A comparative study of vanadium recovery from titaniferous magnetite using salt, sulphate, and soda ash roast-leach processes

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A comparative study of vanadium recovery from titaniferous magnetite (titanomagnetite) using the salt, sulphate, and soda ash roast-leach processes was conducted. The test work entailed laboratory-scale investigations of the best combination of conditions in terms of roasting reagent concentration, time, and temperature for the salt and sulphate roasting options, whereas the data for the soda ash roasting was obtained from previous work conducted at Mintek. The best vanadium extractions were 95%, 86%, and 64% for sulphate, soda ash, and salt roasting options, respectively. When the different roasting reagents are compared on the basis of vanadium extraction only, the sulphate roast-leach process appears to be superior even to the commercially established soda ash roast-leach process. However, for a process to be considered for commercial application it should also claim superior overall techno-economics. Sulphate roasting would possibly be more expensive than the established soda ash roasting process because of special material requirement for building a plant to contain the corrosive SO₃ by-product as well as to withstand higher temperatures and prolonged times. The cost of Na₂SO₄ is also higher than that of Na₂CO₃. However, the economics of sulphate roasting can improve if the SO₃ by-product can be used to produce sulphuric acid. In addition, the intensification of legislation to curb the carbon footprints of industrial processes would also favour the sulphate roasting option.

INTRODUCTION

Titaniferous magnetite (titanomagnetite) resources contain economically significant reserves of vanadium and iron as well as titanium. Titanomagnetite is a primary source of vanadium– about 88% of the world’s vanadium is extracted from titanomagnetite (Fischer, 1975; Roskill, 2010; Zhong et al., 2014). Vanadium is recovered from titanomagnetite by two main processes – the vanadium and steel co-production smelting process (Steinberg et al., 2011; Kelly, 1993; Zhang et al., 2007; Evraz NTMK, 2016) and the roast-leach process for vanadium primary production (Gupta and Krishnamurthy, 1992; Mefos, 2006; Steele and Wilson, 1966; Moskalyk and Alfantazi, 2003; Taylor et al., 2006; Roskill, 2010). In terms of cumulative vanadium recovery, the roast-leach process is reported to be superior to the smelting process (Goso et al., 2016). The conventional roast-leach process entails the roasting of the vanadium-bearing titanomagnetite in the presence of a sodium reagent to produce sodium metavanadate (NaVO₃), which is subsequently leached using water as the lixiviant in a controlled pH system for the effective rejection of impurities. The vanadium from the leachate is typically precipitated as ammonium metavanadate, which is subsequently calcined for the production of the valuable vanadium pentoxide (Rohrmann, 1985; Gupta and Krishnamurthy, 1992; Roskill, 2010).
The success of the roast-leach process is highly dependent on the efficiency of the roasting reaction that converts sodium and vanadium in the titanomagnetite to NaVO₃, as well as the dissolution efficiency of the metavanadate. In support of this view, it has been shown that the leaching extraction efficiency of vanadium from the sodium-titanomagnetite roast is typically about 86%, whereas the cumulative vanadium extraction at the stage of V₂O₅ production is about 82% (Goso et al., 2016; Hukkanen and Walden, 1985). Typical sodium sources include salt (NaCl), sodium sulphate (Na₂SO₄), and soda ash (Na₂CO₃) (Gupta and Krishnamurthy, 1992; Mefos, 2006). The focus of the current study was to compare the effects of the typical sodium sources on the efficiency of the subsequent vanadium extraction from titanomagnetite.

**ROAST-LEACH PROCESS**

As stated above, the conventional roast-leach process involves several stages, namely roasting, leaching, precipitation, and calcination. This paper focuses on the roasting stage and inherently on the leaching stage.

**Roasting**

The reactions of NaCl, Na₂SO₄, and Na₂CO₃ with vanadium in the titanomagnetite to form the water-soluble NaVO₃ are presented in Equations [1] to [4]. The salt roasting can be conducted with and without vapour, in which cases the by-products would be toxic hydrogen chloride and chlorine gases, respectively. From an environmental point of view, the salt roasting route is problematic because of these by-products. However, salt roasting is considered to be the cheapest option due to relatively low reagent costs and operational temperatures. In addition the salt roasting approach uses one of the most selective sodium reagents for reacting with vanadium in the titanomagnetite (Gupta and Krishnamurthy, 1992; Mefos, 2006; Roskill, 2010).

$$2\text{NaCl} + \text{V}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{NaVO}_3 + 2\text{HCl}, \text{salt roasting at 800 – 900°C with vapour}$$ [1]

$$2\text{NaCl} + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{Cl}_2, \text{salt roasting at 800 – 900°C without vapour}$$ [2]

$$\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{SO}_3, \text{sulphate roasting at 1200 – 1230°C}$$ [3]

$$\text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{CO}_2, \text{soda ash roasting at 900 – 1200°C}$$ [4]

General problems associated with the roasting stage include the formation of insoluble vanadates and low-melting complex silicate structures. The optimization of the roasting conditions in the three options generally addresses these challenges. The challenges are further addressed by limiting the free silica and free lime in the roaster feed to <3% and <1%, respectively. Ideally, the free oxygen in the system should be >4% in order to ensure that vanadium in the titanomagnetite is oxidized (Mefos, 2006).

**Leaching**

NaVO₃ can be leached to solubilize the vanadium using sulphuric acid or water as lixiviant. Sulphuric acid is generally less selective and results in the dissolution of impurities like Ca, Mg, and Fe (Mefos, 2006). Water is the most common lixiviant in commercial operations due to its selectivity and NaVO₃ dissolution efficiency as well as its relatively low cost and wide availability. The selectivity and efficiency of the water leaching step can be maximized by controlling the pH of the leach slurry (Goso et al., 2016).
Precipitation and calcination
Vanadium is typically extracted from the pregnant leach liquor by precipitation using excess ammonium sulphate solution to form \( \text{NH}_4\text{VO}_3 \) - ammonium metavanadate (AMV). The precipitation efficiency is typically maximized by controlling the pH of the solution. The AMV precipitate is generally calcined to remove volatiles and produce a high-purity \( \text{V}_2\text{O}_5 \) product (Goso et al., 2016).

EXPERIMENTAL APPROACH

Materials and Equipment
Titanomagnetite mined from the main magnetite layer (MML) of the Bushveld Complex in South Africa was supplied by a client of Mintek. In a separate study, the run-of-mine (ROM) ore was concentrated by magnetic separation. The concentrate, with the bulk chemical composition given in Table I, was used in the current study.

Analytical grade chemicals and reagents were used in the test work. Deionized water was used as a lixiviant in the leaching stage. An electrical-resistance-heated muffle furnace equipped with silicon carbide elements was used for roasting. The bulk chemical compositions of the titaniferous magnetite concentrate, leach residues, and liquors were determined by simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian Vista-PRO CCD instrument. These analyses were used to measure the vanadium extractions after the roast-leach process.

Table I. Bulk chemical compositions of the feed titanomagnetite material (mass %).

<table>
<thead>
<tr>
<th>Fe\text{O}_3</th>
<th>MgO</th>
<th>Al\text{O}_3</th>
<th>Si\text{O}_2</th>
<th>CaO</th>
<th>TiO_2</th>
<th>V\text{O}_3</th>
<th>Cr\text{O}_3</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.4</td>
<td>0.67</td>
<td>3.27</td>
<td>1.44</td>
<td>&lt;0.05</td>
<td>16.1</td>
<td>1.17</td>
<td>0.05</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Experimental Procedures
The purpose of the test work was to evaluate the vanadium extraction from the titanomagnetite concentrate by roasting in the presence of NaCl, Na\text{2SO}_4, and Na\text{2CO}_3. In the current study, only tests with NaCl and Na\text{2SO}_4 were conducted. The Na\text{2SO}_4 and Na\text{2CO}_3 salt concentrations were deduced from the work of Paunova et al. (2003). The vanadium extraction data for Na\text{2CO}_3 was obtained from previous work conducted at Mintek (Goso et al., 2016).

Roasting
The main parameters tested were temperature, concentration of sodium-bearing reagent (for NaCl only), and roasting time. The temperature was varied between 800 and 1200°C, reagent concentration between 5 and 15%, and reaction time between 45 and 240 minutes.

The titanomagnetite concentrate was mixed with a saturated solution of the sodium-bearing reagent in a ratio of 100:5, to form a slurry. The slurry was dried overnight at 110°C. The dried sample was milled to de-agglomerate the friable cake and homogenize the sample. The mixture was weighed into a silicon carbide tray and introduced into a pre-heated furnace operating at the test temperature in air.

Leaching
The leaching conditions were not optimized in the current test work. The scoping leaching procedure and conditions used in the Mintek laboratory were adopted in the current study. The standard leaching conditions entailed leaching using deionized water as lixiviant in a 2 L stainless steel reactor at a pulp density of 20 m/m% and controlled pH of 7.8. The tests were conducted at 70°C for 60 minutes. The reactor was fitted with a thermocouple, pH probe, hot plate, and an overhead stirrer with an impeller. The pH of the slurry was controlled using a solution of 20 g/L H\text{2SO}_4. Slurry temperature, pH, and redox potential were checked at 15-minutes intervals. At the end of each test, the slurry was filtered using a Buchner funnel. The cake was re-slurried and washed three times: first using deionized water with pH adjusted to the alkalinity of the slurry, and thereafter twice with untreated deionized water at a mass ratio of wash water to cake mass of 1:2.5. The leachate and the dried filter cake were stored at
50°C overnight, and were subjected to bulk chemical analysis by ICP-OES.

RESULTS AND DISCUSSION

Salt Roasting

Effect of Reagent Concentration
The effect of NaCl concentration on the vanadium extraction from titanomagnetite was investigated at a standard roasting temperature of 900°C and reaction time of 120 minutes. The NaCl concentration was varied at 5%, 10%, and 15% relative to the mass of the concentrate. The effect of NaCl concentration on the vanadium extraction from titanomagnetite is shown in Figure 1. The vanadium extraction appears to be insensitive to variations in NaCl concentration in the studied range, as shown by the almost constant vanadium extraction of 64% and 63% at NaCl concentrations of 5% and 15%, respectively.

![Figure 1. Effect of NaCl concentration on vanadium extraction by the salt roasting approach](image)

Effect of Roasting Temperature
The effect of roasting temperature on the vanadium extraction using the NaCl roasting approach was studied at a temperature range of 800°C to 1150°C. The NaCl concentration and reaction time were kept constant at 5% and 120 minutes, respectively. The results are shown in Figure 2. The best vanadium extraction of 64% was achieved at the relatively low temperature of 900°C. At 950°C the vanadium extraction seems to still be at saturation point at 65%. These results are in agreement with the literature (Mefos, 2006) in that the best vanadium extraction is achieved when roasting is conducted at temperatures between 800°C and 900°C.
**Effect of Roasting Time**

The effect of roasting time on vanadium extraction was studied between 60 and 240 minutes while the NaCl concentration and roasting temperature were kept constant at 5% and 900°C, respectively. The results of the test work, illustrated in Figure 3, show that the vanadium extraction increases very slightly with increasing roasting time. When roasting is conducted for 60 minutes, the vanadium extraction is 60%, on doubling the roasting time the vanadium extraction increases by only 4%. In addition, there is only a 1% improvement in vanadium extraction when the roasting time is increased from 120 minutes to 240 minutes. Longer roasting periods allowed enough time for diffusion to occur, therefore allowing more vanadium to be extracted. From the perspective of process economics, the vanadium extraction may be regarded as being insensitive to roasting time between 60 and 240 minutes.
Sulphate Roasting

Effect of Roasting Temperature
The effect of roasting temperature on vanadium extraction from titanomagnetite was studied between 1050 and 1200°C, while the Na₂SO₄ concentration and roasting time were kept constant at 5% and 120 minutes, respectively. The results in Figure 4 show that vanadium extraction increases with increasing roasting temperature until a temperatures of 1150°C, where the maximum extraction of 83% is achieved. Increasing the temperature to 1200°C does not seem to improve the vanadium extraction when the roasting time is kept constant.

![Figure 4. Effect of roasting temperature on vanadium extraction by the sulphate roasting approach](image)

Effect of Roasting Time
The effect of roasting time on vanadium extraction was studied between 45 and 180 minutes at temperatures of 1150°C and 1200°C. The inclusion of the test at 1200°C was due to suggestions (Mefos, 2006) that the best vanadium extraction via sulphate roasting of titanomagnetite would be achieved at higher temperatures. In these tests, the concentration of Na₂SO₄ was kept constant at 5%.

At a roasting temperature of 1150°C, the vanadium extraction from the titanomagnetite appears to be insensitive to roasting time in the studied range (Figure 5). At 1200°C, as shown in Figure 6, the vanadium extraction increases with roasting time. A vanadium extraction of 76% is achieved after 45 minutes of roasting, 83% after 120 minutes, and a satisfactory 95% after 180 minutes. These results are in agreement with findings in the literature, where high vanadium extractions are obtained at temperatures between 1200°C and 1230°C as per Equation [3].
Figure 5. Effect of roasting time on vanadium extraction by the sulphate roasting approach at 1150°C

Figure 6. Effect of roasting time on vanadium extraction by the sulphate roasting approach at 1200°C

**Soda Ash Roasting**
As stated previously, vanadium extraction studies using soda ash in the roasting stage was not conducted in the current study, but data from previous work at Mintek was used for the purpose of comparison (Goso et al., 2016).

**Comparison of Vanadium Extractions Using Different Roasting Procedures**
The study focused on the comparison of the efficiencies of typical roasting reagents, *i.e.* NaCl, Na₂SO₄ and Na₂CO₃, on the extraction of vanadium from titanomagnetite. The best combination of conditions for the respective roasting process options were (1) salt roasting using a feed containing 5% NaCl at
900°C for 120 minutes, and (2) sulphate roasting with 5% Na₂SO₄ in the feed at 1200°C for 180 minutes. In the soda ash roasting test work conducted previously at Mintek, the best conditions for vanadium extraction involved roasting of a titanomagnetite feed containing 5% Na₂CO₃ at 1150°C for 60 minutes (Goso et al., 2016). The pulp densities used in the Mintek scoping leaching test work and those established in the previous soda ash roast leach process are 20 mm/m% and 65 m/m%, respectively. A comparison of the two sets of tests with different pulp densities would likely favour the soda ash roast leach with 65% m/m% solids content, as it was shown in the previous work that vanadium extraction increased with increasing solid contents in the range of 30–65 m/m%. However, the NaCl and Na₂SO₄ roast-leach test results obtained with 20 m/m% solids content were compared to the Na₂CO₃ roast leach data obtained with 65 m/m% with reservations that the comparison, in particular with Na₂CO₃, may not be rational.

A comparison of the vanadium extraction efficiencies from the best combination of conditions for the three typical roasting options is presented in graphical form in Figure 7. The graph shows that amongst the three roasting options, salt roasting gives the lowest vanadium extraction efficiency of 64%. The industrially used soda ash roasting option gives the second best vanadium extraction efficiency of 86%. The best vanadium extraction, of 95%, was achieved by the sulphate roasting option.

When the roasting options are compared on the basis of vanadium extraction, sulphate roasting is superior to the salt and soda ash roasting processes. However, in order for the process to be considered for commercial use, it should also exhibit superior overall techno-economics. For a comprehensive techno-economic study of the roast-leach process using different roasting reagents, the budget of costs for the roasting stage would include roaster capital and operating costs, roasting reagent, and waste handling. Capital expenditure for the sulphate roaster is likely to be higher than for the soda ash roaster because sulphate roasting would require special equipment to contain the corrosive SO₃ by-product and withstand high temperatures. The increased roasting time is also likely to require a larger roasting vessel.

Na₂CO₃ is also cheaper and more readily available than Na₂SO₄. The CO₂ by-product of soda ash roasting (Equation [4]) is also less corrosive than the SO₃ produced in sulphate roasting (Equation [3]). However, if the SO₃ by-product could be used to produce sulphuric acid, sulphate roasting would gain ground in terms of economics compared to soda ash roasting. In addition, the intensification of legislation to curb the carbon footprints of industrial processes would also favour the sulphate roasting option.

![Figure 7. Comparisons of vanadium extractions for the different roast-leach processes](image-url)
CONCLUSIONS AND RECOMMENDATIONS

Laboratory experiments were conducted to compare the vanadium extraction from titanomagnetite using the chloride salt, sulphate, and soda ash roast-leach processes. The results have shown that the best vanadium recoveries are achieved with sulphate roasting (95%), followed by soda ash roasting (86%), and lastly by salt roasting (64%). In terms of vanadium extraction efficiencies, sulphate roasting is superior to both the commercially established soda ash and salt roasting options. Before proceeding to development-scale work with a view to commercialization, the proposed process also needs to report the best techno-economics and generate profits. The sulphate roasting produces SO₃ as by-product and operates at relatively high temperature and for long times – these facts may suggest that a sulphate roasting plant would need to be constructed using special materials. Arrangement for the handling and disposal of the SO₃ product would also be needed. In addition, the Na₂SO₄ reagent is more expensive and less readily available than Na₂CO₃. All these factors suggest that the cost of the sulphate roasting will likely be higher than that of the established soda ash roasting process. However, if the SO₃ by-product of sulphate roasting could be used to make sulphuric acid, the product scope of this process option would increase and subsequently increase the overall economics. In addition, the intensification of the legislation in various countries relating to the carbon footprints of industrial processes would also favour further investigation and adoption of the sulphate roasting option.

Further investigations are recommended to repeat the sulphate and soda ash roasting test work using titanomagnetite materials with different vanadium grades. Comprehensive techno-economic studies of the sulphate roasting option would need to be conducted in consideration of the possible recovery and use of SO₃ for the production of sulphuric acid.

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REFERENCES


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I started working at Mintek as a scientist-in-training in 2009. Thereafter, I was appointed as a scientist in the Pyrometallurgy Division in 2010. I completed a BSc in Chemistry in 2003 at the University of Cape Town and further completed a BSc (Hons) in Materials Science in 2004 from the same University. I also completed a Diploma in Advanced Project Management from the same university in 2015. My work experience includes laboratory scale exposure in smelting, converting, roasting and pre-reduction of different ores.