Preliminary investigations into the extraction of vanadium from titaniferous slags using a modified vanadium primary production process

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Vanadium is typically extracted from primary titaniferous magnetite ore using the conventional vanadium primary production process, which is essentially a sodium salt roast-leach process. In this study, a modified roast-leach process using excess stoichiometric sodium salt was investigated for the extraction of vanadium from a titaniferous slag, a by-product of the steel and vanadium coproduction process. A by-product slag produced by the now-defunct EVRAZ Highveld Steel and Vanadium Cooperation containing about 0.9% V_2O_5, was used as a case study. Vanadium extractions from the slag were investigated at 115% and 200% excess stoichiometric Na_2CO_3 and NaOH additions during roasting at temperatures varying between 800°C and 1000°C for 60 to 180 minutes. The highest vanadium extractions were achieved with individual Na_2CO_3 and NaOH during roasting, attaining the respective average vanadium extractions of 75.7% and 73.7% at 200% stoichiometric sodium salt additions. Roasting with a blend of Na_2CO_3 and NaOH did not improve the leaching efficiency of vanadium. There was no significant technical difference between the vanadium extractions using Na_2CO_3 and NaOH. Vanadium extractions using the industrially used Na_2CO_3 salt increased with roasting temperature and time up to 1000°C and 120 minutes, respectively. When roasting was extended to 180 minutes, vanadium extraction decreased due to the slight sintering of the solids. Mineralogical characterisation results showed that the vanadium-bearing spinel and pseudobrookite phases in the starting spinel were decomposed during roasting with individual Na_2CO_3 and NaOH, accompanied by the formation of a new sodium magnesium aluminium silicate phase. However, trace concentrations of spinel, i.e. <5 mass% content, were detected in the roast product and leach solids – the residual vanadium was contained in this trace-level spinel. With optimisation of the roasting conditions to fully decompose the spinel, the leaching efficiency of vanadium can be maximised. Further work is recommended to investigate the upgrading of the leach solids through sequential hydrochloric acid and caustic leaching to produce a marketable titania product.

INTRODUCTION

Titaniferous magnetite (titanomagnetite) deposits typically contain appreciable reserves of iron (Fe), vanadium (V), and titanium (Ti), with concentrations ranging between 16% and 60%, 0.1% and 2%, and 1% and 38%, respectively. Titanomagnetite is composed primarily of ilmenite and magnetite, with hematite, rutile, and perovskite as minor components. The major deposits of titanomagnetite ore are found in Brazil, Russia, China, and South Africa. Titanomagnetite is a primary source of vanadium (Project Blue, 2022; Roskill, 2010). In 2022, about 87% of the world's vanadium production was extracted from titanomagnetite resources, with the remaining 13% extracted from secondary resources such as spent catalysts, uranium and alumina by-products, and coal and petroleum ash (Project Blue, 2022).

The different processes currently used for the extraction of Fe and V include the co-production (smelting) and the primary production (roast-leach) processes. The smelting process can be conducted in the presence or absence of fluxes. In the fluxed smelting approach, the titanomagnetite is typically smelted at high temperatures in the presence of a reductant and fluxes such as dolomite and/ or quartz. Most of the vanadium reports to the pig iron whilst the titania (TiO_2) reports to slag (Steinberg, et al., 2011). This titania slag, also known as titaniferous slag, is discarded since the TiO_2 content is regarded as relatively low for upgrading. The fluxless smelting approach, on the other hand, involves smelting the titanomagnetite ore in the presence of a reductant (Boyd, et al., 1993). During fluxless smelting, reductant addition is lower, to facilitate the production of a high-purity pig iron and the deportment of vanadium to the slag from which it can be extracted. In this scenario, the FeO content in the slag would be high, and would also impart fluxing properties during smelting.

The primary production process involves roasting of titanomagnetite, leaching, precipitation, and calcination mainly for the production of vanadium. Roasting is conducted at high temperatures in the presence of Na reagent for the production of a water-soluble sodium metavanadate ($NaVO_3$). The soluble $NaVO_3$ is leached out using either H_2O or H_2SO_4 as a lixiviant. The leaching stage is followed by impurity rejection treatment before the precipitation of vanadium by the addition of ammonium sulfate. The ammonium metavanadate (AMV) precipitate is further calcined at high temperatures to obtain the V_2O_5 process (Connelly, 2024; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Moskalyk & Alfantazi, 2003).

Although most primary titanomagnetite ores found in China contain only about 0.3% V_2O_5 (Zhang, et al., 2007), China remains the world's largest producer of vanadium (Project Blue, 2022). The content of V_2O_5 in primary titanomagnetite ores from South Africa can be as high as 2% (The MSA Group, 2022). Steinberg *et al.* (2011) reported that the titaniferous slag produced from the vanadium-rich South African titanomagnetite would have as high as 0.9% V_2O_5, which is significantly higher compared to that contained in titaniferous slags produced in other parts of the world, as shown in Table I.

Table I. Chemical compositions of some titaniferous slags produced globally (mass %)

Operation	TiO_2	$\mathbf{V_2O_5}$	FeO	MgO	Al_2O_3	SiO_2	CaO
EHSV$^+$	35.6	**0.90**	1.00	14.1	18.0	16.2	14.1
NMTK and CHMP$^\#$	8-10	**0.18-0.30**	0.6-1.0	11-13	14-15	28-30	30-32
NZS$^\#$	32.1	**0.20**	2.11	13.3	17.8	15.2	15.9
Pangang$^\$$	22.0	**-**	-	7.00	14.0	22.0	27.0

$^+$ (Steinberg, et al., 2011) $^\#$ (Hassell, et al., 2016), $^\$$ (Sui, et al., 2004)

Titaniferous slags typically comprise titanaugite [$(Ca,Mg,Al,Ti,Si)_2O_6$], perovskite ($CaTiO_3$), spinel [$(Mg,Fe)(Al,V,Ti)_2O_4$ or M_3O_4], pseudobrookite [$(Mg,Al,Ti,V)_3O_5$ or M_3O_5] (Goso, et al., 2016; Pistorius, 2011; Zhang, et al., 2007). Vanadium is thus contained in two phases, namely, spinel and pseudobrookite.

The vanadium primary production process is typically used in industrial operations, for the extraction of vanadium from vanadium slags produced from the steel and vanadium co-production process (Project Blue, 2022; Gilligan & Nikoloski, 2020; Roskill, 2010; Taylor, et al., 2006; Moskalyk & Alfantazi, 2003; Gupta & Krishnamurthy, 1992; Rohrmann, 1985). Li and Xie (2012) investigated a direct roasting and soda ash (Na_2CO_3) leaching process for the extraction of vanadium from calcium-rich vanadium slags, in which vanadium was contained in a spinel solid solution that fully decomposed at 800°C. In this process, direct roasting resulted in the formation of calcium vanadate [$Ca(VO_3)_2$], manganese vanadate [$Mn(VO_3)_2$], and iron vanadate ($FeVO_4$), which were subsequently transformed into water-soluble $NaVO_3$ in the Na_2CO_3 lixiviant (Li & Xie, 2012). Yao *et al.* (2023) followed the direct roasting approach to investigate the decomposition of the vanadium ferrospinel in a vanadium-bearing converter slag. This investigation showed that at 900°C, the spinel structure was fully decomposed to facilitate the extraction of vanadium (Yao, et al., 2023). Lee *et al.* (2021) and Xiang *et al.* (2020) also presented consistent results confirming the feasibility of decomposing vanadium-bearing spinel and extracting vanadium from calcium-rich vanadium slags.

Lee *et al.* (2021) also showed that sodium salt roasting may decompose the vanadium-bearing spinel phase contained in a vanadium slag. Sodium salt roasting resulted in the decomposition of the spinel into soluble sodium vanadates such as $NaVO_3$, $Na_4V_2O_7$, and also sodium chromate (Na_2CrO_4). The reported Gibbs free energies of the chemical reactions for the formation of these sodium vanadates and chromate were negative at temperatures of 0°C to 1000°C, indicating that these reactions were thermodynamically favourable (Lee, et al., 2021).

Tawane *et al.* (2021) investigated the extraction of vanadium from the titaniferous slag using the sulfation roasting process. The extraction of vanadium was possible through this process even though the extraction efficiencies were generally low at 12% (Tawane, et al., 2021). Lekobotja et al. (2017) investigated the feasibility of using the conventional vanadium primary production process used industrially for vanadium extraction from titanomagnetite resources, for the extraction of vanadium from titaniferous slag containing about 0.9% V_2O_5. It was reported that at 1100°C, the vanadium-bearing pseudobrookite phase was fully decomposed while the vanadium-bearing spinel was partially decomposed, resulting in the formation of a nepheline phase ($NaAlSiO_4$) and the highest vanadium extraction of 27% (Lekobotja, et al., 2017).

The current study expanded on the work completed by Lekobotja *et al.* (2017). The study involved a preliminary investigation of the technical feasibility of excessive sodium salt addition during the roasting of the vanadium-bearing titaniferous slag to maximise the decomposition of vanadium-bearing phases and the liberation and extraction of vanadium. A preliminary evaluation of the effect of sodium salt composition and addition, roasting temperature, and roasting time on vanadium extraction from titaniferous slags was investigated.

EXPERIMENTAL

The different stages of the vanadium primary production process that were followed for the extraction of vanadium through the roast-leach process are discussed in the following sections.

Materials and equipment

The titaniferous slag used in this study was provided by EHSV, South Africa. The slag sample was crushed to a -1 mm particle size using a laboratory jaw crusher. The crushed sample was sized to a particle size range of -850+106 µm, using laboratory sieves. The sized slag was subjected to mineralogical analysis using a Zeiss EVO® MA15 Scanning Electron Microscopy coupled with a Bruker Energy-Dispersive Spectrometer (SEM-EDS) and a Bruker D8 advanced X-ray Diffraction (XRD). Chemical analysis of the raw and processed materials was carried out using Varian Vista-PRO CCD simultaneous inductively coupled plasma optical emission spectrometer (ICP–OES) and Perkin Elmer PinAAcle™ 900 atomic absorption spectrometer (AAS).

The current study used analytical grade Na_2CO_3 and NaOH supplied by Associated Chemical Enterprises as sodium salts. Deionised water with a conductivity of 0.055 µS/cm at 25°C was produced at Mintek using a Millipore instrument. Deionised water was used as a lixiviant in the current study.

Experimental procedure

The reactions of the vanadium-bearing spinel solid solution $[(Mg,Fe)(Al,Ti,V)_2O_4]$ in the titaniferous slag with Na_2CO_3 and NaOH salts in the air can be described by chemical reactions [1] to [12] (Lv, et al., 2022; Lee, et al., 2021; Parirenyatwa, et al., 2016). Since the solubility of titania in the spinel solid solution of titaniferous slags is limited (Goso, et al., 2024), the main spinel endmembers were assumed to be $MgAl_2O_4$, MgV_2O_4, $FeAl_2O_4$, and FeV_2O_4.

$MgAl_2O_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + MgO + CO_2$ [1]

$MgV_2O_4 + Na_2CO_3 + O_2 \rightarrow 2NaVO_3 + MgO + CO_2$ [2]

$FeAl_2O_4 + Na_2CO_3 + 0.25O_2 \rightarrow 2NaAlO_2 + 0.5Fe_2O_3 + CO_2$ [3]

$FeV_2O_4 + Na_2CO_3 + 1.25O_2 \rightarrow 2NaVO_3 + 0.5Fe_2O_3 + CO_2$ [4]

$MgAl_2O_4 + 2NaOH \rightarrow 2NaAlO_2 + MgO + H_2O$ [5]

$MgV_2O_4 + 2NaOH + O_2 \rightarrow 2NaVO_3 + MgO + H_2O$ [6]

$FeAl_2O_4 + 2NaOH + 0.25O_2 \rightarrow 2NaAlO_2 + 0.5Fe_2O_3 + H_2O$ [7]

$FeV_2O_4 + 2NaOH + 1.25O_2 \rightarrow 2NaVO_3 + 0.5Fe_2O_3 + H_2O$ [8]

Lekobotja et al. (2017) reported that the roasting of titaniferous slag with a sodium salt resulted in the formation of $NaAlSiO_4$. Thus, the formation of $NaAlSiO_4$ can be described by the chemical reaction [9] (Lv, et al., 2022), $NaAlO_2$ formed as shown in chemical reactions [1], [3], [5] and [7].

$2NaAlO_2 + SiO_2 \rightarrow NaAlSiO_4$ [9]

Given the above, the stoichiometric sodium salt additions were calculated using the simplified chemical reactions [10] to [15], with the sodium salts mainly reacting with vanadium, alumina, and silica.

$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2$ [10]

$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$ [11]

$Na_2CO_3 + 2SiO_2 + Al_2O_3 \rightarrow 2NaAlSiO_4 + CO_2$ [12]

$2NaOH + V_2O_5 \rightarrow 2NaVO_3 + H_2O$ [13]

$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$ [14]

$2NaOH + 2SiO_2 + Al_2O_3 \rightarrow 2NaAlSiO_4 + H_2O$ [15]

Table II presents a summary of the formulated test matrix for the preliminary evaluation of the effectiveness of excessive sodium salt additions during roasting on the decomposition of vanadium-bearing phases and vanadium extraction. Sodium salt additions were 15% and 100% above the stoichiometric requirements for the formation of $NaVO_3$, Na_2SiO_3, and $NaAlSiO_4$, according to chemical reactions [10] to [15]. Sodium salt was added as a mixture of Na_2CO_3 and NaOH in mass ratios ranging from 100:0 to 0:100. Tests that produced the highest vanadium extractions for Na_2CO_3 and NaOH were repeated, i.e. Tests 6 and 8.

Table II. Summary of the test matrix

Test	Na_2CO_3	NaOH	Stoichiometric Na addition (%)	Roasting temperature (°C)	Roasting time (min)
1	100	0	115	1000	120
2	85	15			
3	50	50			
4	15	85			
5	0	100			
6	100	0	200	1000	120
6R	100	0			
7	50	50			
8	0	100			
8R	0	100			
9	100	0	200	800	120
10				900	
11	100	0	200	1000	60
12					180

R – Replicate test of the associated test number

Roasting procedure

To complete each test, a mass of 200 g of sized titaniferous slag was mixed with a 40 mL saturated sodium salt solution for effective homogenisation of the test reactants. The slurry with a moisture content of about 20% was dried in an oven at 105°C overnight. After drying, the lumps in the dry solids were broken down manually, using a ceramic rod. The feed was transferred into a SiC tray. The charged tray was placed in a pre-heated chamber furnace operated at the target test temperature. The temperature in the chamber decreased when inserting the SiC tray into the furnace. The counting of the roasting time shown in the test matrix only started when the temperature in the chamber was restored to the target test temperature. At the end of the roasting time, the test tray was removed from the chamber furnace, and placed onto refractory bricks to facilitate the cooling of the sample to room temperature. The masses of the test sample before and after roasting were recorded. Roast products were analysed by ICP-OES and AAS.

Water leaching

Roast products were subjected to a standard set of leaching conditions and procedures. The leaching procedure involved transferring a 200 mL volume of deionised water and 50 g of the roasted sample into a 500 mL round-bottom flask to maintain a solid-to-liquid mass ratio of 1:4 in the slurry. A magnetic stirrer bar was also inserted into the round bottom flask, i.e. the reactor. A condenser was connected to the reactor for condensation of the fumes generated during the leaching. The reactor was immersed in an oil bath and placed on a magnetic hotplate. The temperature of the hotplate and agitation speed of the slurry were adjusted to achieve a constant slurry temperature of 70°C and slurry agitation speed of 350 rotations per minute over a leaching period of 2 hours. At the end of the leaching period, the slurry was filtered whilst still hot using a Buchner funnel equipped with a Whatman 542 hardened ashless filter paper. The volume of the first filtrate was measured. The wet cake was plug-washed with 400 mL of deionised water, and subsequently dried in an oven at 105°C overnight. The first filtrate and dry filter cake were subjected to chemical analyses using ICP-OES and AAS.

RESULTS AND DISCUSSION

Raw material characterisation

The chemical analysis results of the as-received titaniferous slag, shown in Table III, containing about 35% TiO_2 and 0.95% V_2O_5 suggest that this slag was produced from the open slag bath furnaces at EHSV (Steinberg, et al., 2011). However, the iron content in the as-received slag was uncharacteristically high.

Figure 1 and Table IV present the BSE image and EDS analysis results of the different phases identified in the BSE images of the as-received titaniferous slag. XRD analysis results of this slag are also included in Table IV. The identified phases such as spinel, pseudobrookite, titanaugite, and perovskite concur with the phase compositions of titaniferous slags reported in the literature. Moreover, vanadium in the current slag was contained in the spinel and pseudobrookite phases as also reported in the literature (Goso, et al., 2016; Pistorius, 2011). An iron-rich alloy phase was found in the as-received slag. The high iron content observed in the chemical composition of the slag reported in Table III was thus attributed to alloy entrainment. This alloy also contained significant contents of vanadium.

Table III. Chemical composition of the vanadium-bearing titaniferous slag (mass %)

Al_2O_3	CaO	Cr_2O_3	*FeO	MgO	MnO	SiO_2	V_2O_5	TiO_2	S
7.90	14.3	0.38	7.18	9.45	0.64	19.2	0.95	35.6	0.34

*Total Fe expressed as FeO

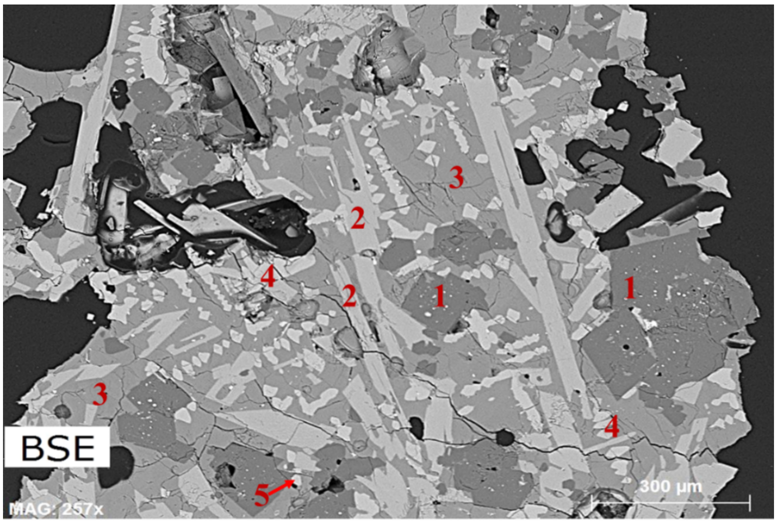

Figure 1. Backscattered electron image of the titaniferous slag

Table IV. EDS analysis results of the BSE phases and XRD phase composition of the as-received slag (mass %)

Spot	O	Mg	Al	Si	Ca	Ti	V	Fe	XRD results
1	44.3	18.2	32.8			4.1	0.5		Spinel
2	40.4	6.7	2.7			49.7	0.5		Pseudobrookite
3	42.3	7.7	8.2	14.7	18.1	8.9			Titanaugite
4	34.9				32.0	33.1			Perovskite
5						1.0	1.5	97.5	Fe-Ti-V alloy

Roasting

The chemical analysis results of the roast products, presented in Table V, show that the chemical species in the starting slag were diluted by sodium. Mineralogical characterisation results shown under the 'phase chemistry' section below suggested a standard stable phase assemblage for all the roast products, namely, spinel, pseudobrookite, perovskite, hematite, and sodium magnesium aluminium silicate ($Na_3MgAlSi_2O_8$). The phase compositions are discussed in more detail for the best results in the above-referenced section. The reported generic phase assemblage of the roast products showed that the vanadium-bearing spinel and pseudobrookite phases were not fully decomposed, if any, and that $Na_3MgAlSi_2O_8$ was formed as a new phase, not the reported nepheline phase ($NaAlSiO_4$) (Lekobotja, et al., 2017).

Table V. Chemical compositions of the roast products (mass %)

Test	Na_2O	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	SiO_2	TiO_2	V_2O_5
1	16.4	14.5	14.5	0.14	4.00	10.1	0.56	12.4	25.8	0.67
2	16.3	14.7	14.3	0.13	3.82	10.2	0.55	12.0	25.3	0.66
3	16.3	14.6	14.5	0.13	4.15	10.1	0.56	12.5	25.8	0.68
4	18.5	14.3	14.6	0.14	4.24	10.1	0.57	12.3	25.8	0.68
5	19.7	13.4	14.2	0.10	3.80	9.93	0.58	11.9	26.4	0.60
6	15.1	11.5	10.4	0.15	5.57	9.58	0.52	13.4	22.8	0.64
6R	16.2	11.0	11.8	0.15	4.45	10.3	0.54	14.5	23.1	0.65
7	14.2	11.7	10.3	0.15	5.78	9.83	0.52	13.5	23.2	0.66
8	14.7	11.8	9.86	0.13	5.39	9.20	0.50	13.1	22.5	0.64
8R	16.6	11.4	10.8	0.14	4.92	9.75	0.52	13.8	22.8	0.58
9	19.5	11.1	10.6	0.19	3.90	8.10	0.46	13.2	20.4	0.63
10	25.8	12.1	11.5	0.20	4.04	8.70	0.49	14.1	21.7	0.67
11	18.9	12.0	12.1	0.19	3.33	9.83	0.54	14.8	22.0	0.65
12	14.3	12.1	12.2	0.18	3.44	9.88	0.54	14.9	22.2	0.67

R – Replicate test of the associated test number

Water leaching

The chemical compositions of the leach solids, shown in Table VI, indicate that vanadium (V_2O_5) contents in the solids after leaching declined significantly, with lower vanadium contents observed in solids produced from 200% compared to 115% stoichiometric sodium additions, i.e. Tests 6 to 12 compared to Tests 1 to 5.

Sodium and silica contents in the solids are generally high, suggesting that these species mainly existed in $Na_3MgAlSi_2O_8$ that is not readily soluble in water, and not in the predicted Na_2SiO_3 that is water-soluble (Gilligan & Nikoloski, 2020).

Table VI. Mass losses and chemical compositions of leach solids (mass %)

Test	Na_2O	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	SiO_2	TiO_2	V_2O_5
1	17.3	14.3	12.6	0.15	2.83	11.6	0.56	15.1	24.8	0.36
2	15.8	13.9	12.0	0.23	4.10	11.2	0.53	15.5	26.0	0.39
3	17.7	14.0	12.5	0.17	3.95	11.4	0.56	14.8	24.2	0.36
4	15.9	13.7	12.2	0.15	4.00	11.1	0.54	15.5	25.5	0.38
5	14.1	13.8	12.9	0.09	3.31	11.7	0.60	15.9	26.6	0.40
6	14.1	10.4	12.4	<0.05	5.50	10.4	0.63	14.8	24.1	0.17
6R	13.8	10.8	12.6	<0.05	5.77	10.8	0.61	15.6	23.7	0.23
7	14.2	10.1	12.3	<0.05	5.60	10.4	0.62	14.9	24.0	0.16
8	14.7	10.2	12.4	<0.05	6.13	10.5	0.63	15.0	24.2	0.15
8R	17.3	14.3	12.6	0.15	2.83	11.6	0.56	15.1	24.8	0.15
9	16.0	10.2	11.8	0.10	3.99	8.8	0.51	15.5	25.1	0.23
10	14.4	12.5	12.1	0.20	3.91	9.1	0.55	15.6	25.4	0.35
11	14.8	11.2	13.1	<0.05	3.61	10.8	0.58	16.1	24.0	0.39
12	14.8	10.9	13.1	<0.05	3.60	10.7	0.58	16.2	24.4	0.13

<0.05 mass% - limit of detection of the analyte on the analytical method

As a preliminary investigation, the estimation of the vanadium extraction was based on the chemical analysis results of the leach solids. Vanadium extraction from the titaniferous slag was therefore calculated using Equation [16].

$$\%V\ \text{extraction} = [1 - (\text{Mass}\ V_{\text{leach solids}}/\text{Mass}\ V_{\text{roast products}})]\ \text{X}\ 100 \qquad [16]$$

Effect of Na_2CO_3: NaOH mass ratio

Figure 2 shows the effect of Na_2CO_3: NaOH mass ratio at 115% and 200% stoichiometric sodium additions on the vanadium extraction from the titaniferous slag. These preliminary results show that vanadium extractions were highest when Na_2CO_3 and NaOH were added individually, at both 115% and 200% stoichiometric sodium additions. Thus, there is no obvious benefit from roasting with a blend of Na_2CO_3 and NaOH salts.

In general, vanadium extractions were higher for roasting with 200% than 115% stoichiometric sodium salt addition. When roasting was conducted with Na_2CO_3 alone, the duplicate vanadium extractions were 76.7% and 74.7%. For NaOH roasting, the duplication vanadium extractions were 76.0% and 71.3%. Lower standard deviations than 5% suggest that the test procedure and results were reproducible. With an average vanadium extraction of 75.7% and a standard deviation of 1.4% for Na_2CO_3, and an average vanadium extraction of 73.7% and a standard deviation of 3.3% for NaOH, the roasting efficiencies of the two salts were similar.

Since the Na_2CO_3 salt is relatively cheaper and more understood as it is used in industrial vanadium primary production operations, it was adopted for investigating the effect of other parameters on the vanadium extraction from the titaniferous slag.

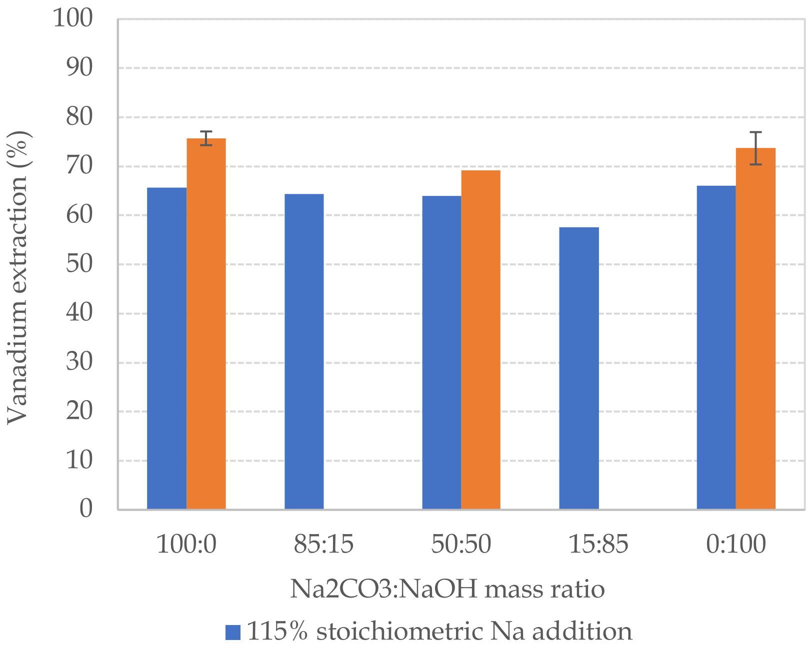

Figure 2. Effect of Na_2CO_3: NaOH mass ratio at 115% and 200% stoichiometric sodium additions on the vanadium extraction from titaniferous slag

Effect of temperature

Vanadium extractions from the titaniferous slag at 200% stoichiometric Na_2CO_3 addition during roasting, as shown in Figure 3, increased with temperature from 800°C to 1000°C. These results agree with those reported by Zhang *et al.* (2019), and Deng *et al.* (2020), in which it was shown that vanadium extraction from various titaniferous concentrates increased with roasting temperature.

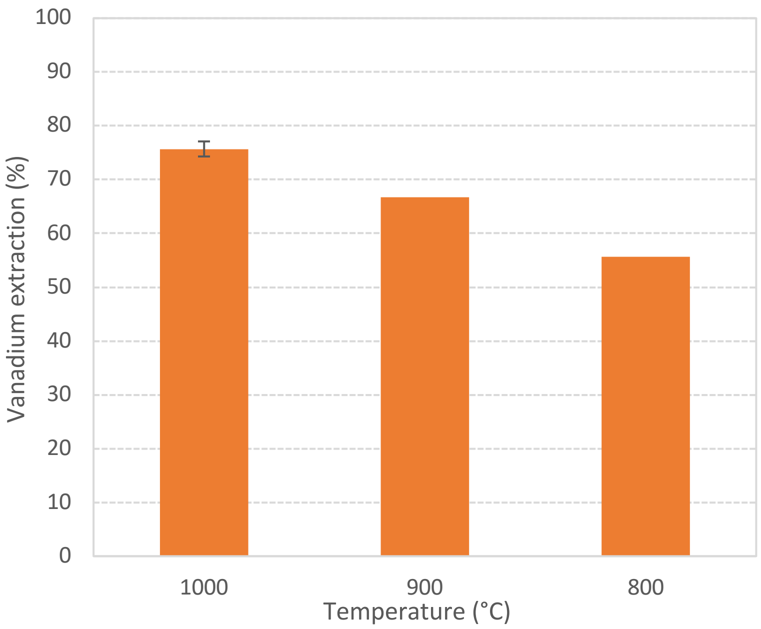

Figure 3. Effect of roasting temperature at 200% stoichiometric Na_2CO_3 addition on the vanadium extraction from titaniferous slag

Effect of time

Vanadium extractions from the titaniferous slag, attained after roasting at different times as shown in Figure 4, increased with roasting time up to 120 minutes and decreased at longer roasting times of 180 minutes. The decrease in vanadium extraction at longer roasting times was attributed to the sintering of the solids when more time was allocated for the residual sodium in the solids to react with slag components. Li *et al.* (2018) also reported lower vanadium extractions at longer roasting times, allegedly due to the sintering of the roast products.

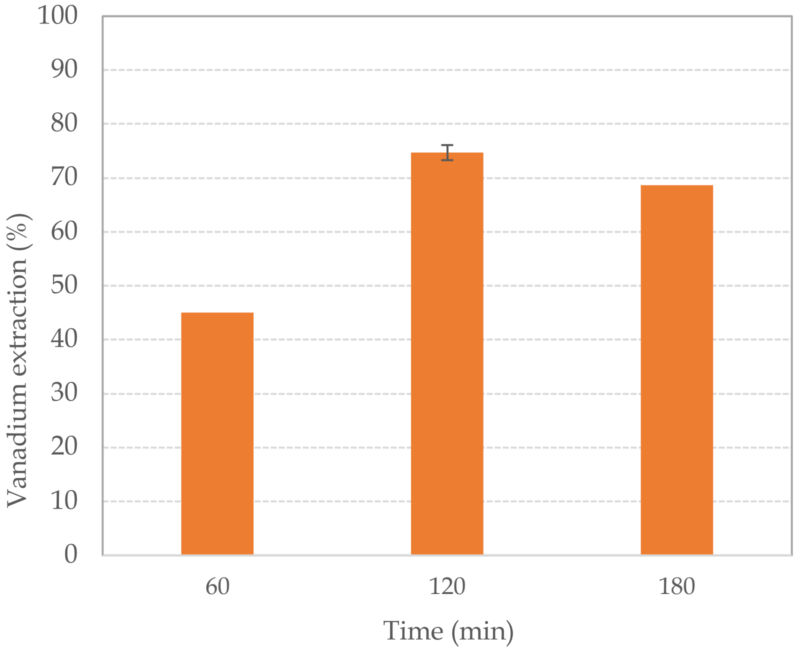

Figure 4. Effect of roasting time at 1000°C for 200% stoichiometric Na_2CO_3 addition on the vanadium extraction from titaniferous slag

Phase chemistry

Roasting with 200% stoichiometric Na_2CO_3 addition

Figure 5 and Table VII present the SEM-EDS and XRD analysis results of the product of roasting with 200% stoichiometric Na_2CO_3 addition. The results show that the vanadium-bearing spinel and pseudobrookite phases were decomposed during roasting, with the spinel phase missed by the SEM-EDS analyses and detected by XRD at trace concentration levels, i.e. <5 mass%. A new phase, i.e. sodium magnesium aluminium silicate ($Na_3MgAlSi_2O_8$), was formed after roasting. Vanadium in the roast product was contained in the titanaugite and $Na_3MgAlSi_2O_8$ phases. The target $NaVO_3$ phase that is water-soluble was not observed on the micrographs and was also not detected by XRD.

Figure 6 and Table VIII present the SEM-EDS and XRD results of the water leach solids of roast produced at 200% stoichiometric Na_2CO_3 addition. The release of vanadium that was present in the starting spinel and pseudobrookite phases resulted in high vanadium extractions. XRD results showed trace concentration levels of the spinel, which was also detected by SEM-EDS. Vanadium after leaching was only detected in this spinel. Further optimisation of the roasting conditions has the potential to facilitate the complete decomposition of the spinel and attainment of even higher vanadium extractions than the reported average extraction of 75.7%.

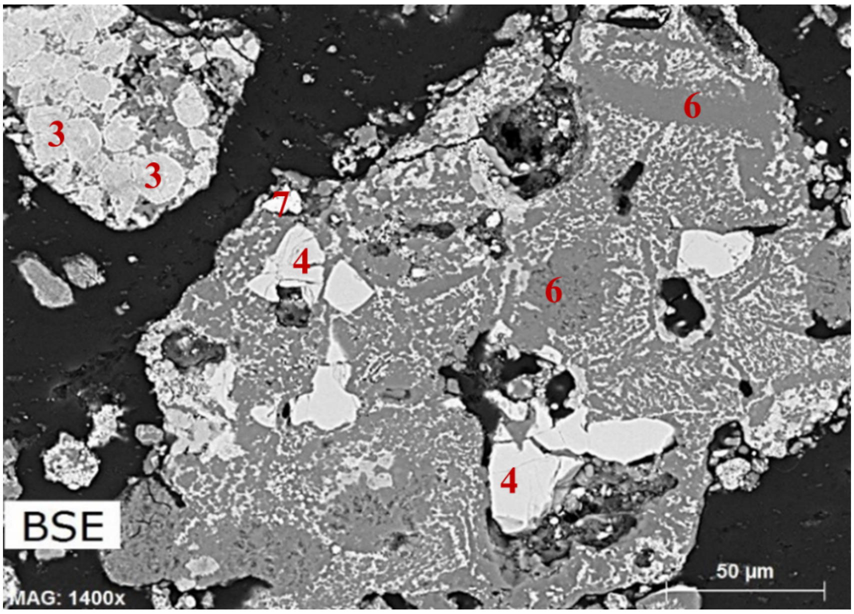

Figure 5. Backscattered electron image of the product of roasting with 200% stoichiometric Na_2CO_3 addition

Table VII. EDS analysis results of the BSE phases and XRD phase composition of roast product at 200% stoichiometric Na_2CO_3 addition (mass %)

Spot	**O**	**Na**	**Mg**	**Al**	**Si**	**Ca**	**Ti**	**V**	**Mn**	**Fe**	XRD results
											Spinel (trace levels)
3	30.5	10.1	3.0	5.2		1.8	13.8	0.5	0.9	34.0	Titanaugite
4	35.4			2.0		30.4	32.1				Perovskite
6	47.2	17.9	7.1	10.2	11.7		3.5	0.2		2.2	$Na_3MgAlSi_2O_8$
7	24.4			4.6						71.0	Iron-Oxide

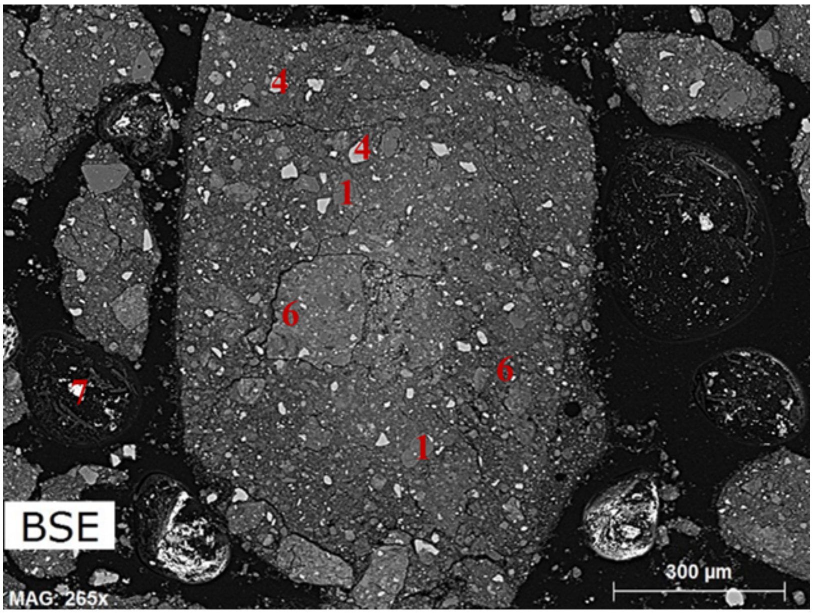

Figure 6. Backscattered electron image of the water leach solids of roast produced at 200% stoichiometric Na_2CO_3 addition

Table VIII. EDS analysis results of the BSE phases and XRD phase composition of the water leach solids of roast produced at 200% stoichiometric Na_2CO_3 addition (mass %)

Spot	O	Na	Mg	Al	Si	Ca	Ti	V	Fe	XRD results
1	44.0		18.9	30.5			6.4	0.2		Spinel
4	35.0					31.3	33.7			Perovskite
6	42.7	2.9	6.7	4.1	14.2	2.5	23.0		3.9	$Na_3MgAlSi_2O_8$
7	22.5						0.8		76.8	Iron-Oxide

Roasting with 200% stoichiometric NaOH addition

Figure 7 and Table IX present the SEM-EDS and XRD results of the product of roasting with 200% stoichiometric NaOH addition. The vanadium-bearing spinel and pseudobrookite phases found in the starting slag were not detected by the two analytical techniques. The vanadium-bearing phases, some of which were eventually leached were completely missed by the SEM-EDS and XRD analyses.

Both EDS and XRD techniques detected the vanadium-bearing spinel in the water leach solids of the roast produced at 200% stoichiometric NaOH addition, as shown in Figure 8 and Table X. XRD results confirmed that the spinel occurred at trace concentration levels of <5 mass%. The residual vanadium that remained in the leach solids was contained in this spinel phase.

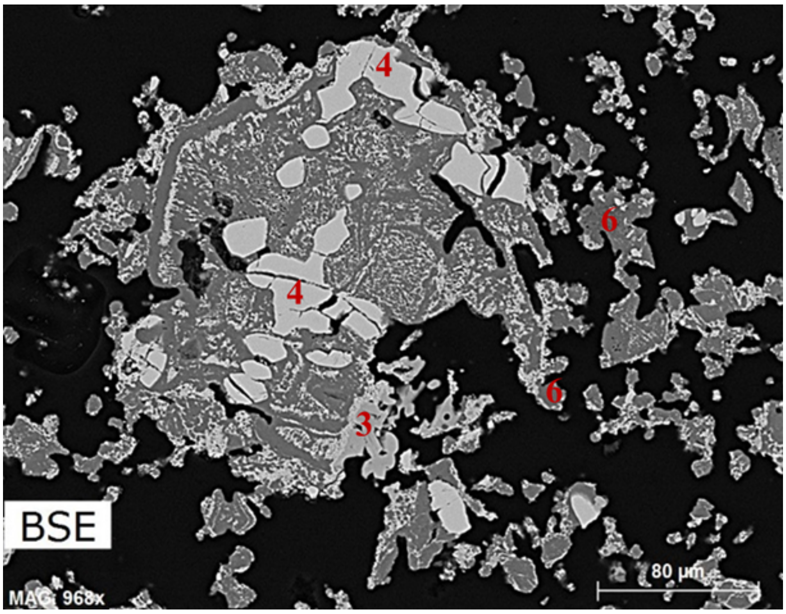

Figure 7. Backscattered electron image of the product of roasting with 200% stoichiometric NaOH addition

Table IX. EDS analysis results of the BSE phases and XRD phase composition of roast product at 200% stoichiometric NaOH addition (mass %)

Spot	O	Na	Mg	Al	Si	Ca	Ti	Mn	Fe	XRD results
3	35.5	10.5	5.1				29.3	8.3	11.3	Titanaugite
4	35.0					31.4	33.6			Perovskite
6	47.0	16.3	8.5	8.4	12.7	0.4	3.8		3.0	$Na_3MgAlSi_2O_8$

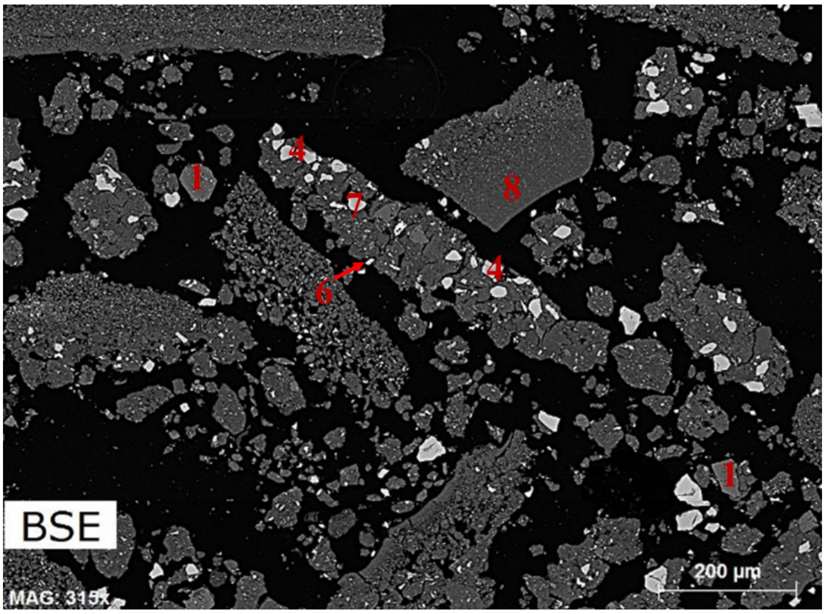

Figure 8. Backscattered electron image of the water leach solids of roast produced at 200% stoichiometric NaOH addition

Table X. EDS analysis results of the BSE phases and XRD phase composition of the water leach solids of roast produced at 200% stoichiometric NaOH addition (mass %)

Spot	O	Na	Mg	Al	Si	Ca	Ti	V	Cr	Fe	XRD results
1	44.2		19.4	31.6			4.4	0.9			Spinel
4	35.0					31.3	33.7				Perovskite
6	42.2	4.0	1.4	6.9	14.1	4.7	21.4			5.3	$Na_3MgAlSi_2O_8$
7	23.8	0.4			0.6		3.4		1.1	70.7	Iron-Oxide
8	38.9	1.6	0.8	0.7	3.1	2.4	46.3			6.2	Rutile

CONCLUSIONS AND RECOMMENDATIONS

Preliminary investigations into vanadium extraction from titaniferous magnetite slags using excess stoichiometric Na_2CO_3 and NaOH salt additions in the vanadium production process resulted in high extractions. The highest vanadium extractions were achieved when roasting was conducted with separate Na_2CO_3 and NaOH, attaining the respective average extractions of 75.7% and 73.7% at 200% stoichiometric sodium salt additions. Roasting with a blend of Na_2CO_3 and NaOH did not improve the vanadium extractions. For both Na_2CO_3 and NaOH roasting, the vanadium extractions improved by increasing the stoichiometric sodium salt addition from 115% to 200%. There was no significant technical difference between roasting with Na_2CO_3 and NaOH. Vanadium extractions using the cheaper and industrially used Na_2CO_3 salt increased with increasing roasting temperature and time up to 1000°C and 120 minutes, respectively. After a roasting time of 180 minutes, vanadium extraction decreased due to the slight sintering of the solids as a consequence of high sodium contents and elongated roasting times.

Mineralogical characterisation results showed that the vanadium-bearing spinel and pseudobrookite phases in the starting spinel were decomposed during roasting with individual Na_2CO_3 and NaOH – only trace concentration levels of spinel were detected in the roast product and leach solids. Unlike in previous work where $NaAlSiO_4$ was reported as a new phase that formed when the vanadium-bearing spinel and pseudobrookite phases were decomposed, $Na_3MgAlSiO_4$ was detected as the new phase that formed in the current study. Further work is recommended to optimise the roasting conditions for effective preconditioning of the feed to the vanadium leaching stage. Leach solids can also be upgraded using sequential hydrochloric acid and caustic leaching stages to a marketable titania product.

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