Extraction of iron, titanium and vanadium from a titaniferous ore with beta-diketones

N.B. Mbhamali and J.H. Potgieter

University of the Witwatersrand, South Africa

Recently, beta-diketones have emerged as a new class of solvents used in hydrometallurgical processes. In this study the extraction of iron, titanium and vanadium from a titaniferous ore was investigated, using β-diketones. The ore was characterised and analysed for mineral phase, bulk chemistry, surface morphology and particle size prior to leaching. The feasibility of various β-diketones (acetylacetone, hexafluoroacetone and 2-thenoyltrifluoroacetone) to extract the metals was first investigated on pure metal oxides. Of the three ligands used in the study, acetylacetone was the most efficient in extraction of the metals from pure oxides. The ore containing 14.24% Fe_2O_3, 1.73% TiO_2 and 0.35% V_2O_5 was subjected to a leaching process with acetylacetone and hexafluoroacetone under the operation conditions of: stirring speed of 100 rpm, temperature of 25°C – 65°C, time of 0 – 12 hours and solid/liquid ratios of 1:1 to 1:20 (g/ml). Under optimised conditions, acetylacetone extracted 73.4% iron and 60.7% vanadium, whereas hexafluoroacetone extracted 34.7% iron and 42.8% vanadium. The extraction percentage for titanium was constant at 2±0.4% throughout the investigation. According to kinetics analysis, the dissolution of iron and vanadium appeared to be controlled by a chemical mechanism, whilst diffusion controlled it for titanium. Overall, this study suggests that the use of β-diketones for direct extraction of metals from their ore as a promising alternative and offers a greener process compared to the use of inorganic acidic solvents. The large difference in extraction between the titanium and iron can point to a potential separation method between these metals.

INTRODUCTION

Metals are the core of modern civilisation and industrialisation, playing a crucial role in various sectors, from infrastructure and technology to energy and healthcare. Their chemical properties such as their ability to form stable oxides and high melting points and physical properties such as high tensile strength and resistant to corrosion have led to metals being used in diverse industries and applications. Iron (Fe), titanium (T) and vanadium (V) are some of the transition metals playing a pivotal role in modern civilisation. Iron is used as a catalyst in the Haber process and alloy steels are used to make bridges, rifle barrels, electricity pylons, etc. Titanium acts as an alloying agent used in manufacturing aircrafts, spacecraft and missiles, and vanadium is used as a steel additive used for armour plates, axles, tools, piston rods, etc.

The elements Fe, Ti and V are typically not found in their pure elemental forms, but rather as compounds in various ores such as titaniferous ores. To date, hydrometallurgy and pyrometallurgy processes have been used for the recovery of metals from their ores. Pyro-metallurgical processes include remelting of the ore in furnaces at elevated temperatures (Sanito *et al.*, 2021). Hydrometallurgical processes involve the use of strong inorganic acidic solvents and lyes to dissolve the ores followed by separation and purification steps (solvent extraction, adsorption and ion exchange) (Bian *et al.*, 2022).

However, the use of acids is often coupled with significant environmental footprints, safety concerns, demanding operating conditions, corrosion of equipment, etc. There is therefore a need for the use of reagents that will mitigate the use of acids.

β-diketones have emerged as a new class of solvents used in hydrometallurgical processes (de Gonzalo and Alcantara, 2021). These solvents are molecules containing two ketones separated by one carbon. These organic solvents are environmentally friendly as they can be recycled and can operate under considerable temperatures of up to 250°C (Shyam-Sunder *et al.*, 2020). In addition, these organic solvents have advantages of easy preparation, low prices, less toxicity and high stability (Plotka-Wasylka *et al.*, 2020; Zhang *et al.*, 2021). Above all, β-diketones have proven to be capable of dissolving metal oxides without any pretreatment steps or additional reducing agents, thus demonstrating their applicability as leaching agents (Han *et al.*, 2023).

Several studies have investigated the ability of metals and metal oxides to dissolve in organic solvents, indicating their possible use in leaching techniques. Kimitaka and Ohiko (1969) studied the feasibility of direct dissolution of various metals in β-diketones reagents (acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoyltrifluoroacetone, 2-furoyltrifluoroacetone and 2-thenoyltrifluoroacetone). Of these five, acetylacetone was the most efficient for the dissolution of the tested metals (iron, aluminium, copper, cobalt, silicon, titanium and chromium). In their study, Watanabe *et al.*, (1995) managed to recover 63.0% of vanadium from an m-Xylene solution using acetylacetone. Furthermore, Potgieter and co-workers (2006) studied the use of acetylacetone in the gas phase to extract iron and vanadium, obtaining extraction yields of up to 63.0% for V and 75.5% for Fe. Moreover, Iwai *et al.*, (2007) used various media such as acetylacetone, methanol, ethanol, and acetic acid to extract iron from low rank coal, obtaining a peak of 41.1% Fe removal.

Narayanan and Palantavida (2020) carried out selective extraction using various bis(-diketone) ligands to recover iron (III) from a waste chloride liquor that contained other metal ions including titanium (IV) and vanadium (V). The authors managed to recover 99.0% of Fe (III) when bis(1-phenyl-3-methyl-5-pyrazolone) was used as an extractant. Recently, Pallei *et al.*, (2024) investigated the ability of fluorinated (1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-l-one) and non-fluorinated (1,3-dimesitylpropane-1,3-dione) β-diketones to form complexes with transition metals (Fe (II), Mn (II), Co (II)) with the aim of treating cancer cells. The authors concluded that metal-fluorinated complexes were more stable. These prior studies concentrated on recovering metals from oxides or liquid solutions, revealing a significant void in research on direct metal extraction from ores using β-diketones without prior treatment of harsh acid leaching.

In this work, the separation of iron, titanium, and vanadium from titaniferous ore using beta-diketones was explored. The composition and structure of the ore was initially studied prior to the separation. Feasibility of various β-diketones to extract the three metals was carried out on the pure metals' oxides. The effects of temperature (kinetically and thermodynamically), solid to liquid ratio on the separation efficiency were investigated. The direct separation of the metals of interest from the ore can provide a new, more economical and environmentally benign route for metal recovery, especially if the lixiviants used can be recovered and recycled.

MATERIALS AND EXPERIMENTAL METHODS

Materials and Sample Characterisation

The sample used in this study originated from a new mine in Mpumalanga, South Africa. The sample obtained from the mine as a composite was collected over a week. The ore is currently processed for its vanadium content. Laboratory sub-sampling and homogenisation were conducted according to the soil sampling protocol published by the US Environmental Protection Agency. Approximately 0.5 kg of each sample was used as the final sample and was dried in an oven for 2 h at 105°C. Size reduction took place by means of laboratory milling and sampling with a particle size ranging from -56 to +38 μm used throughout this experiment.

The composite sample was characterised to assess mineral phases, bulk chemistry, and surface morphology as follows:

- Mineral content: the diffraction patterns associated with the mineral composition of the various samples were obtained (as shown in Figure 1) after the sample was subjected to X-ray diffraction (XRD) analysis using a Rigaku Ultima IV (operated at 40 kV and 30 mA) and the PDXL analysis software; the instrument's detection limit was 2%. The operating conditions of the diffractometer's Cu radiation source were 30 kV and 25 mA. Data were recorded over the range 5° ≤ 2θ ≤ 95°. The powered samples were scanned at 0.5°/in with a step width of 0.01°. The results are shown in Figure 1. The identified major phases were magnetite, vanadium oxide and ilmenite.

- Elemental chemistry: the X-ray fluorescence (XRF) powder method was carried out on a Rigaku-ZSX Primus II in conjunction with the SQX analysis software; operating at a 4 kW, 60 kV, and 150 mA. (Table I displays the elementary chemistry results). The bulk chemistry revealed Si (36%) as the major component of the sample followed Al (26.10%), and Fe (14.24) with traces of Ti (1.73%) and V (0.35%).

- Grain morphology and chemistry: the morphology and surface chemistry analysis were conducted using a scanning electron microscope (TESCAN, operated at 20 kV) in conjunction with energy-dispersive X-ray spectroscopy (EDX) and the corresponding analysis software (performance in nano space). (Figure 2 displays the grain morphology of the ore). Two particular grains were observed, differing in their Fe, Ti and V content

Table I. Bulk chemistry of ore

Elements (Oxides)	**Na**	**Mg**	**Al**	**Si**	**Ca**	**Ti**	**V**	**Fe**	**Others**
w%	1.85	1.90	26.10	36.40	15.02	1.73	0.35	14.24	2.41

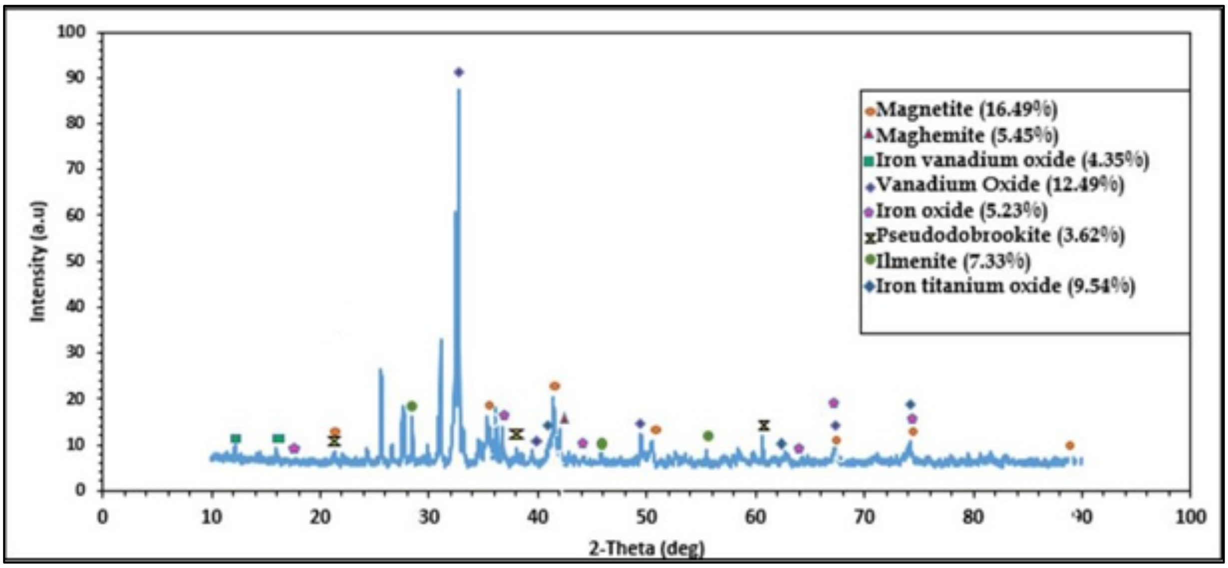
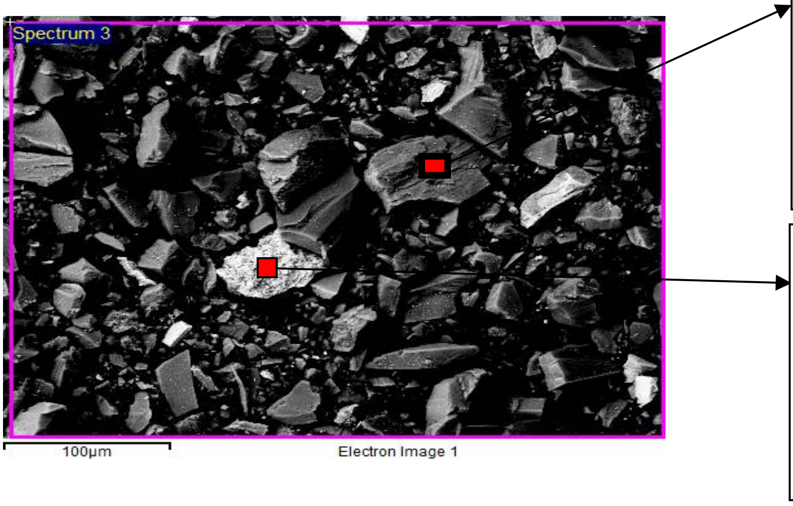


Figure 1. XRD pattern for the mined ore with peaks showing the intensity of minerals with Fe, Ti and V, contained in the ore.



Element	Atomic (%)
Fe	2.17
Ti	0.12
V	0.00
Si	17.42

Element	Atomic (%)
Fe	30.44
Ti	5.27
V	0.77
Si	1.46

Figure 2. SEM-EDS data at 5.00K X and scale of 100 um with the elemental composition of black and white spots.

Leaching experiments

The dissolution was carried out in duplicate with chemical grade β-diketones media including acetylacetone (Acac), 2-Thenoytrifluoroacetone (TTA) and hexafluoroacetylacetone (HFA) and average values reported. Acetylacetone and hexafluoroacetylacetone were purchased in liquid form while 2-thenoytrifluoroacetone was purchased in solid form and was dissolved in ethanol to make a 1 M concentration. Dissolution was first caried out for pure metal oxides (iron oxide, titanium oxide and vanadium oxide) to determine the feasibility of the three β-diketones. For the dissolution of the ore, dissolution parameters such as temperature, solid to liquid ratio and ligand concentration were assessed using atomic absorption flame spectrometry (FAAS) to calculate the extraction percentage. Throughout all experiments a constant speed of agitation was kept at 100 rpm.

RESULTS AND DISCUSSIONS

Dissolution of Pure Metal Oxides

Figure 3 summarises the conducted experiments on pure metal oxides samples. (A), (B) and (C) and display the leaching when using TTA, HFA and Acac respectively. In all cases, high extraction was obtained for vanadium, 12.0, 27.0 and 38.0% was obtained in the various media. On the other hand, iron extraction was found to be 7.0, 17.0 and 34.0% respectively. Lastly, Ti dissolved at amounts of 0.04, 3.0 and 20.0%. The obtained data tend to agree with the previous study conducted by Kimitaka and Ohiko (1969) which attributed Acac'c efficiency to extract more metals due to proton dissociation in Acac and the co-existing water molecule. In their investigation, the authors also concluded that the dissolution of iron is faster in more fluorine-containing β-diketones. This would explain the higher amount of iron extracted in HFA compared to TTA.

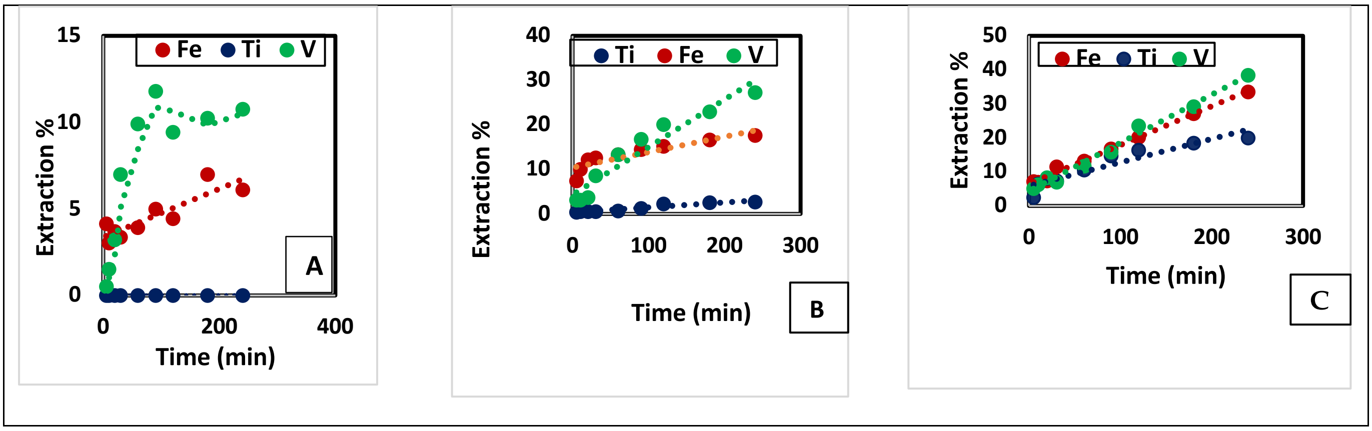


Figure 3. Extraction of Fe, Ti, and V from metal oxides with TTA (A), HFA (B) and Acac (C). Conditions: T= 25 °C, S/L 1:10

Extraction from Ore

Effect of temperature

Based on the preliminary assessment, the dissolution of the ore was performed only using Acac and HFA since the media revealed promising metal recovery. Figure 4 shows the ore dissolution when using the 2 media Acac (A, B & C) and HFA (A1, B1 & C1) based on using the pure oxides. Again, a higher degree of dissolution was obtained with Acac compared to HFA. Raising the temperature revealed a positive response to the rate of metal dissolution and recovery during the dissolution process (Salem, 2023). Its effect appeared to be pronounced when the temperature was increased from 25 to 65°C. From the experimental results in Figure 4, a high extraction of vanadium was reported at 65°C in both media, i.e. 40.0% for Acac (Fig 4 B) and 13.0% for HFA (Fig 4 B1). Iron was reported to have the second highest extraction at 65°C, 6.0% in Acac (Fig 4 A) and 4.0% in HFA (Fig 4 A1). The extraction of titanium yielded the smallest amounts of recovery at 2.4% and 2.0% from Acac and HFA, respectively. Figure 4 illustrates very little change in % extraction recovery after 6 – 7 h, and therefore 7 h was chosen as a sufficient time.

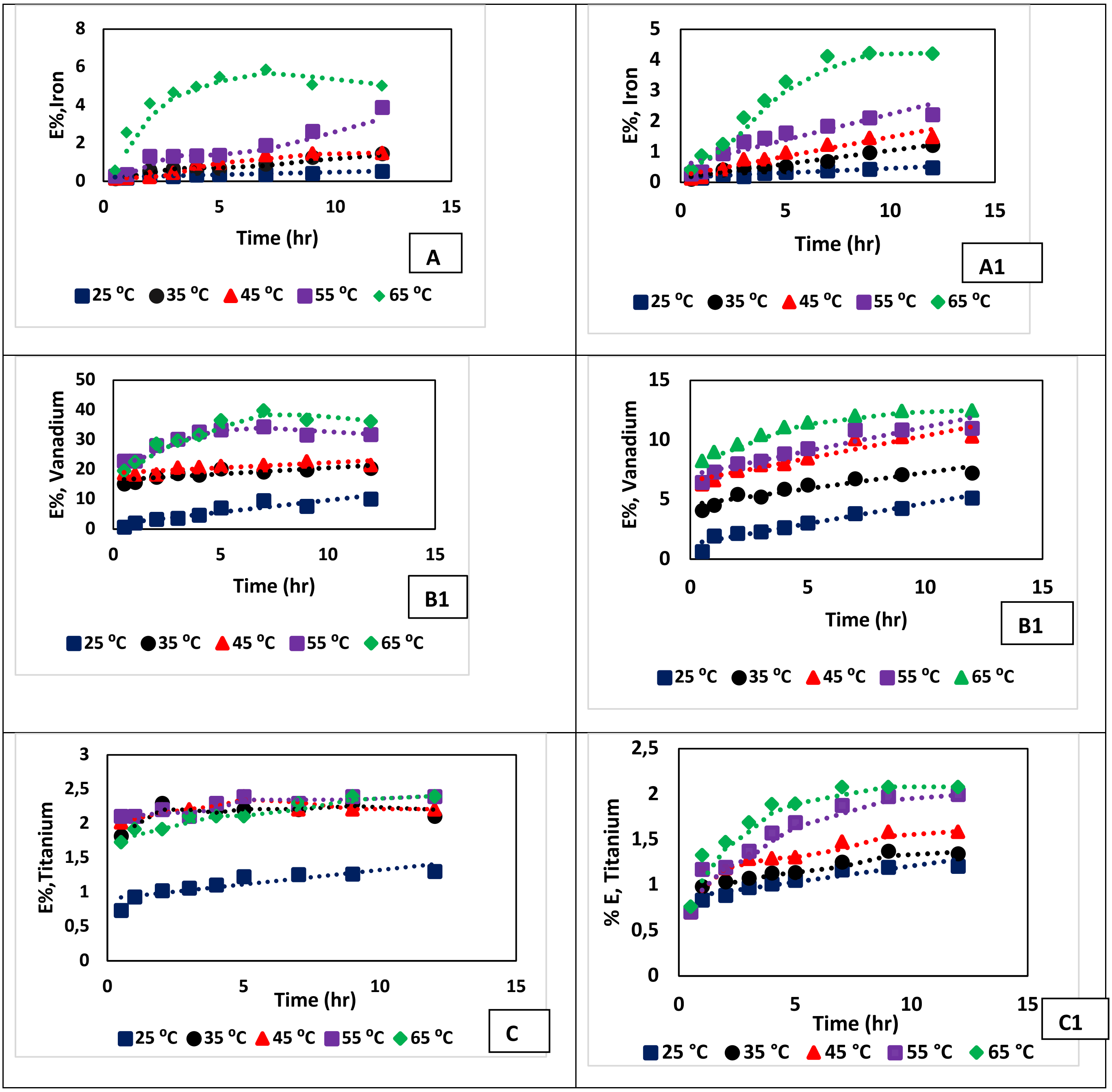


Figure 4. Effect of temperature on the extraction of the three metals from the ore using Acac (A, B & C) and HFA (A1, B1 & C1). Conditions: S/L 1:10 (g/ml), 100% ligand concentration,100 rpm.

Effect of solid to liquid ratio

The effect of solid to liquid ratio on extraction in Acac and HFA media is shown in Figure 5 with the other conditions fixed at a temperature of 65^{0}C, stirring speed of 100 rpm, extraction time of seven hours and concentration of ligand at 100%. In both cases, an increase in the extraction percentage of Fe and V occurs when the solid to liquid ratio changes from of 1:1 to 1:20 (g/ml). In Acac (Fig 5 A), the maximum extraction percentage at 1:20 was 60.7% and 73.4% for V and Fe respectively, whilst for HFA (Fig 5 B), 34.7% Fe and 42.80% V were extracted. The increased ligand volume results in a less dense slurry and results in larger volume/surface area for contact between ore and acac. This leads to higher reaction rates (Shemi *et al*., 2012). However, the extraction percentage for titanium was not affected by the change in solid to liquid ratios.

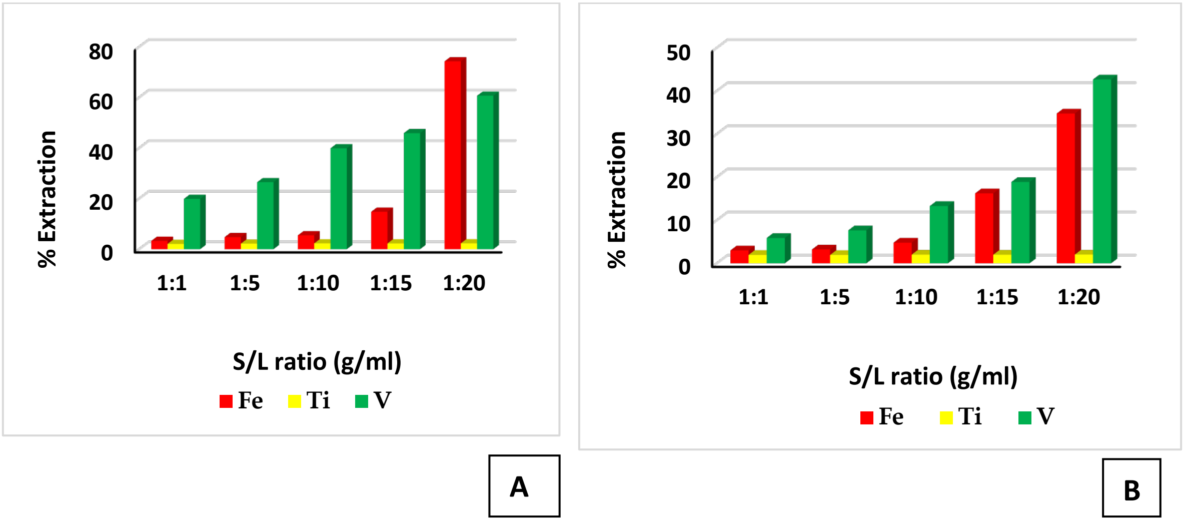


Figure 5. Effects of Solid to Liquid Ratio on extraction percentage of Fe, Ti and V. Conditions: T=65C, time =7hours, 100% acetylacetone (A) and hexafluoroacetylacetone (B) concentration and a stirring speed of 100 rpm.

Kinetics analysis

The behaviour of Fe, Ti and V during extraction from the ore with acetylacetone was studied kinetically to determine the rate at which extraction process occurs. Heterogenous systems are commonly governed by the shrinking core model (Alghanmi *et al.*, 2015). The kinetic dissolution equation of a liquid-solid heterogeneous system is mainly controlled by either one of the mathematical equations for a chemical controlled reaction [1], a diffusion-controlled reaction [2] and a pseudo 1st order homogenous model [3]:

$$1-3(1-A)^{2/3}+2(1-A)=k_r t \qquad [1]$$

$$1-1-(1-A)^{1/3}=k_d t \qquad [2]$$

$$\left(1-\frac{2}{3A}\right)-(1-A)^{2/3}+B\left(1-(1-A)^{1/3}\right)=k_m t \qquad [3]$$

Where A is the fraction of the metal extracted at time t, k_d, k_r and k_m are the rate constants and B is the ratio of k_r/k_d in the mixed control model.

Distinction between the above mathematical models is determined by the activation energy. The relationship between reaction constant and temperature can be determined from activation energy using the Arrhenius equation [4].

$$\ln k=\ln A-\left(\frac{E_A}{RT}\right) \qquad [4]$$

Where A is the frequency factor, k is the reaction constant, and E_A is the activation energy of the dissolution process, T (Kelvin) temperature and R is the universal gas constant (8.314 J/K.mol). A plot of ln k vs the reciprocal of temperature is used to determine the activation energy (E_A = R × slope). An activation energy of <40 kJ/mol indicates a diffusion-controlled mechanism, while activation energy of >40 kJ/mol indicates a chemically controlled mechanism (Salem and Kassab, 2020). The slopes from

Figure 6 indicate that the dissolution of Fe and V was chemically controlled since the activation energies were above 40 kJ/mol, while the dissolution of T was controlled by diffusion since the activation energy was < 40 kJ/mol.

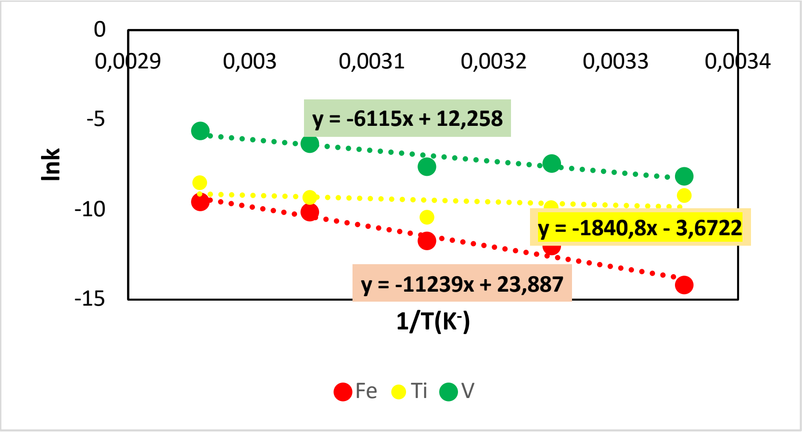
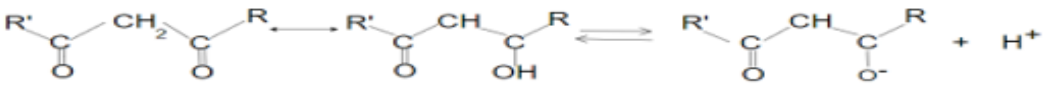
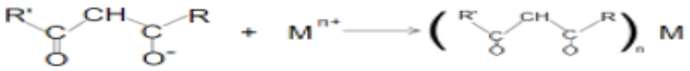


Figure 6. Plot of ln k vs 1/T for determination of activation energy of the dissolution of Fe, Ti and V in Acac.

The mechanism of metal extraction presumably follows a two-step process. In the first step the β-diketone undergoes keto-enol tautomerism and loses a H^+ ion, which can then react with the metal ions to dissolve them. The dissolved metal ions then form a complex with the β-diketone anions. This drives the equilibrium in the first reaction to the right, resulting in more H^+ ions being released from the β-diketone.



[5]



[6]

The difference in the acidic nature of the substituents on the different β-diketones has an influence on the degree of keto-enol tautomerism and subsequent equilibrium in which a H^+ ion and β-diketone tautomerism occurs. Therefore, one observes differences in the amounts of extraction of the different metals, as not only the first reaction step plays a role in the process, but also the case of formation of the metal-β-diketone complex and dissolution of the metal by the released hydrogens ions.

CONCLUSIONS

In this study, the extraction of iron, titanium and vanadium from a titaniferous ore using β-diketones was investigated. This was done through preparation and characterisation of the ore, followed by investigating the ability of the three β-diketones (Acetylacetone, 2-Thenoyfluoroacetone and hexafluoroacetone). The last step involved varying several parameters to optimise the extraction percentages. Acetylacetone was found to be the most efficient extraction ligand, followed by hexafluoroacetylacetone, in the extraction of the three metals from their oxides and the ore. A maximum of 60.7% V and 73.4% Fe in Acac and 34.7% Fe and 42.8% V in HFA were extracted from the ore under the operational conditions of: temperature of 65°C, stirring speed of 100 rpm, time of seven hours, 100% (v/v%) ligand concentration and a solid to liquid ratio 1:20 (g/ml). The investigated parameters did not improve the extraction percentage of titanium as the amount extracted ranged around 2 ± 0.4%. In addition, the kinetic evaluations showed that the dissolution was controlled by a chemical mechanism for Fe and V, but diffusion controlled for Ti. Overall, this study suggests that the use of β-diketones for the direct extraction of metals from their ore can be a promising alternative and offers a greener process compared to the use of inorganic acidic solvents or the usually employed salt roast process. It is also evident then that the separation of Fe and V from a titaniferous ore could be achieved easily using acetylacetone, but an efficient technique must still be investigated for the successful separation of Fe and V from each other. It is also recommended that for future work, a control experiment with traditionally used lixiviants be carried out.

REFERENCES

Alghanmi, S.I., Al Sulami, A.F., El-Zayat, T.A., Alhogbi, B.G. and Abdel Salam, M. (2015). Acid leaching of heavy metals from contaminated soil collected from Jeddah, Saudi Arabia: kinetic and thermodynamics studies. International Soil and Water Conservation Research, 3(3), pp.196–208.

Bian, Z., Ning, Z., Zhao, K., Gao, R., Li, W., Chao Lv, Yu, Y. and Li, H. (2022). Recovery of vanadium, titanium, and iron from vanadium titanomagnetite concentrate through ammonium sulfate cascade roasting with potassium pyrosulfate. Journal of Sustainable Metallurgy, 8(4), pp.1988–2000.

Chen, D., Zhao, H., Hu, G., Qi, T., Yu, H., Zhang, G., Wang, L. and Wang, W. (2015). An extraction process to recover vanadium from low-grade vanadium-bearing titanomagnetite. Journal of Hazardous Materials, 294, pp.35–40.

de Gonzalo, G. and Alcántara, A.R. (2021). Recent developments in the synthesis of β-Diketones.Pharmaceutical,14(10),pp.1043-106

Devi, R.K.B., Devi, S.P. and Singh, R.K.H. (2012). Synthesis, characterization and DNA interaction study of a new oxovanadium (IV) complex containing acetylacetone and dicyandiamide as ligands. *Spectroscopy Letters*, 45(2), pp.93–103.

Han, K., Kim, R. and Kim, J. (2023). Recent Advancements in Hydrometallurgy: Solubility and Separation. Transactions of the Indian Institute of Metals.

Iwai, Y., Okamoto, N., Ohta, S., Arai, Y. and Kinya Sakanishi (2007). Extraction of iron and calcium from low rank coal by supercritical carbon dioxide with entrainers. Journal of Supercritical Fluids, 40(2), pp.227–231.

Kimitaka, S. and Ôhiko, K. (1969). Studies of the Direct Dissolution of Metal in a β-Diketone Reagent. Bulletin of the Chemical Society of Japan, 42(10), pp.2778–2790.

Maria, H.A. and Lago, R.M. (2012). Investigation of iron oxide reduction by ethanol as a potential route to produce hydrogen. Applied Catalysis B-Environmental, 115-116, pp.45–52.

Narayanan, R.P. and Palantavida, S. (2020). Selective extraction and solid-state complexation of iron (III) with bis(β-diketone) ligand. Materials Today: Proceedings, 41(2021), pp.638–643.

Pellei, M., Jo' Del Gobbo, Caviglia, M., Gandin, V., Marzano, C., Karade, D.V., Anurag Noonikara Poyil, Dias, R. and Santini, C. (2024). Synthesis and Investigations of the Antitumor Effects of First-Row Transition Metal (II) Complexes Supported by Two Fluorinated and Non-Fluorinated β-Diketonates. International Journal of Molecular Sciences, 25(4), pp.2038–2038.

Płotka-Wasylka, J., de la Guardia, M., Andruch, V. and Vilková, M. (2020). Deep eutectic solvents vs ionic liquids: Similarities and differences. Microchemical Journal, 159, p.105539.

Potgieter, J.H., Kabemba, M.A., Teodorovic, A., Potgieter-Vermaak, S.S. and Augustyn, W.G. (2006). An investigation into the feasibility of recovering valuable metals from solid oxide compounds by gas phase extraction in a fluidised bed. Minerals Engineering, 19(2), pp.140–146.

Radzyminska-Lenarcik, E., Pyszka, I. and Kosciuszko, A. (2021). Separation and recovery of gold (III), palladium (II) and platinum (IV) by solvent extraction using a new β-diketone derivative from acidic solutions. Materials, 14(16), pp.4436–4448.

Salem, A.R. (2023). Efficient leaching process of valuable elements from gibbsite ore materials in Talet Seleim, Southwestern, Sinai, Egypt using green and ecofriendly lixiviant agent: optimization, kinetic and thermodynamic study. Analytical Chemistry Letters, 13(2), pp.141–158.

Salem, A.R. and Kassab, W.A. (2020). Uranium and rare earth elements leaching characteristics from El-Sella mineralized Granite, Eastern Desert, Egypt. *International Journal of Environmental Analytical Chemistry*, 102(19), pp.7498–7522.

Sanito, R.C., You, S.J. and Wang, J.F. (2021). Application of plasma technology for treating e- waste: A review. Journal of Environmental Management, 288(188), p.112380.

Shemi, A., Mpana, R.N., Ndlovu, S., van Dyk, L.D., Sibanda, V. and Seepe, L. (2012). Alternative techniques for extracting alumina from coal fly ash. Minerals Engineering, 34, pp.30–37.

Shyam Sunder, G.S., Adhikari, S., Rohanifar, A., Poudel, A. and Kirchhoff, J.R. (2020). Evolution of Environmentally Friendly Strategies for Metal Extraction. Separations, 7(1), pp.4– 31.

Ntuthuko Buke Mbhamali

Student
University of the Witwatersrand, Johannesburg

Ntuthuko is a Master of Science in Engineering (Metallurgy and Materials) candidate at the University of the Witwatersrand. He holds a BSc in Chemical Engineering from the University of the Witwatersrand. His research work focuses on the use of organic solvents for leaching and recovery of metals from low-grade ores. He has done research on the use of beta- diketones for the extraction of iron, titanium and vanadium from a titaniferous ore at undergraduate level. Currently, researching the use of organic acids in the extraction of copper and cobalt.