

# Kinetics of Vanadium Bearing Slag Leaching with a Mixture of Organic Acids

J. Ntita, W.Nheta and O. O. Ola-omole

**Abstract**— An environmentally-friendly method based on hydrometallurgy was examined for the extraction of Vanadium (V) from vanadium steel slag using a mixture of organic acids. This method was utilized to mimic a bioleaching process of vanadium slag with microorganisms such as *Pseudomonas putida* which produce organic acids that act as leaching agents. A slag roasted with sodium carbonate was leached using a mixture of Gluconic, Citric and Oxalic acid (mixed in equal volumes of similar concentration) under the growing conditions of the microorganisms considered. The impact of various parameters such as acid concentration, solid-liquid ratio, particle size and temperature were examined. It was discovered that leaching with the mixed organic acids in the optimum conditions gave a V dissolution of 78%. The kinetics of the leaching process revealed 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 initial ten minutes of the leaching process. After 10 minutes, the dissolution is a diffusion controlled reaction with an activation energy of 13kJ/mol. The main impurity (Al) was remarkably co-leached at an average of 66%.

**Keywords**— Bioleaching, waste treatment, leaching kinetics, vanadium extraction.

## I. INTRODUCTION

Extraction of metals from waste materials and by-products from industries have been broadly investigated for the purpose of environmental compliance and economic gain. The growing amount of valuable by-products such as slags has made the steelmaking industry more interested in this research area [1], [2]. Hazardous components such as V contained in the slags make the examination of their ecological impact and the possible mitigation thereof vital [3]. Vanadium imparts properties such as fatigue resistance, tensile strength and hardness to ferrous and nonferrous alloys.

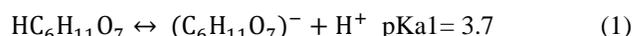
Distinctive techniques have been proposed to extract V from ores and slag. V extraction by roast-leaching of slag was detailed by [4]. As indicated by this technique, addition of a sodium compound (sodium salt) helps to alter the vanadium

calcium oxide ( $\text{Ca}_2\text{V}_2\text{O}_7$ ) phase to a vanadium sodium oxide ( $\text{NaVO}_3$ ), which is more leachable by acids. The calcium is then found in a new phase ( $\text{CaCO}_3$ ) which can be calcined into CaO and  $\text{CO}_2$  at high temperatures ( $825^\circ\text{C}$ ). Such techniques of extraction led to large acid consumption and creation of expensive volumes of potentially hazardous liquid and volatile waste. The prominent cost and harmful effect of these recovery techniques has prompted examination of bioleaching as an innovative option for V extraction from solid wastes.

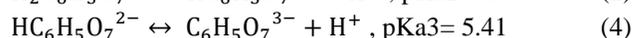
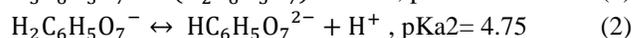
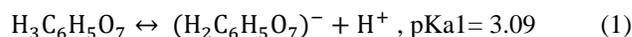
Many researchers have been researching the leaching of vanadium using microorganisms, but few materials have been displayed on the leaching of V with organic acids. Bioleaching depends on the capacity of microorganisms to produce acids from the metabolism of organic or inorganic compounds, which in turn can be utilised for the leaching of solid compounds [1]. Chemolitho-autotrophic microorganisms from the Acidithiobacillus and Leptosperillum species generally produce acidic ferric solution from iron and sulphur-bearing minerals which is used for the leaching of value-bearing sulphides. Some Heterotrophic bacteria and fungi such as Penicillium and Aspergillus species have also been used to recover metals from non-sulphide ores and minerals [5].

Microorganisms can mobilise metals by the formation of organic acids from organic nutrients, oxidation-reduction reactions, extraction by complexing agents and by chelate formation. Bioleaching with ferric ions is not appropriate for the leaching of solid waste materials in oxide, carbonate or silicate form. Such waste can rather be leached by organic acids (such as citric, oxalic or gluconic acid), which are produced by heterotrophic microorganisms such as Aspergillus niger [6].

The dissociation of organic acids relies on the functional group present. Gluconic acid is dissociated in one step as shown in equation (1), producing only one mole of  $\text{H}^+$  per mole of gluconic acid.



Citric acid can be dissociated according to the three steps shown in equations (2) to (4), thereby producing three  $\text{H}^+$  ions in solution [7].



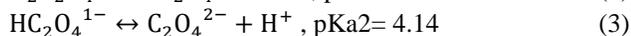
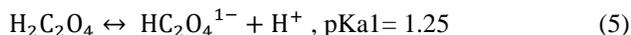
Oxalic acid dissociates in two steps giving two moles of  $\text{H}^+$  per mole of acid used in the leaching process according to equations 5 and 6.

Manuscript received October 14, 2014. This work was supported by University of Johannesburg.

J. Ntita, is with Mineral Processing Research and Technology center Metallurgy Department, University of Johannesburg, South Africa.

W. Nheta, is with Mineral Processing Research and Technology center Metallurgy Department, University of Johannesburg, South Africa..

O. O. Ola-omole, is with Mineral Processing Research and Technology center Metallurgy Department, University of Johannesburg, South Africa.



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 the pathway by which the reaction happens or as the rate controlling step (kinetic mechanism) of the reaction. The slowest step is the rate-limiting step of the overall leaching process. During leaching, the rate-limiting step could change, from being a chemical reaction limited to fresh material for example to being limited by diffusion through the product layer at an advanced stage of the leaching process.

The shrinking core model (SCM) is frequently used to analyse kinetic data. This model assumes that the leaching process is controlled either by external diffusion, chemical reaction or diffusion through the ash layer. Using the SCM model, the leaching kinetics can be depicted by the following expressions:

If diffusion through the liquid film is the controlling mechanism, equation 7 is usually applicable assuming spherical geometry of the ore particle.

$$\alpha = k_1 \cdot t \quad (7)$$

Where  $k_1$  is the rate 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:

$$1 - (1 - \alpha)^{1/3} = k_1 \cdot t \quad (8)$$

If diffusion through the ash layer is the controlling mechanism for small particles in the stokes regime, equation (9) is applied.

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = k_2 \cdot t \quad (9)$$

Where  $k_2$  is the rate constant and  $\alpha$  the leaching fraction of the metal.

The distinction in the leaching rate at two stages suggest a different controlling step in each stage. The controlling mechanism's plot is linear with time (t).

In this paper, leaching of V from a V-slag was investigated using a mixture of gluconic, citric and oxalic acids. Low acid concentrations were used to simulate a bioleaching process. The impact of different parameters such as acid concentration, solid/liquid ratio, particles size and temperature on the rate of dissolution were investigated. This study is aimed at determining the kinetics of the dissolution reactions.

## II. EXPERIMENTAL

### A. Instruments and reagents

The slag was obtained from a vanadium steel making plant situated in North West province, South Africa. All reagents (organic acids and sodium carbonate) used were analytical grade (99% purity) and sourced from Merck, South Africa. The elemental composition of the raw and roasted slag was

determined using X-ray Fluorescence Spectrometer (XRF) Rigaku ZSX Primus II. The mineralogy of the slag was investigated using X-ray Diffraction (XRD) Rigaku Ultima IV and the study of the slag morphology was processed using SEM/EDX Vega 3 XMU.

### B. Leaching experiments

The slag sample was ground to 100% passing 75 $\mu\text{m}$  in a pulveriser to completely expose all metal surface to the leaching solution. It was then blended with sodium carbonate in a weight proportion of 80% Slag – 20%  $\text{Na}_2\text{CO}_3$  and roasted at 900°C according to our recent work [2].

The leaching tests were executed in a water bath using 250ml conical flasks under different conditions. Once the experimental temperature (25, 35 or 45°C) was reached, the slag (mass depending on the solid/liquid ratio) was added and stirring was initiated at 150 rpm.

After leaching, the slurry was filtered and the filtrate was analysed using a Thermo scientific atomic absorption spectrometer (AAS). The % dissolution of V was calculated using equation 10.

$$\% \text{ dissolution} = [\text{Vs}] \cdot \text{Vol[s]} / (\text{m} \cdot \text{V[g]}) \cdot 100 \quad (10)$$

where [Vs]: Vanadium concentration in solution [mg/L]

Vol[s]: Volume of the solution [L]

m: Mass slag [mg]

V[g]: Vanadium grade in slag

### C. Kinetic studies

The kinetic studies were done during the bioleaching simulation to determine the mechanism controlling the dissolution process. To achieve this, the shrinking 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 these results, the terms  $\alpha$ ,  $1 - (1 - \alpha)^{1/3}$  and  $1 - 2/3\alpha - (1 - \alpha)^{2/3}$  were calculated corresponding to the diffusion through the liquid layer, chemically and diffusion through the ash layer controlled reactions. The terms  $\alpha$ ,  $1 - (1 - \alpha)^{1/3}$  and  $1 - 2/3\alpha - (1 - \alpha)^{2/3}$  vs time were then plotted.

## III. RESULTS AND DISCUSSION

### D. Slag Characterisation

The chemical composition of the roasted slag according to the procedure detailed by [2] was analysed using XRF and the results are shown in Table 1.

TABLE I: CHEMICAL COMPOSITION OF THE ROASTED SLAG

Component	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>
% Oxide	3.25	7.03	61.49	1.54	18.94	4.58	0.84

The slag contains a considerable amount of V which can be recovered. The Al oxide content in the slag was very high due to the preceding smelting process where Al was added as a reagent to react with V<sub>2</sub>O<sub>5</sub> flasks to form ferrovanadium.

The XRD analysis was done to assess the phases in the roasted slag and the results are shown in Fig. 1. With an

increase of the temperature to 900°C, sodium vanadate ( $\text{NaVO}_3$ ) peaks intensity improved with elimination of vanadium oxide ( $\text{V}_2\text{O}_5$ ) peaks. At this temperature, there is an increase in sodium aluminium ( $\text{Na}_2\text{Al}_2(\text{Si})\text{O}_4$ ) peak with a slight decrease of spinel phase ( $\text{MgAl}_2\text{O}_4$ ) confirming the breakdown of the spinel phase.

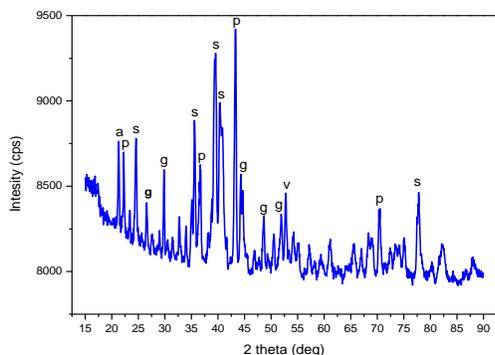


Fig.1. XRD pattern of roasted slag

Where p is spinel ( $\text{MgAl}_2\text{O}_4$ ), g: grossite ( $\text{CaAl}_4\text{O}_7$ ), a: sodium aluminium oxide ( $\text{Na}_2\text{Al}_2\text{O}_4$ ), s: sodium vanadate ( $\text{NaVO}_3$ ), c: calcium aluminosilicate ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ .) and v: vanadium oxide ( $\text{V}_2\text{O}_5$ ).

The SEM analysis as well as EDX were performed on the roasted sample to investigate both the morphological aspect as well as the distribution of components and the results are shown in Fig. 2 and Table 2. It was noticed that on the roasted sample, the surface exposure of the sample throughout the medium was increased by the fact that there was formation of pores. The SEM/EDX of the roasted sample also revealed the presence of V and Na scattered throughout the matrix of the slag confirming the formation of a sodium vanadium phase from the roasting process.

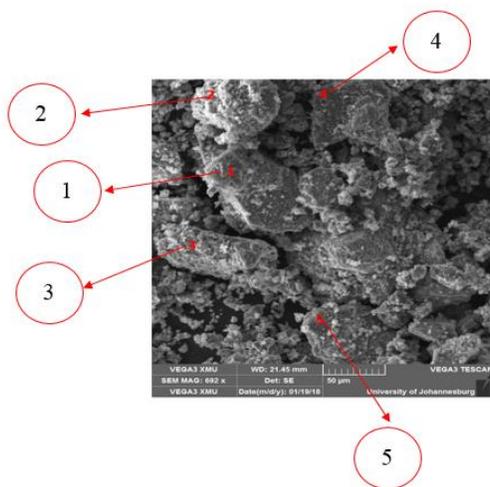


Fig. 2. Micrograph of the roasted slag

TABLE II: CHEMICAL COMPOSITION OF POINTS (1-5) OF THE ROASTED SLAG USING EDX

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

From Table 2, the presence of sodium vanadate phases and some impurity leaching phases such as sodium aluminate or sodium silicon were confirmed.

#### E. Acid leaching experiments using a mixture of acids

V leaching was investigated using roasted slag (900°C, wt. 20%  $\text{Na}_2\text{CO}_3$ ) with the mixture of the three organic acids under the conditions of a bioleaching process. The effects of acid concentration, solid/liquid ratio, particles size and temperature on the leaching process were determined.

#### F. Effect of acid concentration on V dissolution

The effect of acid concentration on the dissolution of V was examined and the results are shown in Fig. 3. It can be seen that variation of acid concentration does not strongly affect the leaching process of V from the slag. The extraction was nearly the same from 50 to 150mM with an increase at 200mM. This increase might be due to the sufficient protons ( $\text{H}^+$ ) which destroys the sodium vanadate lattice. After the leaching process, 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:  $\text{V}(\text{OH})_2^+$ ,  $\text{V}(\text{OH})_3$ ,  $\text{VO}(\text{OH})^+$ ,  $\text{VO}_2(\text{OH})_2^-$ , and  $\text{VO}_3(\text{OH})_2^-$ . The sample leached at 200mM had the highest V dissolution (54%).

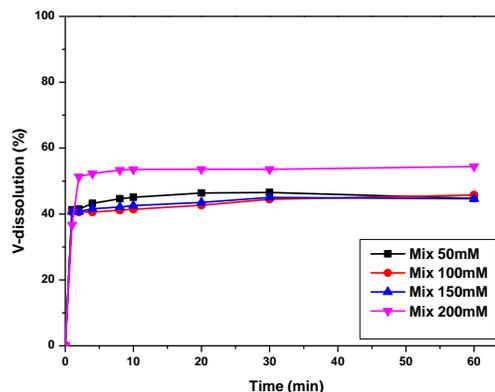


Fig. 3. Effect of acid concentration on V-dissolution

#### G. Effect of solid-liquid ratio on V dissolution

The impact of solid-liquid ratio was investigated and the results are illustrated in Fig. 4. Although the amount of the dissolved solid per unit liquid increased with an increase in

solid/liquid (S/L) ratio, the leaching rate decreased. High solid-liquid ratio gave low V dissolution. 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 S/L ratio render the diffusion of ions slower resulting in low leaching efficiencies. The lower S/L ratio (2%) was the optimum and had the highest V dissolution (59%).

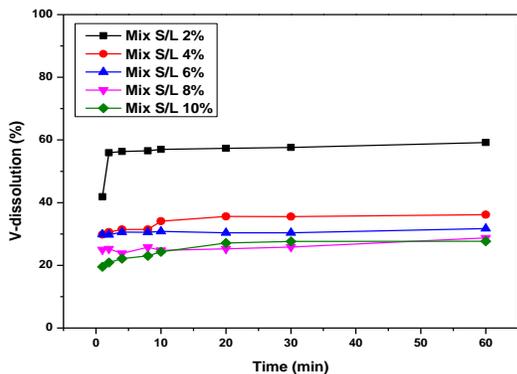


Fig. 4. Effect of solid-liquid ratio on V dissolution

H. Effect of particles size on V dissolution

The effect of slag particle size on V dissolution was investigated and the results are presented in Fig. 5. The outcomes demonstrate that V dissolution increases with decreasing particles size. This is because of the increase in the contact surface area per unit weight of solid. In general, smaller particle size yields faster leaching kinetics.

For chemically controlled leaching, the dependence is proportional to 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 larger particle sizes.

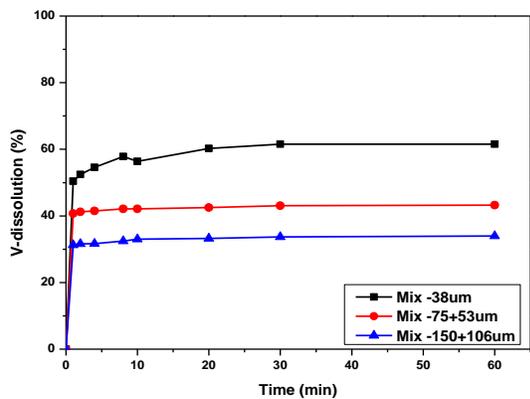


Fig. 5. Effect of slag particle size on V dissolution.

I. Effect of leaching temperature on V dissolution

The effect of leaching temperature on dissolution of V was explored and the outcomes are shown in Fig. 6. The results showed that dissolution of V increases with increase in temperature. This is because of 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 respectively.

The 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 [8].

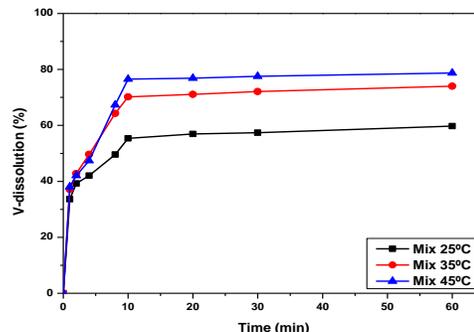
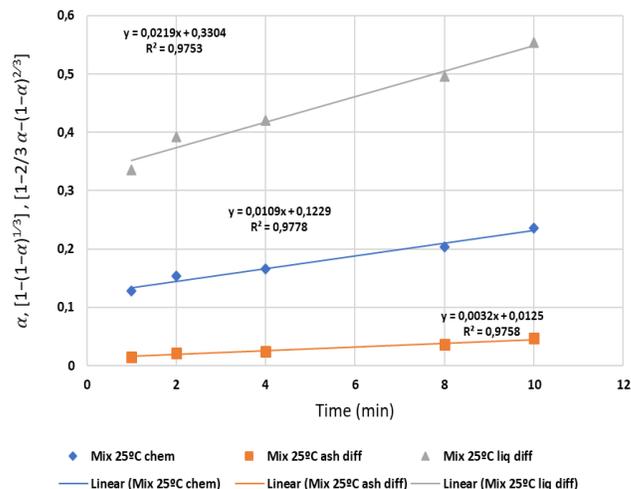


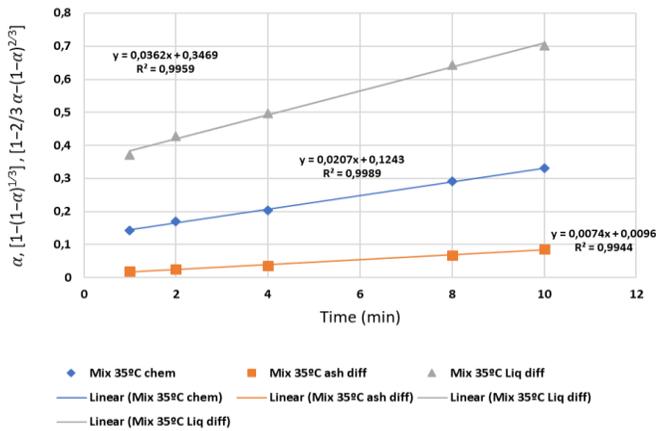
Fig. 6. Effect of temperature on V dissolution

J. Kinetics studies of V dissolution

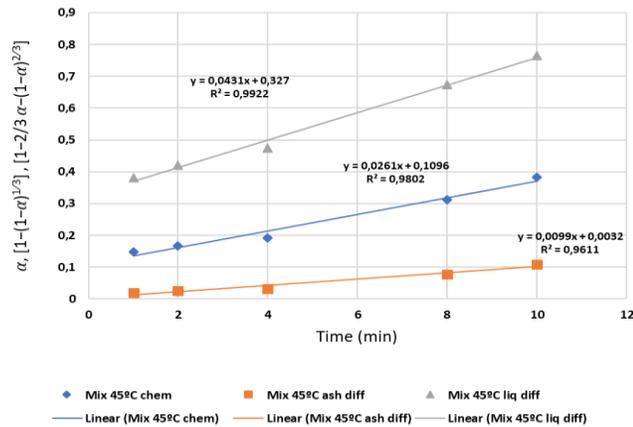
The dissolution kinetics for the initial ten minutes of the leaching process was analysed and the results are shown in Fig. 7. From Fig. 7, it can be seen that the chemically controlled mechanism gives the most probable fittings. There is therefore a linearity between the term  $1 - (1 - \alpha)^{1/3}$  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 the  $\alpha$  value not zero at the beginning.



7(a)



7(b)



7(c)

Fig. 1. Curves of  $\alpha$ ,  $1 - (1 - \alpha)^{1/3}$  and  $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$  vs time at different temperatures

It can be noticed from Figures 7 (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 Fig. 7 are equal to the rate constant which obeys to the law of Arrhenius:

$$k = A e^{\frac{-E_a}{RT}} \quad (11)$$

Where  $E_a$  is the activation energy,  $T$  the temperature in K and  $R$  the ideal-gas constant (8.314J/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 Fig. 8 (a).

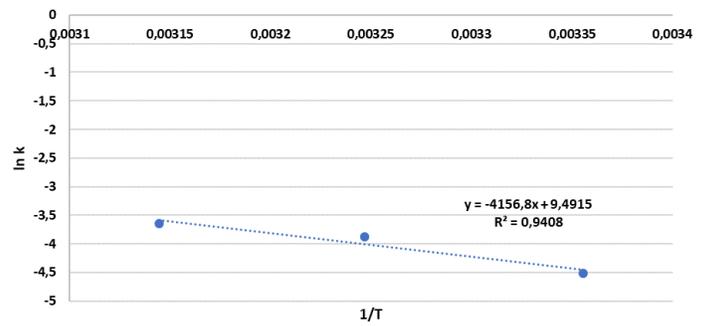


Figure 8 (a)

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  $-E_a/R$  as shown on Fig. 8 (b).

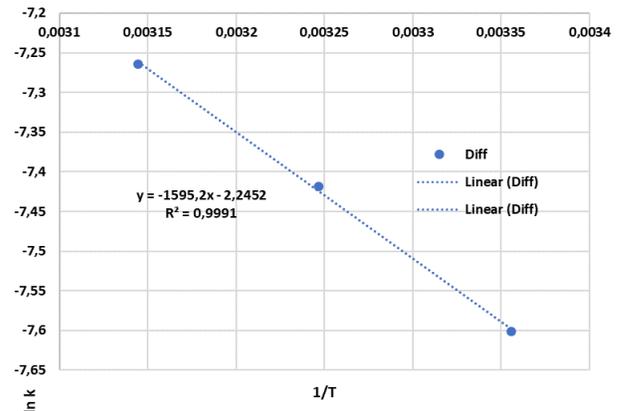


Figure 8 (b)

Fig. 8. Arrhenius curve for the first 10 minutes (a) and after 10 minutes (b) of the leaching process

From Fig. 8 (a), the slope of the graph is -4156.8 which equals the term  $(-E_a/R)$ . The activation energy was found to be 34 kJ/mol by multiplying the value of the slope by R.

As indicated by [9], 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 Fig. 7.

### K. Aluminium co-leaching in mixed acids

The use of sodium carbonate in the roasting process has the potential of destroying the refractory spinel phase ( $MgAl_2O_4$ ) in the slag. This will lead to leaching of impurities such as the aluminium and magnesium from the slag. Co-leaching of Al was investigated after leaching for 1 hour, at 25, 35 and 45°C and the results are illustrated in Table 3.

TABLE III: EFFECT OF TEMPERATURE ON ALUMINIUM DISSOLUTION LEACHING CONDITIONS AL (%)

Leaching conditions	Al (%)
Mix 200mM, 25°C, 2% (S/L), 1h	45,72
Mix 200mM, 35°C, 2% (S/L), 1h	56,99
Mix 200mM, 45°C, 2% (S/L), 1h	66,29

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 temperatures which is beneficial to the leaching reaction as described by [10].

#### L. Mineralogical composition of the leaching residues

The XRD analysis of the residues after leaching was done and results are illustrated in Fig. 9. 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.

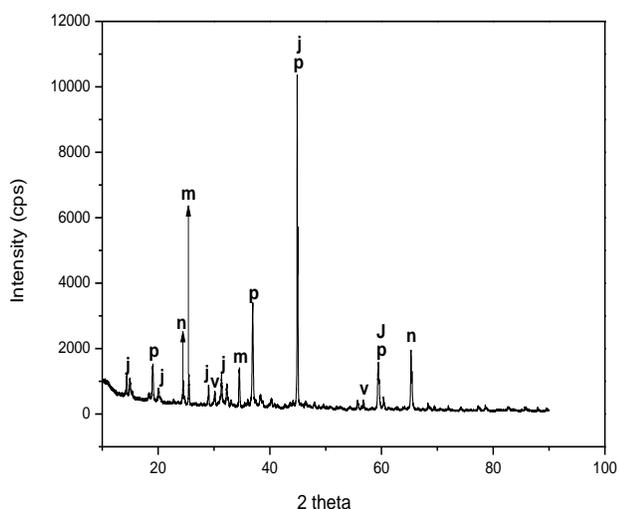


Fig. 9. XRD pattern of residue after leaching

Where p is spinel ( $MgAl_2O_4$ ), j: jadeite [ $NaAl(Si_2O_6)$ ], n: sodium magnesium silicate [ $Na(Mg Si)(Si_2O_6)$ ], m: magnesium silicate ( $MgSiO_3$ ) and v: vanadium oxide ( $V_2O_5$ ).

The presence of  $V_2O_5$  in the residue can be justified by a small amount of vanadium oxide which may have not been converted into sodium vanadate during the roasting process.

#### IV. CONCLUSION

In this research, leaching kinetics of V from a vanadium bearing slag was investigated using commercial organic acids and mimicking a bioleaching process. The leaching parameters were optimised and leaching kinetics was investigated systematically. The kinetic studies revealed that the leaching process was an intermediate between a diffusion and

chemically controlled reaction within the first 10 minutes of leaching with an activation energy of 34 kJ/mol. With further leaching, the process became a diffusion controlled reaction with an activation energy of 13kJ/mol. Dissolution of V increased with increase in leaching temperature as well as that of Al that was co-leached. Further work needs to be done leaching the V bearing slag using microorganism and on the removal of Al from the slag.

#### ACKNOWLEDGMENT

The authors would like to acknowledge the University of Johannesburg for funding of the project.

#### REFERENCES

- [1] C. Erust, A. Akcil, Z. Bedelova, K. Anarbekov, A. Baikonurova, and A. Tuncuk, "Recovery of vanadium from spent catalysts of sulfuric acid plant by using inorganic and organic acids: laboratory and semi-pilot tests," *Waste Management*, vol. 49, pp.455-461, 2016. <https://doi.org/10.1016/j.wasman.2015.12.002>
- [2] J. Ntita, W. Nheta, and P.V. Staden, "Selective Leaching of Vanadium from Vanadium Slag using Organic Acids. Parys, South Africa, 9th Int'l Conference on Advances in Science, Engineering, Technology & Waste Management (ASETWM-17), 2017.
- [3] E.N. Malenga, A.F. Mulaba-Bafubiandi, and W. Nheta, "Alkaline leaching of nickel bearing ammonium jarosite precipitate using KOH, NaOH and  $NH_4OH$  in the presence of EDTA and  $Na_2S$ ," *Hydrometallurgy*, vol. 155, pp.69-78, 2015. <https://doi.org/10.1016/j.hydromet.2015.04.004>
- [4] B. Rohrmann, "Vanadium in South Africa (Metal Review Series no. 2)". *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 85, no 5, pp.141-150, 1985.
- [5] K.M.M. Aung, and Y.P. Ting, "Bioleaching of spent fluid catalytic cracking catalyst using *Aspergillus niger*," *Journal of biotechnology*, vol. 116, no. 2, pp. 159-170, 2005. <https://doi.org/10.1016/j.jbiotec.2004.10.008>
- [6] P. Rasoulnia, S.M. Mousavi, S.O. Rastegar, and H. Azargoshasb, "Fungal leaching of valuable metals from a power plant residual ash using *Penicillium simplicissimum*: Evaluation of thermal pretreatment and different bioleaching methods," *Waste Management*, vol. 52, pp. 309-317, 2016. <https://doi.org/10.1016/j.wasman.2016.04.004>
- [7] R. Ciriminna, F. Meneguzzo, R. Delisi, and M. Pagliaro, "Citric acid: emerging applications of key biotechnology industrial product," *Chemistry Central Journal*, vol. 11, no. 1, pp. 22, 2017. <https://doi.org/10.1186/s13065-017-0251-y>
- [8] P. Fonseca, R. Moreno, and F. Rojo, "Growth of *Pseudomonas putida* at low temperature: global transcriptomic and proteomic analyses," *Environmental microbiology reports*, vol. 3, no 3, pp. 329-339, 2011. <https://doi.org/10.1111/j.1758-2229.2010.00229.x>
- [9] E.A. Abdel-Aal, "Kinetics of sulfuric acid leaching of low-grade zinc silicate ore," *Hydrometallurgy*, vol. 55, no. 3, pp. 247-254, 2000. [https://doi.org/10.1016/S0304-386X\(00\)00059-1](https://doi.org/10.1016/S0304-386X(00)00059-1)
- [10] H.Y. Li, K. Wang, W.H. Hua, Z. Yang, W. Zhou, and B. Xie, "Selective leaching of vanadium in calcification-roasted vanadium slag by ammonium carbonate," *Hydrometallurgy*, vol. 160, pp. 18-25, 2016. <https://doi.org/10.1016/j.hydromet.2015.11.014>