3-} + 3H^+ \quad \text{Equation 2.26}
\]

\[
5(C_6H_5O_7)^{3-} + 3M^{5+} \leftrightarrow M_3(C_6H_5O_7)_5 \quad \text{Equation 2.27}
\]
C. Oxalic acid

Oxalic acid C\textsubscript{2}H\textsubscript{2}O\textsubscript{4} also known as Ethanedioic acid was first detected by Johann Christian Wiegleb in 1769. It is a relatively strong acid having two carboxyl groups with reactions:

\[ C_2O_4H_2 \rightleftharpoons C_2O_4H^- + H^+ \quad pKa = 1.27 \quad Equation 2.28 \]

\[ C_2O_4H^- \rightleftharpoons C_2O_2^{2-} + H^+ \quad pKa = 4.27 \quad Equation 2.29 \]

The atomic structure of Oxalic acid is given in the figure 2.6.

![Oxalic acid structure](image)

*Figure 2. 6: Oxalic acid structure (George, et al., 1999)*

The general characteristics of Oxalic acid are described in Table 2.7.

**Table 2. 7: General characteristics of Oxalic acid (Mensah, et al., 2009)**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative molecular mass</td>
<td>90.03 g mol(^{-1}) (anhydrous)</td>
</tr>
<tr>
<td></td>
<td>123.065 g mol(^{-1}) (dihydrate)</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}</td>
</tr>
<tr>
<td>Synonym</td>
<td>Ethanedioic</td>
</tr>
<tr>
<td>pKa</td>
<td>1.25, 4.14</td>
</tr>
<tr>
<td>Melting point (50 % solution)</td>
<td>189 to 191°C</td>
</tr>
<tr>
<td>Density</td>
<td>1.90 g cm(^{-3}) (anhydrous)</td>
</tr>
<tr>
<td></td>
<td>1.653 g cm(^{-3}) (dihydrate)</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colorless crystalline solid</td>
</tr>
<tr>
<td>Solubility</td>
<td>143g/L (25°C)</td>
</tr>
</tbody>
</table>
Likewise, Oxalic acid contains two carboxyl groups which are:

\[
H_2C_2O_4 \leftrightarrow HC_2O_4^{1-} + H^+ \quad pK_a1 = 1.25 \quad \text{Equation 2.30}
\]

\[
HC_2O_4^{1-} \leftrightarrow C_2O_4^{2-} + H^+ \quad pK_a2 = 4.14 \quad \text{Equation 2.31}
\]

Therefore, possible oxalate complex of vanadium will be V(C$_2$HO$_4$)$_2$ and V(C$_2$O$_4$).

The literature on the topic suggests that the leaching efficiency of heterotrophic microorganisms is directly proportional to the production of organic metabolites excreted into the culture medium and which lower the pH of medium. This has a consequence on the dissolution of metals into the solution (Behera, et al., 2011).

2.6 Previous kinetic studies on V leaching

Some studies have been accounted to examine the kinetics of V leaching. Kinetics of V leaching from a steelmaking slag was investigated by (Aarabi, et al., 2010). It was proved that the first 15 minutes of the leaching process was quicker (fast leaching rate) compared to the last minutes of the leaching process (over 30 minutes). V leaching rate was chemically controlled at low temperatures whilst diffusion through the solid product layer was the controlling mechanism at higher temperatures.

Amer, (1994) demonstrated that the most positive conditions for the extraction of 95% of the V 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 demonstrated that the V leaching was mixed controlled and the activation energy of the reaction was around 30 kJ/mol. On the other hand, Li, et al., (2012) discovered that oxidative conditions can enhance the leaching process of V from a blend of vanadium (V) and (III) oxides. The kinetic study reported an activation energy value of 40.1 kJ/mol.

Zhou, et al., (2012) extracted vanadium from pure vanadium trioxide using sulfuric acid under an oxidative pressure. It was demonstrated that vanadium trioxide can be totally leached in around 20 minutes by 1M sulfuric acid, oxygen partial pressure 1MPa, and 140°C. The activation energy was around to be 43.46 kJ/mol. Calcium vanadate was leached using Na$_2$CO$_3$ and higher pH values gave higher reaction rate constant compared to lower. The activation energy was found to be 38.98 kJ/mol (Wang-xing, et al., 2010).
Chapter 3: EXPERIMENTAL METHODOLOGY

3.0 Introduction

This chapter describes the experimental approach used to simulate the bioleaching of V from the V-bearing slag as well as the mechanism taking place. It consists of three major sections. The first section presents the characterisation of the slag and reagents used, the second describe different types of analytical techniques used during the project while the third elaborate on the pre-treatment prior to leaching and the bioleaching simulation of the dissolution of V from the slags.

3.1 Materials and reagents

3.1.1 Materials

The V-bearing slag used in the present project was provided by a steel making plant in North West province, South Africa and was generated from a steelmaking plant according to the procedure presented and described in chapter 1 section 1.1.

3.1.2 Reagents

All reagents used in the present project were provided by MERCK, South Africa and they were of high analytical purity of 99%. Na₂CO₃ was used for the roasting of the slag in order to transform V into a water-soluble form. Commercial Gluconic, Citric and Oxalic acids were used in place of organic acids produced by microorganisms during the dissolution of oxide minerals for leaching of V from the slag.

3.2 Characterisation

Several analytical techniques have been used to characterise and analyse the as received sample, the pre-treated and final products after leaching in different conditions.

3.2.1 Chemical composition of the slag sample

The chemical composition of the slag before and after pre-treatment was determined using X-ray fluorescence (XRF) model RigakuZSX Primus II equipped with SQX analysis software. 10 g of the pulverized sample was weighed and pelletized by applying 15 mega-pascal pressure to make pellets of 2.5 mm thickness and 35 mm diameter. The pellets were then incubated at 50°C for 20 minutes to remove all moisture prior to analysis and loaded in the spectrometer for elemental analysis.
3.2.2 Mineralogical composition of the slag sample

The mineralogical phases of the raw slag, the mineralogical changes during pre-treatment and that of the residues were obtained using X-ray diffractometer (XRD) model “Rigaku UltimaI V” X-ray diffractometer equipped with PDXL analysis software equipped with a graphite monochromator in the diffracted beam. The sample was oven dried for approximately 24 hours, grounded manually with mortar and pestle and placed in a specimen sample holder prior to testing.

3.2.3 Surface morphology of the slag sample

The surface morphology of the slag samples was observed using Scanning Electron Microscopy (SEM) model while the Energy Dispersive X-Ray (EDX) was used to give the point by point analysis and the elemental percentage composition of the samples. For this purpose, the sample was mounted in the resin then polished for analysis. The polished sample was coated under vacuum with a thin layer of carbon to make the surface conductive. The coated samples were analysed using the SEM TESCAN loaded with Vega 3 software while the EDX used Inca software performing in Nanospace at 15 kV. Based on the difference in contrast and the EDX, the distribution of the V bearing phases was identified. SEM/EDX and Coating instruments used are shown in the Figure 3.1.

![SEM and EDX](image)

*Figure 3.1 Scanning Electron Microscopy (SEM) with EDX (a) and a coating chamber (b)*

3.2.4 Chemical composition of leachate

The atomic absorption spectrophotometer “Thermo Scientific ICE 3000 series & Varian” was used to determine the amount of elements dissolved into the solution. After each leaching experiment at different conditions, the liquors were collected and analysed for V and the major impurity Al.
3.3 Pre-treatment and dissolution tests

3.3.1 Alkali-roasting of the slag sample (Goso, et al., 2016)

The sample was crushed, blended and pulverised to 80% passing 75μm to liberate the V from slags for a better leaching process.

After pulverisation, the slag was then mixed with sodium carbonate in different mass ratios (10, 20, 30 and 40% wt). The mixture was pelletized and then oven dried for 24 hours at 100 ºC. After 24 hours, the dried pellets were roasted using the muffle furnace shown in Figure 3.2. at different temperatures (800, 900 and 1000ºC) for a fixed time of two hours.

![Muffle furnace](image)

Figure 3. 2: Muffle furnace

The calcined slag was then pulverised and analysed for chemical composition using XRF and for change in mineral phases using XRD.

3.3.2 Validation test work

To confirm the formation of water soluble compounds, different roasted samples were leached using a mixture of Gluconic, Citric and Oxalic acids and the leachate analysed using AAS.

3.4 Bioleaching simulation of V dissolution from the slag

The leaching experiments were done using a mixture of Gluconic, Citric and Oxalic to simulate the bacterial leaching of oxide minerals. A water bath shown in Figure 3.4 was used for all leaching experiments to maintain the leaching temperatures. In fact, as elaborated in the previous works, during the dissolution of oxide minerals using strain such as Pseudomonas...
*putida*, production of organic acids such as Gluconic, Citric and Oxalic occurs. These acids promote the dissolution of the metal (Strasser, et al., 1994).

To determine the dissolution of V in each individual organic acid, the dissolution was done as well using individual acid separately.

![Water bath](image)

**Figure 3.3: Water bath**

3.4.1 Mixed acid leaching experiments

The simulation was done using the mixture of the three organic acids in equal volumes of similar concentration while leaching according to the following conditions:

- Concentration: 50, 100, 150 and 200 (mM);  
- Solid-liquid ratio: 2, 4, 6, 8, 10 (%);  
- Particles size: -38; -75+53; -150+106 (μm);  
- Temperature: 25, 35, 45 (ºC);  
- Time: 1, 2, 4, 8, 10, 20, 30, 60 (min);  
- Volume of the lixiviant: 100ml;  
- Volume of the conical flask: 250ml;  
- Agitation: 150rpm;  
- Condition: aerobic;  
- Pressure: atmospheric pressure

The study was conducted by changing one parameter while keeping others constant. It must be noted that samples were collected at intervals of 1, 2, 4, 8, 10, 20, 30 and 60 minutes during the leaching process. These sample were filtered using filter papers and the filtrate analysed using AAS. Reported results are the average of three leach tests per sample.
3.4.2 The kinetic studies of the leaching process

The kinetic studies were done during the bioleaching simulation to determine the mechanism controlling the dissolution process. To achieve this, the shirking core models were used to analyse the experimental data. A good data fit is a minimum requirement for validity of the model, however it does not guarantee that it is indeed valid. To check that the model applies to our results, the terms $\alpha$, $1 - (1 - \alpha)^{1/3}$ and $1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3}$ were calculated corresponding to the diffusion through the liquid layer, chemically and diffusion through the ash layer controlled reactions (Al-Hamamre, 2001). The terms $\alpha$, $1 - (1 - \alpha)^{1/3}$ and $1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3}$ vs time were then plotted.

3.4.3 Leaching in individual acid

The leaching in individual acid was done to evaluate the V dissolution in each acid. This was done using the same leaching parameters as in the mixed ones.

➢ Note: in both cases the V was assessed together with Al prompt to co-leaching.

3.4.4 Evaluation of the leaching experiments

The % metal dissolution was calculated using the formula described in the equation 3.1 to evaluate the efficiency of the leaching process.

\[
\% = \frac{(M*V)}{(m*G)} * 100 \quad \text{Equation 3.1}
\]

Where M: Metal solution [mg/L]
V: Volume of the solution [L]
m: Mass slag [mg]
G: Grade of the metal in slag

The experimental procedure flowsheet is summarized in Figure 3.4.
Figure 3.4: Flowsheet of the experimental procedure
Chapter 4: RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents the findings of the study generated based on the methodology, discusses and interprets the findings of the results.

4.1 Characterisation of the raw slag

4.1.1 Chemical composition of the slag

The average elemental analysis results of the V slag using XRF are present in Table 4.1. The slag contains a considerable amount of V which can be recovered. The Al oxide content in the slag is considerably very high due to the smelting process where Al was added as a reagent to react with V$_2$O$_5$ flasks to form ferrovanadium.

Table 4.1: Chemical composition of the as received slag

<table>
<thead>
<tr>
<th>Component</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>V$_2$O$_5$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Oxide</td>
<td>3.25</td>
<td>7.03</td>
<td>61.49</td>
<td>1.54</td>
<td>18.94</td>
<td>4.58</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Elemental analysis was also done on different particle size range of the slag to access the V distribution in the slag and the results shown in Table 4.2. It was noticed that the bigger particle sizes are richer in V than the smaller once, hence there was need for further pulverisation of the bigger particles of the slag to free the locked V. This confirms findings of previous researches such as Balasubramanian, (2015).

Table 4.2: Vanadium deportment in different size ranges of the raw sample

<table>
<thead>
<tr>
<th>Size range (µm)</th>
<th>%Wt. V$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-350+212</td>
<td>5.9</td>
</tr>
<tr>
<td>-212+150</td>
<td>5.9</td>
</tr>
<tr>
<td>-150+106</td>
<td>4.7</td>
</tr>
<tr>
<td>-106+75</td>
<td>4.6</td>
</tr>
<tr>
<td>-75+53</td>
<td>5.69</td>
</tr>
<tr>
<td>-53+38</td>
<td>4.1</td>
</tr>
<tr>
<td>-38</td>
<td>3.1</td>
</tr>
</tbody>
</table>
4.1.2 Mineralogical composition of the slag

The mineralogical analysis done by XRD showed the presence of V phases such as calcium divanadate (IV), V oxide and other phases such as spinel, grossite, calcium magnesium as illustrated in Figure 4.1. V and Al are in phases which are stable and difficult to leach. V is present in the phases such as calcium vanadate and vanadium oxide which are very difficult to leach in aqueous media as confirmed in previous works by (Aarabi, et al., 2010) who also found presence of V in a form of calcium vanadium oxide (Ca₂V₂O₇) in the slag.

![XRD pattern of the raw slag](image)

*Figure 4.1: XRD pattern of the raw slag*

4.1.3 Surface morphology of the slag sample

The surface morphology of the slag sample was investigated using SEM on five different points and confirms the presence of the phases revealed in XRD as illustrated in the Figure 4.2. Different phases such as spinel, grossite, magnesioculsonite, calcium magnesium vanadium oxide, aluminium vanadium oxide, calcium divanadate (IV), vanadium oxide and larnite are present with grossite as the major phase. Pure metal V was also found incrusted in the slag. Vanadium is mostly find in phases which are difficult to leaching.
Figure 4.2: Micrographs of the raw slag

The selected point A, B, C, D and E were analysed using EDX and the Table 4.3 gives their composition.

Table 4.3: Composition of different points of the raw slag using

<table>
<thead>
<tr>
<th>POINT</th>
<th>Oxide Percentage</th>
<th>Phase Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V₂O₅</td>
<td>MgO</td>
<td>CaO</td>
</tr>
<tr>
<td>A</td>
<td>4.32</td>
<td>27.35</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.37</td>
<td>28.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>21.56</td>
<td>78.44</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.70</td>
<td>34.74</td>
<td>60.42</td>
</tr>
<tr>
<td>E</td>
<td>95.7</td>
<td>0.35</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It was also noticed that on the raw sample, the distribution of components was not homogeneous on the surface of the sample and the sample was not porous enough to promote the dissolution of V.

4.2 Characterisation of the roasted slag

4.2.1 Chemical composition of the roasted slag

All the roasted slags were analysed using XRF to investigate variation of the chemical composition throughout the roasting process and the results are shown in the Table 4.4. The chemical composition change depended on the amount of sodium carbonate used in the roasting process. All samples with same percentage of sodium carbonate added have almost same chemical composition.

Table 4. 4: Chemical composition of the roasted slag

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>%wt Na2CO3</th>
<th>Na2O</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>CaO</th>
<th>V2O5</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>10</td>
<td>14.76</td>
<td>7.39</td>
<td>54.78</td>
<td>0.95</td>
<td>16.46</td>
<td>4.05</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.55</td>
<td>5.99</td>
<td>50.09</td>
<td>0.76</td>
<td>16.45</td>
<td>3.76</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>26.50</td>
<td>6.67</td>
<td>46.39</td>
<td>0.80</td>
<td>14.00</td>
<td>3.83</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40.45</td>
<td>5.20</td>
<td>37.8</td>
<td>0.67</td>
<td>11.21</td>
<td>3.17</td>
<td>0.61</td>
</tr>
<tr>
<td>900°C</td>
<td>10</td>
<td>11.60</td>
<td>8.26</td>
<td>57.06</td>
<td>0.72</td>
<td>16.76</td>
<td>3.98</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.49</td>
<td>6.24</td>
<td>52.26</td>
<td>0.65</td>
<td>15.97</td>
<td>3.72</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>23.82</td>
<td>8.08</td>
<td>47.04</td>
<td>1.08</td>
<td>14.65</td>
<td>3.68</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40.94</td>
<td>6.51</td>
<td>35.05</td>
<td>1.02</td>
<td>11.22</td>
<td>3.36</td>
<td>0.77</td>
</tr>
<tr>
<td>1000°C</td>
<td>10</td>
<td>11.87</td>
<td>7.73</td>
<td>56.89</td>
<td>0.71</td>
<td>17.04</td>
<td>4.03</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>21.44</td>
<td>5.07</td>
<td>52.10</td>
<td>0.64</td>
<td>15.36</td>
<td>3.82</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>25.53</td>
<td>7.98</td>
<td>45.91</td>
<td>0.83</td>
<td>14.35</td>
<td>3.90</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40.18</td>
<td>6.11</td>
<td>37.22</td>
<td>0.77</td>
<td>10.69</td>
<td>3.52</td>
<td>0.73</td>
</tr>
</tbody>
</table>

4.2.2 Mineralogical composition of the roasted slag

a. Roasting at 800°C

The XRD analysis were done to compare the raw sample to the roasted slag at 800°C with the addition of different ratio of sodium carbonate (10, 20, 30, 40% in weight) and the results are shown on Figure 4.3. The results revealed formation of the new phases such as
sodium aluminium oxide (\(\text{Na}_2\text{Al}_2(\text{Si})\text{O}_4\)) and sodium vanadate (NaVO_3) within the slag structure dominated by phases of calcium vanadium oxide, grossite and spinel.

![XRD pattern of roasted slag at 800ºC](image)

**Figure 4.3: XRD pattern of roasted slag at 800ºC**

Where a is sodium aluminium oxide (\(\text{Na}_2\text{Al}_2(\text{Si})\text{O}_4\)), g: grossite (CaAl_4O_7), p: spinel (MgAl_2O_4), s: sodium vanadate (NaVO_3) and v: (calcium) vanadium oxide (Ca_2V_2O_7).

It is observed that roasting at this temperature results in much change in the structure of the slag while adding 10% sodium carbonate. The increase in sodium carbonate-slag ratio announces slight increase in peak corresponding to sodium vanadate. Nevertheless, presence of V less soluble phases such as vanadium oxide and calcium vanadate is still noticed after roasting at 800ºC. This confirms the findings in previous work of other researchers such as Fedorov, et al., (1978) and Li, et al., (2011) while investigating the solubility of magnesium and calcium vanadate.

**b. Roasting at 900ºC**

The XRD analysis were done to compare the raw sample to the roasted slag at 900ºC with the addition of sodium carbonate in different ratio (10, 20, 30, 40% in weight). With an increase of the temperature to 900ºC, sodium vanadate (NaVO_3) peaks intensity improved with
elimination of vanadium oxide (V\textsubscript{2}O\textsubscript{5}) peaks. At this temperature, there is an increase in sodium aluminium (Na\textsubscript{2}Al\textsubscript{2}(Si)O\textsubscript{4}) peak with a slight decrease of spinel phase (MgAl\textsubscript{2}O\textsubscript{4}) as shown in Figure 4.4 confirming the breakdown of the spinel phase.

![Graph showing XRD pattern of roasted slag at 900°C](image)

*Figure 4.4: XRD pattern of roasted slag at 900°C*

Where p is spinel (MgAl\textsubscript{2}O\textsubscript{4}), g: grossite (CaAl\textsubscript{4}O\textsubscript{7}), a: sodium aluminium oxide (Na\textsubscript{2}Al\textsubscript{2}O\textsubscript{4}), s: sodium vanadate (NaVO\textsubscript{3}), c: (calcium, silicon, aluminium) oxide (CaO, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}) and v: vanadium oxide (V\textsubscript{2}O\textsubscript{5}).

c. **Roasting at 1000°C**

The XRD analysis was done to compare the raw sample to the slag roasted at 1000°C with addition of different ratios of sodium carbonate (10, 20, 30, 40% in weight) and the results are shown in Figure 4.5.

At 1000°C, more soluble phases of V are noticed while there is a significant formation of soluble phases of impurities containing aluminium and silicon coming from the decomposition of other phases such as spinel, grossite and calcium aluminium. Peaks of aluminium vanadate are more intense proving their high formation compared to sodium vanadate. This might allow leaching of more impurities as proven by (Padillar & Sohn, 1985).
Where p is spinel (MgAl$_2$O$_4$), g: grossite (CaAl$_4$O$_7$), a: sodium aluminium oxide (Na$_2$Al$_2$O$_4$), s: sodium vanadate (NaVO$_3$), c: (calcium, silicon, aluminium) oxide (CaO, SiO$_2$, Al$_2$O$_3$) and v: vanadium oxide (V$_2$O$_5$).

After roasting at different temperature while changing the ratio of sodium carbonate, it was noticed that there are important phase changes at the temperatures of 900ºC and 1000ºC more than 800ºC. This favours the formation of sodium soluble compounds of V as well as that of impurities (aluminium and silicon) as compared to the one roasted at 800ºC. This behaviour is attributed to the fact that in the high temperature range, semi fusion or melting of the blend occurs, quickening the dissemination procedure of ions and therefore an expansion in the interactions between Na$_2$CO$_3$ and V$_2$O$_5$ (Kolta, et al., 1973).

### 4.2.3 V Dissolution tests

All the samples (raw and roasted slag) were leached in same conditions using 50mM Gluconic, Citric, Oxalic and a mixture of the three organic acids. This was done to confirm the formation of soluble V phases after roasting and results are presented in Figure 4.6. The dissolution of V was very low when leaching from the raw sample than from the roasted. This is due to the natural refractoriness of V and the way V is enclosed in the slag structure.
After roasting at 800°C a slight dissolution of V was observed (30%). The low solubility of V may be due to the high percentage of the remaining calcium vanadate and vanadium oxide which are non-soluble as confirmed by the XRD results in Figure 4.3 and this is in agreement with the results found by Li, et al., (2011). At 900°C and 1000°C more V was dissolved as compared to the raw and the 800°C roasted sample. At this temperature, the probability of forming more soluble compounds such as sodium vanadate was achieved as shown in the Figures 4.4 and 4.5. The same observations were noted by Padillar & Sohn, (1985). It was noticed that more V was leached from the sample roasted at 900°C with a ratio of 20% added sodium carbonate. For this specific sample, the dissolution was 54%, 39%, 35% and 37% for Gluconic, Citric, Oxalic and mixed acids respectively. On the other hand, leaching of other samples show good V leaching as well but with a higher level of impurities. The dissolution tests results are shown in the Figure 4.6.
Figure 4.6: Dissolution tests of raw and roasted slag in 50mM of Gluconic, Citric, Oxalic and Mixed acids
Where Gl is Gluconic, Cit: Citric, Ox: Oxalic and Mix: Mixed

It can be noticed that the high V dissolution is given by Gluconic, followed by Citric, Oxalic and then mixed acids. On the other hand, Oxalic acid gives the higher leaching of Al followed by Citric, Mixed and Gluconic.

The chosen sample used for the succeeding leaching processes experiments is therefore the one that was roasted at 900°C, 20% wt. Na$_2$CO$_3$ and has a chemical composition presented in Table 4.5.

Table 4.5: Chemical composition of the roasted slag at 900°C, 20% wt Na$_2$CO$_3$

<table>
<thead>
<tr>
<th>Component</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>V$_2$O$_5$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide %</td>
<td>14.76</td>
<td>7.39</td>
<td>54.78</td>
<td>0.95</td>
<td>16.46</td>
<td>4.05</td>
<td>0.73</td>
</tr>
</tbody>
</table>

The chemical composition of this sample showed an average of 4% V$_2$O$_5$ which is considerable amount to recover V from.

4.2.4 Surface morphology of the selected roasted sample

The SEM as well as the EDX were performed on the selected roasted sample to investigate both the morphological aspect as well as the distribution of component and the results are shown in Figure 4.7. It was noticed that on the roasted sample, the surface exposure of the sample through the medium was increased by the fact that there was formation of pores. The EDX results revealed that after roasting, components were homogeneously distributed on the all bulk of the sample.

The SEM/EDX of the selected roasted sample have revealed presence of V and Na scattered through the matrix of the slag confirming the formation of a sodium vanadium phase from the roasting process as shown in Figure 4.7 and Table 4.6.
Table 4.6: Chemical composition of different points of the roasted slag using EDX

<table>
<thead>
<tr>
<th>Element</th>
<th>Point 1</th>
<th>Point 2</th>
<th>Point 3</th>
<th>Point 4</th>
<th>Point 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>17.91</td>
<td>25.80</td>
<td>21.28</td>
<td>18.57</td>
<td>17.08</td>
</tr>
<tr>
<td>Mg</td>
<td>12.40</td>
<td>3.76</td>
<td>13.96</td>
<td>16.25</td>
<td>11.96</td>
</tr>
<tr>
<td>Al</td>
<td>32.97</td>
<td>47.49</td>
<td>41.37</td>
<td>52.28</td>
<td>39.09</td>
</tr>
<tr>
<td>Si</td>
<td>0.97</td>
<td>0.79</td>
<td>0.64</td>
<td>0.56</td>
<td>0.58</td>
</tr>
<tr>
<td>Ca</td>
<td>25.31</td>
<td>17.03</td>
<td>17.81</td>
<td>9.54</td>
<td>26.72</td>
</tr>
<tr>
<td>V</td>
<td>9.49</td>
<td>4.18</td>
<td>3.02</td>
<td>2.19</td>
<td>4.06</td>
</tr>
<tr>
<td>Fe</td>
<td>0.95</td>
<td>0.95</td>
<td>1.91</td>
<td>0.61</td>
<td>0.51</td>
</tr>
</tbody>
</table>

From Table 4.6, the presence of sodium vanadate phases and some impurities leaching phases such as sodium aluminate or sodium silicon were confirmed.
4.3 Acid leaching experiments using a mixture of acids

V leaching was investigated using the chosen roasted slag (900°C, wt. 20% Na₂CO₃) with the mixture of the three organic acids in the conditions of the bioleaching process.

4.3.1 Effect of acid concentration on V dissolution

The effect of acid concentration on the dissolution of V was investigated (25°C, 2% S/L, particles sizes -75µm, 150rpm) and the results are shown in Figure 4.8. It can be seen that variation of acid concentration does not have a strong effect on the leaching process of V from the slag. The extraction was almost the same from 50 to 150mM with an increase at 200mM. This increase might be due to the sufficient protons (H⁺) which destroys the sodium vanadate lattice. After leaching, the pH value ranged from around 9 for 50mM to 4 for 200mM and the potential ranged from -0.2 to 0.2 V. Based on the Pourbaix diagram, the possible species of V stable in this region are: V(OH)_2⁺, V(OH)_3, VO(OH)_3⁺, VO₂(OH)_2⁻, and VO₃(OH)_2⁻ (Takeno, 2005). Sample leached at 200mM had the highest V extraction (54%).

![Figure 4.8: Effect of acid concentration on V-dissolution.](image-url)
4.3.2 Effect of solid-liquid ratio on V dissolution

The effect of solid-liquid ratio was investigated (25°C, 200mM, particles sizes -75µm, 150rpm), and the results are illustrated in Figure 4.9. Although the amount of the dissolved solid per unit liquid increases with solid/liquid ratio increase, the leaching rate decreased. High solid-liquid ratio gives low V extraction.

This is due to the fact that at low S/L ratio, the reaction is more complete and there is no acid starvation. Apart from that, high viscosity of the leaching slurry due to the high solid-liquid ratio render the ions diffusion slower resulting in low leaching efficiencies (Ntita, et al., 2017). The lower solid-liquid ratio (2%) was the optimum. Sample leached at 2% had the highest V extraction (59%).

![Figure 4.9: Effect of solid-liquid ratio on V dissolution](image)

4.3.3 Effect of slag particles size on V dissolution

The effect of slag particles size on V dissolution was investigated (25°C, 200mM, 2% S/L, 150rpm) and the results are shown in Figure 4.10. The results demonstrate that V dissolution increases with decreasing particles size. This is due to the increase in the contact surface per unit weight of solid. This has been proven by many other researchers (Sandström, 2006; Bayrak, et al., 2010; Li, et al., 2016) who demonstrated that the particles size has an
impact on the leaching kinetics in different ways during chemically and diffusion-controlled reactions respectively. In general, smaller particle size yields faster leaching kinetics.

- For chemically controlled leaching, the dependence is proportional to $\frac{1}{r}$
- For diffusion-controlled leaching, the dependence is proportional to $\frac{1}{r^2}$

Where $r$ is the radius of particles

The particle size of -38µm gave the highest leaching efficiency (61.55%) compared to the higher particle sizes.

![Graph showing effect of leaching temperature on V dissolution](image)

**Figure 4.10: Effect of slag particles size on V dissolution.**

### 4.3.4 Effect of leaching temperature on V dissolution

The effect of leaching temperature on dissolution of V was investigated (200mM, 2% S/L, particles sizes -38µm, 150rpm) and the results are shown in Figure 4.11. The results illustrate that dissolution of V increases with increase in temperature. This is in agreement with many researchers (Zhu, et al., 2012; Tavakolikhaledi, 2014; Bayrak, et al., 2010). This is due to the increase in the ions diffusion rate between the leaching reagents and the slag. A dissolution of 59, 74 and 78% of V were obtained at 25, 35 and 45°C for mixed acid.
Temperature was not increased over 45°C because the growth temperature of the microorganisms (*Pseudomonas putida* and *Aspergillus niger*) here mimicked is not over 45°C (Fonseca, et al., 2011; Astoreca, et al., 2007).

![Graph](image)

*Figure 4.11: Effect of temperature on V dissolution.*

### 4.4 Kinetics studies of V dissolution

The dissolution kinetics for the first ten minutes of the leaching process were investigated as the leaching recoveries vary very quickly during this range of time and stabilise afterwards. The results shown in Figure 4.12. From Figure 4.12, it can be seen that the chemically controlled mechanism gives the most probable fittings. There is therefore a linearity between the term $1 - (1 - \alpha)^{1/2}$ and the time of leaching. The curves are not of the type $y = a\alpha$ which would start from the origin of axes but of the type $y = a\alpha + b$. This is justified by the immediate dissolution of the slag sample which makes that $\alpha$ value is not zero at the beginning (Samson, 2009).
\[ y = 0.0109x + 0.1229 \]
\[ R^2 = 0.9778 \]

\[ y = 0.0032x + 0.0125 \]
\[ R^2 = 0.9758 \]

\[ y = 0.0219x + 0.3304 \]
\[ R^2 = 0.9753 \]

\[ \alpha, [1-(1-\alpha)^{\frac{1}{3}}], [1-2/3\alpha-\alpha^{\frac{2}{3}}] \]

\[ y = 0.0207x + 0.1243 \]
\[ R^2 = 0.9989 \]

\[ y = 0.0074x + 0.0096 \]
\[ R^2 = 0.9944 \]

\[ y = 0.0362x + 0.3469 \]
\[ R^2 = 0.9959 \]

\[ y = 0.0207x + 0.1243 \]
\[ R^2 = 0.9989 \]

\[ y = 0.0074x + 0.0096 \]
\[ R^2 = 0.9944 \]
It can be noticed from Figures 4.12 (a), (b) and (c) that very similar correlations (between chemical and diffusion control) were found, however the chemically controlled mechanism gives the best fit in 2 out of the 3 cases plotted.

The slope of the curves in Figure 4.12 are equal to the rate constant which obeys to the law of Arrhenius:

$$k = A e^{-\frac{E_a}{RT}} \quad \text{Equation 4. 1}$$

Where $E_a$ is the activation energy, $T$ the temperature in K and $R$ the ideal-gas constant (8.314 J/Kmol).

This law allows the determination of the activation energy $E_a$ which is the minimal energy required for the reagents to react and be transformed into leaching products.

$\ln k$ vs $1/T$ was then plotted to find the value $-E_a/R$ and the results are shown in Figure 4.13 (a).
For the leaching time proceeding from 10 minutes to 60 minutes, the diffusion controlled was found to be the most probable fitting and its Ln k vs 1/T was also plotted to find the value -Ea/R as seen on Figure 4.13 (b).

**Figure 4.13 (a)**

**Figure 4.13 (b)**

*Figure 4. 13: Arrhenius curve for the first 10 minutes (a) and after 10 minutes (b) of the leaching process*
From Figure 4.13 (a), the slope of the graph is -4156.8 which equals the term \(-\frac{E_a}{R}\). The activation energy was found to be 34 kJ/mol by multiplying the value of the slope by R.

According to Abdel-Aal, (2000), when the activation energy is between 4.2 and 12.6 kJ/mol, then the reaction is diffusion controlled and when the energy is over 42 kJ/mol, the control is purely chemical. The value found for V dissolution for the first 10 minutes is intermediate between a diffusion and chemically controlled reaction. However, the value of the activation energy from 10 to 60 minutes was 13kJ/mol which falls under the diffusion controlled reactions. The Arrhenius plots showed chemical reaction limitation initially which changes to diffusion controlled later. This is a possible explanation for the inability to distinguish entirely between chemical and diffusion control based on the plots of Figure 4.12.

4.5 Aluminium co-leaching in mixed acids

The use of sodium carbonate in the roasting process has the potential of destroying the refractory spinel phase \((\text{MgAl}_2\text{O}_4)\) in the slag. This will lead to leaching of impurities such as the aluminium and magnesium from the slag (Lasheen, 2008). Co-leaching of Al was investigated after leaching for 1 hour, at 25, 35 and 45°C and the results are illustrated in Table 4.7.

Table 4.7: Effect of temperature on Aluminium dissolution

<table>
<thead>
<tr>
<th>Leaching conditions</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 200mM, 25°C, 2% (S/L), 1h</td>
<td>45.72</td>
</tr>
<tr>
<td>Mix 200mM, 35°C, 2% (S/L), 1h</td>
<td>56.99</td>
</tr>
<tr>
<td>Mix 200mM, 45°C, 2% (S/L), 1h</td>
<td>66.29</td>
</tr>
</tbody>
</table>

An average of 45, 56 and 66% Al was dissolved at 25, 35 and 45°C respectively. This increase in Al leaching is justified by the increase in the solubility of Al at higher temperature which is beneficial to the leaching reaction as described by Li, et al. (2016).

4.6 Mineralogical composition of the residues

The XRD analysis of the residues after leaching was done and results are illustrated in Figure 4.14. Vanadium phases have almost disappeared due to the leaching process of V in a form of sodium vanadate. The residue is mostly composed with unreacted spinel which
contains magnesium and other phases such as sodium magnesium silicon and magnesium silicon oxide which justify the insignificant leaching of magnesium and silicon.

*Figure 4. 14: XRD pattern of residue after leaching*

Where p is spinel (MgAl$_2$O$_4$), j: jadeite [NaAl(Si$_2$O$_6$)], n: sodium magnesium silicon [Na(MgSi)(Si$_2$O$_6$)], m: magnesium silicon oxide (MgSiO$_3$) and v: vanadium oxide (V$_2$O$_5$).

The presence of V$_2$O$_5$ in the residue can be justify by a small amount of vanadium oxide which may have not been converted into sodium vanadate during the roasting process.

**4.7 pH values of the leaching solutions**

The pH of the solutions was measured before leaching and the results are shown in Figure 4.15. It is seen from Figure 4.15 that the pH value varies slightly with the different concentration. The Gluonic acid’s pH values are slightly basic while the Citric and Oxalic acid are acidic in nature (Pangayao, et al., 2013). Gluonic acid has an initial pH of 6.7 at 50mM and 7.13 at 200mM. On the other hand, Citric acid has an initial pH of 2.2 at 50mM and 1.87 at 200mM.
Finally, Oxalic acid has initial pH of 2.33 at 50mM and 1.86 at 200mM. The pH values after leaching were 11.9 and 12.3 for 50mM and 200mM of Gluconic acid while 11.9 and 12.3 for 50mM and 200mM of Citric acid and 9.6-4.97 for 50mM and 200mM of Oxalic acid were obtained.

4.8 Vanadium leaching with Gluconic, Citric and Oxalic acids separately

The acid leaching study was performed using Gluconic, Citric and Oxalic acids separately to investigate the V dissolution in each acid at optimum conditions.

4.8.1 Effect of individual acid concentration on V dissolution

The roasted slag was leached using 50, 100, 150 and 200 Mm of Gluconic, Citric and Oxalic acid (25°C, 2% S/L, particles sizes -75µm, 150rpm). The V dissolution by the three acids is represented in Figure 4.16.
Figure 4.16: Effect of acid concentration on V dissolution

Figure 4.16 indicates that the leaching of V from the roasted slag with Gluconic, Citric and Oxalic acid enhanced with the increasing acid concentrations until 150mM for Gluconic and 100mM for Citric and Oxalic acid. Increasing Citric acid and Oxalic acid concentration over 100mM did not lead to an increase V dissolution. Hence, it is more economical to use low concentration of these acids. At these concentrations, the leaching is quicker in the first few minutes but the overall extraction does not increase quickly as seen in Figure 4.17 a, b and c. This might be due to a later dissolution of more impurities because of high concentrations.

Figure 4.17 (a)
Figure 4.17: Effect of time on V dissolution at different concentrations

Gluconic leaching was more efficient than Citric and Oxalic acids. From the E-pH diagram of V as reported in the section 2.2.4 of the chapter 2, the species V (V) is more stable in alkaline media while the species (IV) and (III) are more stable in acidic medium. V from NaVO₃ being in a form of V (V), the Gluconic acid leach more of V (V) than Citric and Oxalic acids.
V dissolution increased rapidly within the first 10 minutes and remained relatively constant after 20 minutes. The dissolution of V at 150mM of Gluconic acid after one hour was 84% and for 100mM of Citric and Oxalic acid were respectively 66% and 47%.

4.8.2 Effect of solid-liquid ratio on V dissolution in individual acid

Variation of solid-liquid ratio was investigated with a constant concentration of 150mM for Gluconic acid and 100mM for Citric and Oxalic acids (25ºC, particles sizes -75µm, 150rpm).

The V recoveries are represented in Figure 4.18. V dissolution decrease with the increase of the solid-liquid ratio. Decreasing the solid-liquid ratio increases the diffusion in the reaction medium which causes the reaction to be more complete and benefit the leaching process.

![Figure 4.18: Effect of solid-liquid ratio on V dissolution for Gluconic, Citric and Oxalic acids](image)

4.8.3 Effect of particles size on V dissolution in individual acid

The effect of particles size was investigated in different particles size fractions and the results are illustrated in Figure 4.19 (25ºC, 2% S/L, 150rpm). It is shown that the particles size
has substantial effect on the dissolution of V. The leaching rate greatly increases with decreasing particles size. This is due to the increase in the contact surface per unit weight of solid. The particle size of -38µm gave the highest leaching efficiency compared to the higher particles size used for all the three acids.

![Graph showing the effect of particles size on V dissolution for Gluconic, Citric and Oxalic acids](image)

**Figure 4.19: Effect of particles size on V dissolution for Gluconic, Citric and Oxalic acids**

**4.8.4 Effect of leaching temperature on V dissolution in individual acid**

The dissolution of V is represented in Figure 4.20 (2% S/L, particles sizes -38µm, 150rpm). Results showed temperature to be of importance for leaching yields of V with a positive effect. V dissolution enhanced with the temperature increase. This is due to the raising of the ions diffusion rate between the leaching reagents and the slag (Ntita, et al., 2017). An average of 90, 88 and 80% recovery of V were obtained at 45°C for Gluconic, Citric and Oxalic acids respectively.
Figure 4. 20: Effect of leaching temperature on V dissolution for Gluconic, Citric and Oxalic acids

4.9 Aluminium co-leaching in individual acid

An investigation was done on the co-leaching of Al during the leaching process using individual acid in their optimum leaching conditions and results are presented on Table 4.8.

Table 4. 8: Al leaching in Gluconic, Citric and Oxalic acids at the optimum V leaching conditions

<table>
<thead>
<tr>
<th>Leaching conditions</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gl 150mM, 45°C, 2% (S/L), -38um, 1h</td>
<td>60.31</td>
</tr>
<tr>
<td>Cit 100mM, 45°C, 2% (S/L), -38um, 1h</td>
<td>72.80</td>
</tr>
<tr>
<td>Ox 100mM, 45°C, 2% (S/L), -38um, 1h</td>
<td>73.71</td>
</tr>
</tbody>
</table>

Gluconic acid leached less Al followed by Citric and Oxalic acid. Leaching of Al with Gluconic acid was proved to be effective by Amin & Refat. (2013) who showed that the possible reaction of Al with Gluconic acid can be summarized as followed:

\[ Al + G^- \rightleftharpoons Al(G)_{ads}^- \]

\[ Al(G)_{ads}^- + nH_2O \rightleftharpoons Al(H_2O)_n^{3+} + G^- + 3e^- \]

where Eq. 4.2 is the dissolution step and Al(H_2O)_n^{3+} represents the solvated Al^{3+} ion.
The slight difference in percent dissolution of Al in Citric acid as compared to Oxalic acid might have been caused by inhibition of Al leaching in Citric acid as demonstrated by Solmaz, et al., (2013). Oxalic acid was much more efficient in Al leaching and this confirms results found by Urík, et al. (2018) and Kyriakogona, et al. (2017).
CONCLUSIONS

This research has been done to investigate the recovery of V from a V bearing slag using commercial organic acids mimicking a bioleaching process. After reception, the slag was characterised using XRF, XRD, SEM/EDX and the results showed presence of V in a form of insoluble V-oxide at a percentage of 4.58.

V slag was then submitted to a sodium carbonate roasting in order to convert the insoluble V-oxide phase in a soluble sodium vanadate phase before the leaching process. The optimum roasting conditions were found to 900ºC with 20% wt of Na$_2$CO$_3$.

Roasted V slag was submitted to a leaching process using a mixture of Gluconic, Citric and Oxalic acid in equal volumes of similar concentration. The optimum conditions were found to be 200 mM of concentration, 2% S/L ratio, -38um particles size and 45ºC with an average V dissolution percentage of 78%.

The kinetics study of the leaching process using the mixed acid revealed that the first ten minutes of the leaching process was intermediate between a diffusion and chemically controlled reaction (activation energy of 34 kJ/mol) while the last leaching period was diffusion controlled (activation energy of 13kJ/mol).

Leaching in individual acid revealed that all acids leached V efficiently with a dissolution of 90, 88 and 80% for Gluconic, Citric and Oxalic acid respectively. Dissolution of V enhanced with increase in concentration of Gluconic acid until a concentration of 150mM whilst maximum dissolution of V in Citric and Oxalic acid was at a concentration of 100mM.

Aluminium co-leaching was also noticed during the leaching process with Oxalic acid revealing the highest contribution (73%) followed by Citric (72%) and then Gluconic acid (60%).

RECOMMENDATIONS

The study was about mimicking a bioleaching process, it is recommended that studies can be carried out using microorganisms to evaluate this simulation and study the leaching mechanism. Further studies can be carried to try and separate V from Al in order to purify the leachate.
**APPENDIX**

**APPENDIX 1: DISSOLUTION TESTS RESULTS**

Table 1.A: Dissolution tests of raw and slag roasted at 800°C in 50mM of Gluconic, Citric, Oxalic and Mixed acids

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>800°C, 10% Na₂CO₃</th>
<th>800°C, 20% Na₂CO₃</th>
<th>800°C, 30% Na₂CO₃</th>
<th>800°C, 40% Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gl</td>
<td>cit</td>
<td>ox</td>
<td>mix</td>
<td>Gl</td>
</tr>
<tr>
<td>V</td>
<td>1.97</td>
<td>2.53</td>
<td>3.89</td>
<td>2.70</td>
<td>18.21</td>
</tr>
</tbody>
</table>

Table 1.B: Dissolution tests of slag roasted at 900°C in 50mM of Gluconic, Citric, Oxalic and Mixed acids

<table>
<thead>
<tr>
<th></th>
<th>900°C, 10% Na₂CO₃</th>
<th>900°C, 20% Na₂CO₃</th>
<th>900°C, 30% Na₂CO₃</th>
<th>900°C, 40% Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gl</td>
<td>Ct</td>
<td>Ox</td>
<td>Mix</td>
</tr>
<tr>
<td>V</td>
<td>37.43</td>
<td>23.23</td>
<td>20.49</td>
<td>20.02</td>
</tr>
<tr>
<td>Al</td>
<td>17.45</td>
<td>17.73</td>
<td>32.17</td>
<td>16.00</td>
</tr>
</tbody>
</table>

Table 1.C: Dissolution tests of slag roasted at 1000°C in 50mM of Gluconic, Citric, Oxalic and Mixed acids

<table>
<thead>
<tr>
<th></th>
<th>1000°C, 10% Na₂CO₃</th>
<th>1000°C, 20% Na₂CO₃</th>
<th>1000°C, 30% Na₂CO₃</th>
<th>1000°C, 40% Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gl</td>
<td>cit</td>
<td>ox</td>
<td>mix</td>
</tr>
<tr>
<td>V</td>
<td>43.07</td>
<td>38.80</td>
<td>34.95</td>
<td>36.40</td>
</tr>
<tr>
<td>Al</td>
<td>37.11</td>
<td>36.61</td>
<td>46.11</td>
<td>37.62</td>
</tr>
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</table>
APPENDIX 2: ACID LEACHING EXPERIMENTS USING A MIXTURE OF GLUCONIC, CITRIC AND OXALIC ACIDS

Table 2.A: Effect of acid concentration on V dissolution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>50mM</th>
<th>100mM</th>
<th>150mM</th>
<th>200mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41,27</td>
<td>40,62</td>
<td>40,74</td>
<td>36,75</td>
</tr>
<tr>
<td>2</td>
<td>41,50</td>
<td>40,58</td>
<td>40,69</td>
<td>51,32</td>
</tr>
<tr>
<td>4</td>
<td>43,23</td>
<td>40,60</td>
<td>41,59</td>
<td>52,26</td>
</tr>
<tr>
<td>8</td>
<td>44,64</td>
<td>41,18</td>
<td>42,11</td>
<td>53,34</td>
</tr>
<tr>
<td>10</td>
<td>45,09</td>
<td>41,46</td>
<td>42,58</td>
<td>53,49</td>
</tr>
<tr>
<td>20</td>
<td>46,37</td>
<td>42,69</td>
<td>43,50</td>
<td>53,56</td>
</tr>
<tr>
<td>30</td>
<td>46,55</td>
<td>44,47</td>
<td>45,03</td>
<td>53,54</td>
</tr>
<tr>
<td>60</td>
<td>44,77</td>
<td>45,75</td>
<td>44,66</td>
<td>54,44</td>
</tr>
</tbody>
</table>

Table 2.B: Effect of solid-liquid ratio on V dissolution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>2%</th>
<th>4%</th>
<th>6%</th>
<th>8%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41,88</td>
<td>29,79</td>
<td>29,86</td>
<td>24,96</td>
<td>19,56</td>
</tr>
<tr>
<td>2</td>
<td>55,94</td>
<td>30,61</td>
<td>29,73</td>
<td>25,28</td>
<td>20,86</td>
</tr>
<tr>
<td>4</td>
<td>56,33</td>
<td>31,44</td>
<td>30,63</td>
<td>23,79</td>
<td>22,14</td>
</tr>
<tr>
<td>8</td>
<td>56,56</td>
<td>31,45</td>
<td>30,57</td>
<td>25,75</td>
<td>23,04</td>
</tr>
<tr>
<td>10</td>
<td>56,99</td>
<td>34,06</td>
<td>30,82</td>
<td>24,76</td>
<td>24,34</td>
</tr>
<tr>
<td>20</td>
<td>57,31</td>
<td>35,61</td>
<td>30,36</td>
<td>25,28</td>
<td>27,11</td>
</tr>
<tr>
<td>30</td>
<td>57,60</td>
<td>35,54</td>
<td>30,40</td>
<td>25,81</td>
<td>27,65</td>
</tr>
<tr>
<td>60</td>
<td>59,18</td>
<td>36,16</td>
<td>31,70</td>
<td>28,75</td>
<td>27,68</td>
</tr>
</tbody>
</table>

Table 2.C: Effect of particles size on V dissolution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>-38um</th>
<th>-75+53um</th>
<th>-150+106um</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50,42</td>
<td>40,70</td>
<td>31,26</td>
</tr>
<tr>
<td>2</td>
<td>52,44</td>
<td>41,22</td>
<td>31,62</td>
</tr>
<tr>
<td>4</td>
<td>54,55</td>
<td>41,52</td>
<td>31,68</td>
</tr>
<tr>
<td>8</td>
<td>57,81</td>
<td>42,12</td>
<td>32,44</td>
</tr>
<tr>
<td>10</td>
<td>56,39</td>
<td>42,14</td>
<td>33,00</td>
</tr>
<tr>
<td>20</td>
<td>60,25</td>
<td>42,51</td>
<td>33,25</td>
</tr>
<tr>
<td>30</td>
<td>61,52</td>
<td>43,05</td>
<td>33,67</td>
</tr>
<tr>
<td>60</td>
<td>61,55</td>
<td>43,23</td>
<td>33,97</td>
</tr>
</tbody>
</table>
Table 2.D: Effect of leaching temperature on V dissolution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mix 25ºC</th>
<th>Mix 35ºC</th>
<th>Mix 45ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.62</td>
<td>37.12</td>
<td>38.05</td>
</tr>
<tr>
<td>2</td>
<td>39.27</td>
<td>42.78</td>
<td>42.06</td>
</tr>
<tr>
<td>4</td>
<td>42.06</td>
<td>49.62</td>
<td>47.36</td>
</tr>
<tr>
<td>8</td>
<td>49.56</td>
<td>64.28</td>
<td>67.31</td>
</tr>
<tr>
<td>10</td>
<td>55.37</td>
<td>70.16</td>
<td>76.51</td>
</tr>
<tr>
<td>20</td>
<td>56.94</td>
<td>71.06</td>
<td>76.88</td>
</tr>
<tr>
<td>30</td>
<td>57.36</td>
<td>72.08</td>
<td>77.55</td>
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<tr>
<td>60</td>
<td>59.72</td>
<td>74.02</td>
<td>78.72</td>
</tr>
</tbody>
</table>

APPENDIX 3: KINETICS STUDIES

Table 3.A: Shrinking core model terms calculation

<table>
<thead>
<tr>
<th>Temperature º C</th>
<th>Time (min)</th>
<th>Vanadium Leached fraction (α)</th>
<th>$1 - (1 - \alpha)^{1/3}$</th>
<th>$\frac{2}{3}\alpha - (1 - \alpha)^{2/3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25ºC</td>
<td>1</td>
<td>0.33</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.39</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.42</td>
<td>0.17</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.49</td>
<td>0.20</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.55</td>
<td>0.24</td>
<td>0.05</td>
</tr>
<tr>
<td>35ºC</td>
<td>1</td>
<td>0.37</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.42</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.49</td>
<td>0.20</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.64</td>
<td>0.29</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.70</td>
<td>0.33</td>
<td>0.08</td>
</tr>
<tr>
<td>45ºC</td>
<td>1</td>
<td>0.38</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.42</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.47</td>
<td>0.19</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.67</td>
<td>0.31</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.76</td>
<td>0.38</td>
<td>0.10</td>
</tr>
</tbody>
</table>
APPENDIX 4: VANADIUM LEACHING WITH INDIVIDUAL ACIDS

Table 4.A: Effect of individual acid concentration on V dissolution

<table>
<thead>
<tr>
<th>Concentration mM</th>
<th>V dissolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gluconic</td>
</tr>
<tr>
<td>50</td>
<td>55.41</td>
</tr>
<tr>
<td>100</td>
<td>68.14</td>
</tr>
<tr>
<td>150</td>
<td>84.04</td>
</tr>
<tr>
<td>200</td>
<td>85.94</td>
</tr>
</tbody>
</table>

Table 4.B: Effect of solid-liquid ratio on V dissolution with individual acids

<table>
<thead>
<tr>
<th>S/L</th>
<th>V dissolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gluconic</td>
</tr>
<tr>
<td>2</td>
<td>85.18</td>
</tr>
<tr>
<td>4</td>
<td>74.11</td>
</tr>
<tr>
<td>6</td>
<td>53.75</td>
</tr>
<tr>
<td>8</td>
<td>49.66</td>
</tr>
<tr>
<td>10</td>
<td>47.38</td>
</tr>
</tbody>
</table>

Table 4.C: Effect of particles size on V dissolution with individual acids

<table>
<thead>
<tr>
<th>S/L</th>
<th>V dissolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-38µm</td>
<td>81.28</td>
</tr>
<tr>
<td>-75+53µm</td>
<td>41.94</td>
</tr>
<tr>
<td>-150+106µm</td>
<td>39.33</td>
</tr>
</tbody>
</table>

Table 4.D: Effect of leaching temperature on V dissolution with individual acids

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>V dissolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gluconic</td>
</tr>
<tr>
<td>25</td>
<td>81.28</td>
</tr>
<tr>
<td>35</td>
<td>90.43</td>
</tr>
<tr>
<td>45</td>
<td>91.79</td>
</tr>
</tbody>
</table>
APPENDIX 5: pH OF ORGANIC SOLUTIONS

Table 5.A: pH of the Gluconic, Citric and Oxalic acids solutions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Gluconic pH</th>
<th>Citric pH</th>
<th>Oxalic pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mM</td>
<td>6.73</td>
<td>2.2</td>
<td>2.33</td>
</tr>
<tr>
<td>100 mM</td>
<td>6.88</td>
<td>2.02</td>
<td>2.05</td>
</tr>
<tr>
<td>150 mM</td>
<td>7.01</td>
<td>1.94</td>
<td>1.96</td>
</tr>
<tr>
<td>200 mM</td>
<td>7.13</td>
<td>1.87</td>
<td>1.86</td>
</tr>
</tbody>
</table>

APPENDIX 6: ROASTING EXPERIMENTAL CONDITIONS

Table 6.A: Roasting experimental conditions

<table>
<thead>
<tr>
<th>Na$_2$CO$_3$</th>
<th>800 ºC</th>
<th>900 ºC</th>
<th>1000 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>20%</td>
<td>30%</td>
<td>40%</td>
</tr>
<tr>
<td>10%</td>
<td>20%</td>
<td>30%</td>
<td>40%</td>
</tr>
<tr>
<td>10%</td>
<td>20%</td>
<td>30%</td>
<td>40%</td>
</tr>
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Jose , L. T., Santamaria, R. & Gregorio, F. O., 2007. Tin–carbon composites as anodic material in Li-ion batteries obtained by copyrolysis of petroleum vacuum residue and SnO2. 7(45), pp. 1396-1409.


Tirado L, J. et al., 2007. Tin–carbon composites as anodic material in Li-ion batteries obtained by copyrolysis of petroleum vacuum residue and SnO2. j.carbon., 7(45), pp. 1396-1409.


