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EXTERNAL REPORT

8226

PRELIMINARY INVESTIGATION INTO VANADIUM EXTRACTION FROM SELECTED EHSV BY-PRODUCTS USING THE ROAST-LEACH PROCESS

By

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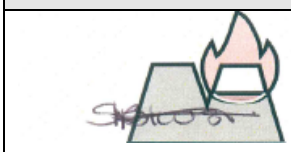	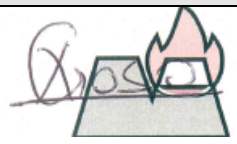	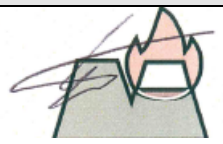
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SUMMARY

Ukhozi Africa Technologies (Pty) Ltd. (Ukhozi) are interested in the valorisation of the waste dumps generated by the defunct Evraz Highveld Steel and Vanadium Corporation (EHSV) for the production of ammonium metavanadate (AMV) intermediate product that will subsequently be used as feedstock for the production of vanadium electrolyte used in the vanadium redox flow batteries (VRFBs). Ukhozi contracted Mintek to undertake a high level study to test the technical feasibility of vanadium extraction from the concentrated by-product materials with concentrations of 1% to 4% V_2O_5 using the conventional roast-leach process. The concentrations of V_2O_5 in these by-products are significantly higher than 0.39% V_2O_5 concentration in the Chinese titaniferous magnetite, which is used as feedstock for the production of steel and vanadium, which accounts for the world's single largest vanadium production by country.

Scouting tests using the un-optimised roast-leach conditions were conducted on five client samples, namely; 'Red dust', '1A', '1B', 1D-S/N' and '1E'. The scouting test conditions involved the roasting of a blend of the vanadium bearing sample and soda ash (Na_2CO_3) in a mass ratio of 100: 5 using a chamber furnace at 1000°C for 60 minutes, followed by leaching in de-ionised water in a slurry with solid content of 65 wt% at 70°C for 60 minutes. Samples labelled 1A, 1B, 1D-S/N and 1E performed the worst as only 2% to 5% vanadium extraction efficiencies were achieved. Hence, for any chance of the extraction of vanadium from these materials, a systematic study incorporating mineralogical characterization and intense roasting conditions may be required.

Red dust material was different to the other samples: it had higher V_2O_5 and Fe concentrations and low titania concentrations. Though, the vanadium extraction efficiencies from the red dust using the un-optimised roast-leach conditions were also low at about 11%, the relatively higher V_2O_5 concentration compared to other samples and relatively low roasting temperature requirement (to avoid sintering) made the processing of red dust more attractive. Roasting of the red dust at temperatures of 900°C and above resulted in the formation of sinters which were responsible for low vanadium extraction efficiencies. Hence, the scouting roast-leach conditions were reviewed for the red dust material. The vanadium extraction efficiencies from the red dust were evaluated further under the following conditions: roasting of a blend of red dust and 115% stoichiometric Na_2CO_3 amount equivalent for the formation of $NaVO_3$ and Na_2SiO_3 at 800°C for 60, 120, 180 and 240 minute tests. The vanadium extraction from the red dust was generally sensitive to roasting time. The best vanadium extraction efficiency of about 69% was achieved after roasting for 240 minutes – the extraction efficiency had not reached the saturation point.

The vanadium pregnant leachate was subjected to impurity rejection, and subsequently vanadium precipitation as AMV, which would be used by the client for marketing purposes. XRD analysis only detected the existence of AMV phase in the vanadium precipitate – thus, the concentrations of other phases would be less than 3%, which is the limit of detection of the XRD instrument employed in the current study.

During the vanadium production using the conventional roast-leach process, the impurity rejection and vanadium concentration stages typically do not result in vanadium losses. The vanadium precipitation or recovery efficiency to AMV is generally about 95%. Thus, the cumulative vanadium extraction from the red dust material to AMV through the roast-leach vanadium primary production process would be 66%. It is thus estimated that for a 100 kg red dust material processed through the conventional roast-leach process, about 3.1 kg AMV would be precipitated.

The current preliminary study has shown that AMV can be produced from the red dust. Further work is therefore proposed to optimise the roast-leach process conditions, particularly the roasting time and sodium reagent type and addition. Further work can also be conducted to investigate the potential application of the leach residue. Techno-economic evaluation of the proposed roast-leach process flowsheet for the red dust material for the determination of the minimum commercial scale of production of AMV is also recommended. The techno-economic study will take into consideration the mass and energy balance for the process flowsheet. The minimum or desirable production scale for reasonable and practical net present value (NPV), internal rate of return (IRR) and payback period (PP) or return of investment would be established.

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1. INTRODUCTION

Ukhozi Africa Technologies (Pty) Ltd. (Ukhozi) are interested in the valorisation of the waste dumps generated by the defunct Evraz Highveld Steel and Vanadium Corporation (EHSV) for the production of ammonium metavanadate (AMV) intermediate product that will subsequently be used as feedstock for the production of vanadium electrolyte used in the vanadium redox flow batteries (VRFBs). Ukhozi identified five possible by-products for the production of the AMV intermediate product, namely; 'Red dust', '1A', '1B', 1D-S/N' and '1E'.

Ukhozi contracted Mintek to undertake a high level study to test the feasibility of vanadium extraction from the by-product materials with concentrations of 1% to 3.7% V_2O_5 using the conventional roast-leach process. The concentrations of V_2O_5 in some of the by-product materials are significantly higher than 0.39% V_2O_5 concentration in the Chinese titaniferous magnetite used as feedstock for the production of steel and vanadium, which accounts for the world's single largest vanadium production by country.

At first, the five samples were subjected to exploratory roast-leach test conditions established at Mintek in the past on a South African titaniferous magnetite concentrate. The preliminary tests indicated that the vanadium was relatively easier to extract from the red dust compared to other samples. Hence, the scope of work mainly focused on the processing of the red dust. The testwork included the roasting of the red dust material in the presence of a sodium reagent, followed by leaching of vanadium into solution. The vanadium pregnant solution was subjected to impurity rejection and concentration before the precipitation of vanadium as AMV. The testwork was conducted as shown in the block flow diagram in Figure 1, using the red dust as feedstock for AMV production.

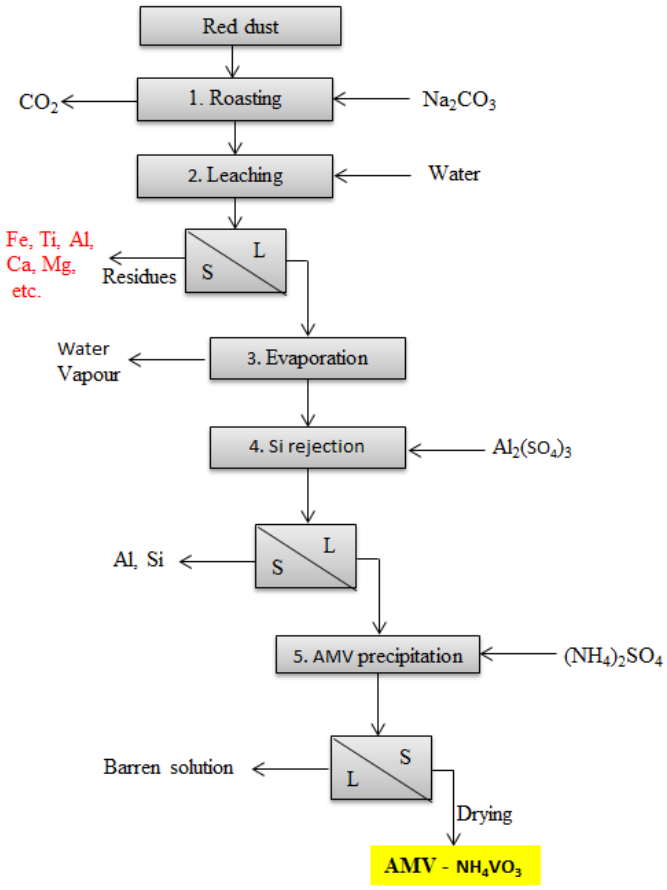

Figure 1 Block flow diagram of the completed testwork

2. EXPERIMENTAL PROCEDURES

2.1. Sample receipt and characterisation

Ukhozi provided Mintek with five samples for the testwork. The samples were contained in respective 3-litre buckets as shown in Figure 2. The respective samples labelled 'Red dust', '1A', '1B', 1D-S/N' and '1E'were weighed, and the masses are recorded in Table 1. The samples were dried in an oven at 105°C overnight. The dry samples were crushed, milled and split into 6 subsamples. The respective samples were milled to a top size of 1 mm. A split subsample of each material was subjected to bulk chemical analysis by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and semi-quantitative X-Ray fluorescence (XRF). Other subsamples were used for the roast-leach testwork.

The client provided Mintek with an additional sample of the red dust in order to complete the bulk test for the production of the AMV. The mass of the additional sample is also included in Table 1.

Figure 2 Photograph of the as received samples from Ukhozi

Table 1 Masses of the as received samples (grams)

Sample identification	Mass of sample and bucket (grams)	Additional sample (grams)
Red dust	3126.9	5265.5
1A	3254.2	
1B	2949.3	
1D-S/N	3449.9	
1E	3187.2	

2.2. Scouting roast-leach testwork

The scouting roast-leach conditions that were used as basis for the beneficiation of the client samples for the vanadium extraction included (1) blending of the vanadium bearing sample and soda ash (Na_2CO_3) in a mass ratio of 100: 5, (2) roasting in a pre-heated furnace at 1100°C, and keeping the sample at temperature for 60 minutes before removal from the furnace and allowing to cool down to room temperature, and (3) leaching of the roast product in de-ionised water in a slurry with solid content of 65 wt% at 70°C for 60 minutes.

2.2.1. Roasting

The objective of the roasting stage in the conventional roast-leach process is to convert vanadium in the resource to the water soluble sodium metavanadate ($NaVO_3$) as shown in reaction equation [1].

$$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2, \quad [1]$$

A mass of 200 g of the split vanadium bearing material was weighed and mixed with sodium carbonate (Na_2CO_3) at a mass ratio of 100:5. The mixtures were placed in respective SiC trays, and subsequently put into the preheated chamber furnace at target test temperatures. When the roasting was conducted at 1100°C, the respective mixtures formed hard sinters that generally hamper the extraction of vanadium during the subsequent leaching stage. Hence, the roasting temperatures were reviewed. At the end, all samples were successfully roasted at 1000°C, with the exception of the red dust, which still sintered after roasting at 1000°C and 900°C. All the samples were roasted at the target temperature for a period of 60 minutes. The roast products

were subjected to bulk chemical analysis using ICP-OES. The test matrix for the preliminary roasting tests is shown in Table 2.

Table 2 Test matrix for samples roasted at different temperatures

Test	Sample	Temperature (°C)
1*	Red Dust	1100
3#	Red Dust	1000
8#	Red Dust	900
2*	1A	1100
4	1A	1000
5	1B	1000
6	1D-S/N	1000
7	1E	1000

*Samples sintered significantly, #test with sinters that could adversely affect V extraction

2.2.2. Leaching

The roast products, including the somewhat sintered red dust samples, were subjected to leaching in de-ionised water at 70°C over 60 minutes in a pulp density of 65 m/m%. During leaching on a hot-magnetic plate, the slurry was agitated at 350 rotations per minute (rpm) using a magnetic bar. Upon completion of each test, the slurry was filtered. The residue was washed with excess de-ionised water to remove the possibly attached vanadium onto the solid particles – the washing was conducted until a clear solution of water was observed as filtrate. The leach residue was then dried in an oven at 105°C overnight. The first undiluted filtrate and the dry residue were subjected to bulk chemical analyses by ICP-OES.

The vanadium extraction efficiencies from the respective roasted materials were determined using equation [2].

$$\%V_{extraction} = \frac{\text{mass } V_{filtrate}}{\text{mass } V_{feed}} \times 100 \qquad [2]$$

$\%V_{extraction}$: vanadium extraction efficiency from the roasted vanadium material

mass $V_{filtrate}$: mass of vanadium in the first undiluted filtrate/ leachate

mass V_{feed}: mass of vanadium in the roasted vanadium material/ feed to leaching

2.3. Red dust processing to AMV

In the testwork with one of the objectives being the production of the AMV intermediate product for marketing purposes, the elemental mass balance determinations fell outside the scope of the current study.

2.3.1. Small scale roast-leach testwork

Since the red dust formed hard sinters after roasting at temperatures of 900°C and above, in this part of the testwork the roasting temperature was lowered to 800°C. In this work, the red dust was mixed with 115% stoichiometric Na_2CO_3 for the chemical reactions in equations [3] and [4]. The roasting procedure reported in section 2.2.1 was followed to complete the current roasting tests. The roasting time was varied between 60 and 240 minutes, with repeat tests conducted for 120, 180 and 240 minute tests. A matrix of roasting tests is shown in Table 3.

$$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2 \quad [3]$$

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \quad [4]$$

Table 3 Test matrix for samples roasted at different temperatures

Test	Temperature (°C)	Time (min)	
1	800	60	
2 3	800	120	Duplicates
4 5	800	180	Duplicates
6 *7	800	240	Duplicates

*Bulk test in a rotary kiln

The leaching tests of the roast products was altered slightly. In the current testwork, the roasts were subjected to leaching in de-ionised water at 70°C over 60 minutes in a pulp density with solid to liquid mass ratio of 1:4. To complete the leaching test, the slurry was heated using a hot plate while being agitated using an overhead stirrer at 350 rpm. Upon completion of each test, the slurry was filtered. The residue was washed with excess de-ionised water to remove the possibly attached vanadium onto the solid particles – the washing was conducted 3 times at a mass ratio of 1:5. The leach residue was then dried in an oven at 105°C overnight. The dry residues were subjected to bulk chemical analysis by ICP-OES to facilitate the quantification of the vanadium extraction efficiencies.

2.3.2. Bulk roast-leach testwork

A red dust sample of 1.5 kg in mass was mixed with 115% stoichiometric Na_2CO_3 for roasting in the rotary kiln. The charge was placed in the kiln and the temperature was increased at 10°C/ minute to 800°C and kept at temperature for a period of 240 minutes. The temperature of the sample bed inside the furnace was monitored with a K-type thermocouple connected to a data acquisition unit. At the end of the test duration, the roast material was collected for downstream processing.

The leaching of the bulk sample was conducted using the procedure described in section 2.3.1. The only difference was that the bulk sample was leached in two equal batches. Figure 3 show the typical appearance of the leachates and wash liquids produced during the processing of the bulk sample. The yellow colour of the leachate and the initial washes is indicative of vanadium in solution. It should be noted that the leaching conditions were not optimised in the current testwork.

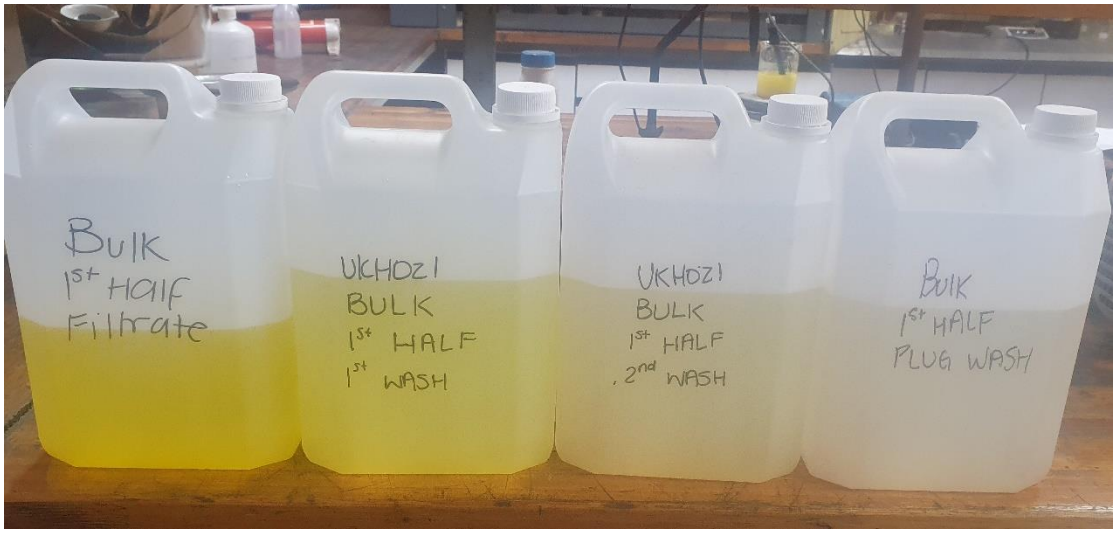

Figure 3 Typical appearance of the vanadium pregnant leachates of the roasted red dust material

2.3.3. Vanadium concentration

Before the precipitation of vanadium, the vanadium concentration in the solution should be between 35 and 40 g/L. The concentration of vanadium in the solution was achieved by evaporating some of the solution at 70°C, in order to avoid the losses of vanadium to the steam. When the target V concentration was achieved, the solution was cooled down to room temperature through natural heat loss of the container. After reaching the required volume after evaporation, the target vanadium concentration was achieved.

During the concentration of vanadium, vanadium losses to the steam generally do not occur.

2.3.4. Impurity rejection

The aim of the impurity rejection step was to remove Si and Al from the solution. The vanadium pregnant solution was heated up to 70°C using a hot plate. A mass of aluminium sulphate which was calculated to target Si content of ~0.05 g/ L in the final solution was added into the vanadium pregnant solution. The solution pH was immediately adjusted to pH 7.8 using concentrated sulphuric acid. The solution was agitated softly using a stirrer bar onto a hot-magnetic plate. After an hour, the slurry containing presumably the precipitates of aluminium silicate was allowed to cool down to room temperature. The slurry was filtered using a Buchner system. The solution was recovered for downstream processing.

2.3.5. AMV precipitation

The objective of this step of the testwork is to demonstrate the production of high purity AMV from the red dust. The de-silicated solution was used as a feed to the AMV precipitation testwork. AMV precipitation from the pregnant solution required adjusting of the pH to 8.4 using sulphuric acid. Ammonium sulphate was added to the pregnant solution at an amount equivalent to 200% for the stoichiometric requirement satisfying equation [5].

$$(NH_4)_2SO_4 + 2NaVO_3 \rightarrow 2NH_4VO_3 + Na_2SO_4 \quad [5]$$

The mixture was gently agitated to allow precipitation to complete, where after the AMV was separated from the barren solution using a millipore filtration system. The AMV filter cake

was washed with de-ionised water to remove excess sodium sulphate around the AMV particles.

3. RESULTS AND DISCUSSION

3.1. Bulk chemical compositions of the head samples

The bulk chemical compositions of the as-received samples from the defunct EHSV dump sites are included in Table 4. The total chemical compositions of the five samples are fairly close to 100%; thus, the deviation from the 100% total chemical composition may be attributed to the analytical measurement uncertainty.

Table 4 Bulk chemical analysis results of the as-received materials (mass %)

Sample	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	SiO_2	TiO_2	V_2O_5	ZnO	Total
Red dust	2.84	7.27	0.79	71.1	2.18	0.60	7.66	1.74	3.64	0.42	98.30
1A	12.9	15.1	0.22	6.15	13.8	0.75	17.4	30.7	1.36	<0.05	98.38
1B	12.5	15.4	0.18	4.46	14.5	0.76	19.7	30.6	1.07	<0.05	99.17
1D-S/N	11.6	15.0	0.18	6.89	13.4	0.68	17.8	28.9	1.06	<0.05	95.51
1E	12.2	15.8	0.20	4.53	14.9	0.80	18.7	31.2	1.43	<0.05	99.76

<0.05%: analyte concentration is below the limit of detection of 0.05% in the analytical method

3.2. Scouting roast-leach

3.2.1. Roasting

The typical appearance of the roasted red dust and 1A samples at 1100°C is shown in Figure 4. The samples formed hard sinters. The formation of sinters has a potential to adversely affect the leaching of vanadium due to a possible limitation of lixiviant penetration into the core of the sinter. Hence, the roasting test temperatures were lowered until sinters or hard agglomerates of the feed were not observed. All the samples were successfully roasted at 1000°C, with the exception of the red dust material which still formed sinters. The roasting temperature for the red dust sample was further reduced to 900°C – the photograph of the roast product is shown in Figure 5. The photograph shows that the red dust material still sintered at 900°C.

However, all the samples that were roasted at 1000°C were subjected to the scouting leaching testwork. In one leaching test, the sintered red dust feed was milled, while in another test it was not milled.

Figure 4 Appearance of the red dust and 1A samples after roasting at 1100°C

Figure 5 Appearance of red dust material after roasting at 900°C

The bulk chemical compositions of the roasted samples at 1000°C and 900°C are given in Table 5. The chemical analysis results of the roasted red dust sample are generally lower than the total chemical composition of 100%, suggesting that the chemical analysis results may be associated with measurement uncertainty. For the preliminary testwork conducted in this current test programme, a decision was taken to continue with the downstream processing of the red dust samples.

Table 5 Bulk chemical compositions of the roasted materials (mass %)

Sample	Temp (°C)	Na_2O	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	SiO_2	TiO_2	V_2O_5	Zn	Total
Red dust	1000	3.87	3.31	6.41	0.75	59.69	3.23	0.61	8.15	5.09	2.71	0.31	94.13
Red dust	900	4.11	3.19	6.31	0.76	60.85	3.32	0.62	7.70	5.04	2.87	0.36	95.14
1A	1000	3.79	13.08	14.27	0.22	6.12	13.37	0.68	18.48	29.53	1.09	<0.05	100.63
1B	1000	3.81	12.57	14.41	0.18	4.04	13.32	0.68	21.09	29.20	0.87	<0.05	100.18
1D-S/N	1000	3.81	12.38	14.55	0.18	6.65	13.28	0.63	19.64	28.36	0.89	<0.05	100.38
1E	1000	3.06	12.45	14.97	0.20	4.05	14.20	0.74	19.98	30.03	1.18	<0.05	100.86

<0.05%: analyte concentration is below the limit of detection of 0.05% in the analytical method

3.2.2. Leaching

The typical appearance of the slurry for the leaching of the un-milled sintered red dust is shown in Figure 6. As shown in the figure, the agitation of the slurry was not feasible when the un-milled red dust roast material was leached. However, the yellowish colour of the solution indicates that the leaching of vanadium from the sinter was happening – the leaching efficiencies were anticipated to be low due to the possible limitation of lixiviant penetration into the core of the hard sinter particles.

Figure 6 Appearance of the leach slurry of the un-milled roasted red dust sample at 1000°C

The bulk chemical compositions of the residues and filtrates from the leaching testwork are included in Table 6 and Nd – not determined as the sample sintered (higher temperature roast product chemical analysis was conducted for comparison with other samples)

Table 7, respectively. The chemical analysis results of the leach residues of the roasted red dust samples are still lower than the total chemical compositions of 100%.

Nevertheless, the V_2O_5 concentrations in the leach residues (Table 6) are not significantly different from the V_2O_5 concentrations in the leach feeds (Table 5), suggesting that leaching of vanadium into solution was also not significant. The chemical analysis results of the leachates in Nd – not determined as the sample sintered (higher temperature roast product chemical analysis was conducted for comparison with other samples)

Table 7 show notable concentrations of Al, Si and V.

Table 6 Bulk chemical compositions of the residues produced after leaching (mass %)

Sample	Temp (°C)	Na_2O	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	SiO_2	TiO_2	V_2O_5	Zn	Total
Un-milled red dust	1000	2.99	3.27	6.45	0.76	61.11	3.43	0.62	7.81	5.16	2.55	0.35	94.50
Milled red dust	1000	2.70	3.31	6.46	0.76	61.24	3.45	0.62	7.79	5.19	2.46	0.36	94.33
Red dust	900	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	
1A	1000	2.86	12.81	13.92	0.20	6.11	13.32	0.68	18.03	29.70	1.07	<0.05	98.71
1B	1000	2.90	11.64	14.41	0.18	6.96	12.87	0.68	19.23	29.03	0.87	<0.05	98.78
1D-S/N	1000	2.87	12.79	14.55	0.18	4.22	13.76	0.70	20.43	29.70	0.89	<0.05	100.09
1E	1000	2.72	12.30	14.69	0.19	4.04	14.13	0.74	19.36	30.03	1.14	<0.05	99.35

Nd – not determined as the sample sintered (higher temperature roast product chemical analysis was conducted for comparison with other samples)

Table 7 Bulk chemical compositions of the filtrates produced after leaching (ppm)

Sample	Temp (°C)	Al	Ca	Cr	Fe	Mg	Mn	Si	Ti	V (wt%)	Zn
Un-milled red dust	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.40	<2
Milled red dust	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.40	<2
Red dust	900	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
1A	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.10	<2
1B	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.06	<2
1D-S/N	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.05	<2
1E	1000	0.01	<2	<2	<2	<2	<2	0.01	<2	0.12	<2

<2ppm: Analyte concentration is below the limit of detection of 2 ppm in the analytical method
Nd – not determined as the sample sintered

3.2.3. Vanadium extraction efficiencies

Vanadium extraction efficiencies were calculated from the residue analysis results and are summarised in Table 8. The vanadium leaching efficiencies from the various materials was generally very low. A systematic study incorporating mineralogical characterization and intense roasting conditions may be required in order to maximize the extraction of vanadium from these materials.

Nevertheless, the vanadium extraction efficiencies from the relatively high V_2O_5 red dust material, which is also chemically different from the other samples, are somewhat disappointing. However, the available results for vanadium extractions from the sintered red dust material roasted at 1000°C (milled and un-milled) were anticipated to produce poor results due to the possible limitation of the lixiviant penetration into the roast product particles.

The focus of the investigations was redirected to the red dust material due to its relatively high V_2O_5 concentration.

Table 8 Summary of the vanadium extraction efficiencies from various Ukhozi samples

Sample	Roasting temperature (°C)	Vanadium extraction efficiency
Un-milled red dust	1000	8%
Milled red dust	1000	11%
1A	1000	4%
1B	1000	2%
1D-S/N	1000	2%
1E	1000	5%

3.3. Red dust processing to AMV

3.3.1. Roasting

Photographs showing the appearance of the red dust samples roasted at 800°C for 60, 120, 180 and 240 minutes are shown in Figure 7. The starting light brown sample colour became darker with increasing the roasting time from 60 to 240 minutes.

Red dust – 60 min

Red dust – 120 min

Red dust – 180 min

Red dust – 240 min

Figure 7 Photographs showing the appearance of the red dust samples after roasting at 800°C for 60, 120, 180 and 240 minutes.

The bulk chemical compositions of the roasted red dust material are given in Table 9.

Table 9 Bulk chemical compositions of the roasted materials (mass %).

Test	Na_2O	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	MnO	NiO	SiO_2	TiO_2	V_2O_5	ZnO	Total
1	10.66	1.74	4.83	0.72	*65.4	1.48	0.52	0.06	4.69	1.54	2.85	0.48	94.9
2	10.50	1.78	5.11	0.73	68.6	1.51	0.53	0.07	4.94	1.55	2.97	0.48	98.8
3	11.64	1.82	5.08	0.72	69.2	1.54	0.54	0.07	5.11	1.59	2.92	0.48	100.7
4	10.48	1.77	5.13	0.75	69.3	1.50	0.54	0.07	5.01	1.49	2.79	0.51	99.3
5	11.38	1.81	5.05	0.86	66.2	1.54	0.54	0.14	5.05	1.64	3.01	0.51	97.7
6	10.78	1.84	5.10	0.72	68.2	1.55	0.54	0.07	4.98	1.56	3.15	0.52	99.0
#7	10.65	1.83	5.09	0.71	67.5	1.53	0.55	0.08	5.03	1.53	3.23	0.50	98.2

*chemical analysis value appears to be an outlier, resulting in lower chemical composition total than 100%
#Bulk sample

3.3.2. Leaching tests

The bulk chemical compositions of the leach residues are included in Table 10. Low chemical analysis totals were attributed to measurement uncertainty. Though the vanadium concentrations as V_2O_5 are significant in the leach residues, it is still evident that the vanadium concentrations in the leach residues decrease with increasing the roasting time. Thus, the vanadium extraction from the red dust under the evaluated roast-leach conditions is sensitive to the roasting time.

Table 10 Bulk chemical compositions of the leach residues (mass %)

Test	Na_2O	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3	MgO	MnO	NiO	SiO_2	TiO_2	V_2O_5	ZnO	Total
1	4.67	1.81	5.32	0.64	70.9	1.58	0.55	0.06	4.82	1.65	1.97	0.51	94.52
2	5.12	1.63	5.33	0.76	72.1	1.46	0.61	0.07	3.55	1.87	1.74	0.54	94.74
3	7.84	1.68	5.28	0.31	71.7	1.49	0.66	0.07	3.91	2.01	1.19	0.54	96.69
4	5.11	1.60	5.34	0.75	71.8	1.45	0.61	0.07	3.49	1.85	1.76	0.55	94.38
5	7.79	1.70	5.31	0.35	70.9	1.53	0.66	0.08	3.95	2.05	1.17	0.56	96.05
6	7.88	1.74	5.35	0.45	68.9	1.50	0.75	0.09	4.05	2.32	0.98	0.53	94.54
#7	7.95	1.77	5.39	0.49	69.3	1.53	0.71	0.08	3.98	2.45	1.03	0.54	95.22

#Bulk sample

3.3.3. Vanadium extraction efficiencies from the red dust

The vanadium extraction efficiencies from the red dust material using the different roast-leach conditions were calculated based on residue chemical analysis results using equation [2]. The effect of roasting time on the vanadium extraction from the red dust material are reported in Figure 8. It appears that the vanadium extraction efficiencies increase with increasing the roasting time. After roasting for 240 minutes, the maximum extraction efficiency of about 69% was achieved (at both small and bulk scales); however, the extraction efficiency had not reached a saturation point. Thus, further tests at longer roasting times are required in order to maximize the vanadium extraction from the red dust material.

The reproducibility of the duplicate tests was generally satisfactory.

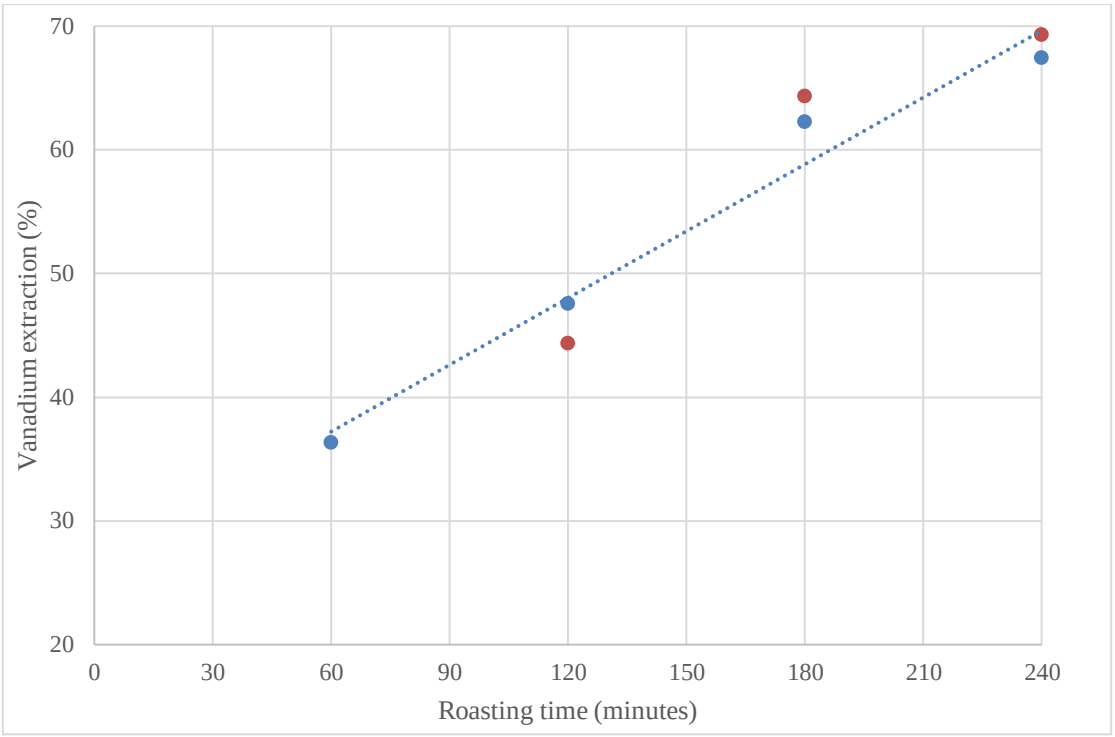

Figure 8 Effect of roasting time on the vanadium extraction efficiencies from the red dust material

3.3.4. Concentration of vanadium in the solution

A photograph showing the typical appearance of the concentrated vanadium solution is shown in Figure 9. As specified earlier, the testwork was preliminary in nature. Thus, the chemical composition of the vanadium pregnant solution was estimated using the chemical analysis results of the leachates.

Figure 9 Photograph showing the vanadium pregnant solution

3.3.5. Impurity rejection

The concentrations of Al and Si impurities in the vanadium pregnant solution were deduced from the chemical compositions of the feed leachates. The chemical analyses of the purified vanadium pregnant solution and the Al and Si bearing precipitate would need to be conducted for the quantification of the mass balance at this stage of the process. Moreover, it is always advisable to quantify the reagent consumption.

3.3.6. AMV precipitate

The typical appearance of the AMV precipitate produced in the current testwork is shown in Figure 10. The XRD analysis results of the AMV are shown in Figure 11. The results show that the product is mainly AMV. If present, the impurity phases are below 3%, which is the detection limit of the employed XRD instrument.

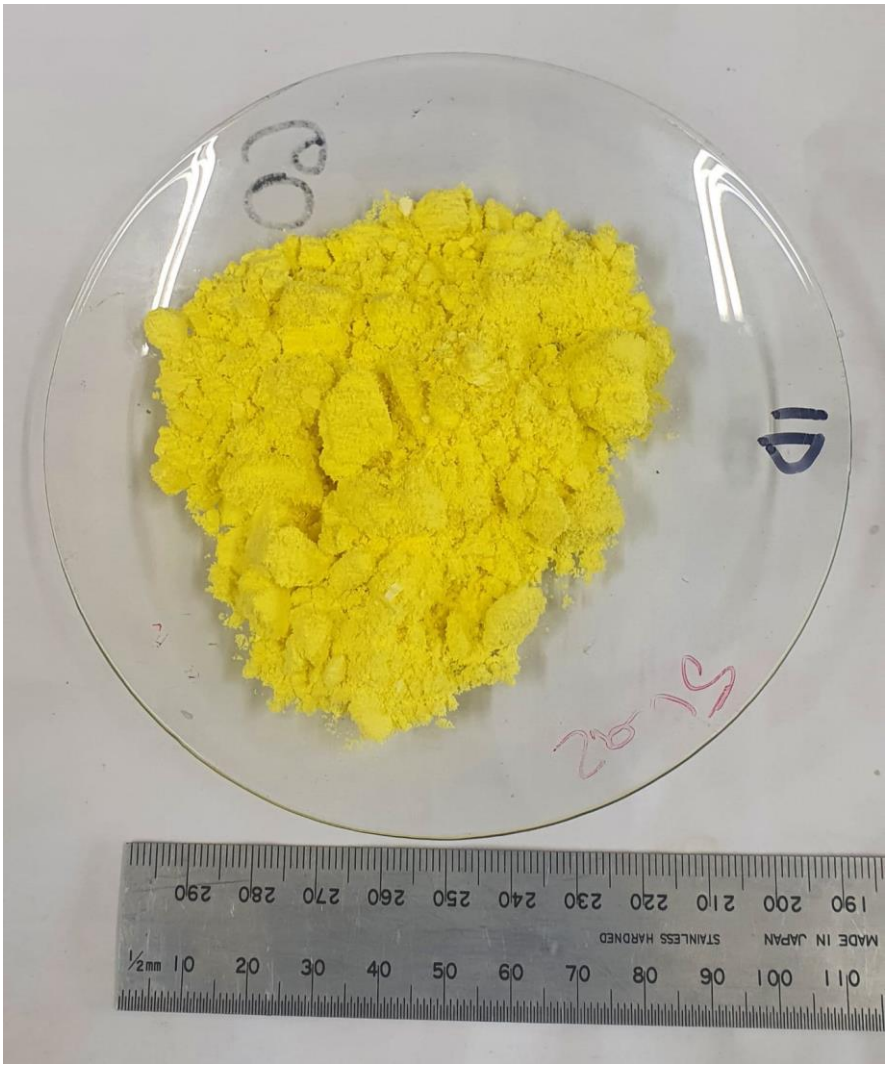

Figure 10 Photograph of the AMV intermediate product

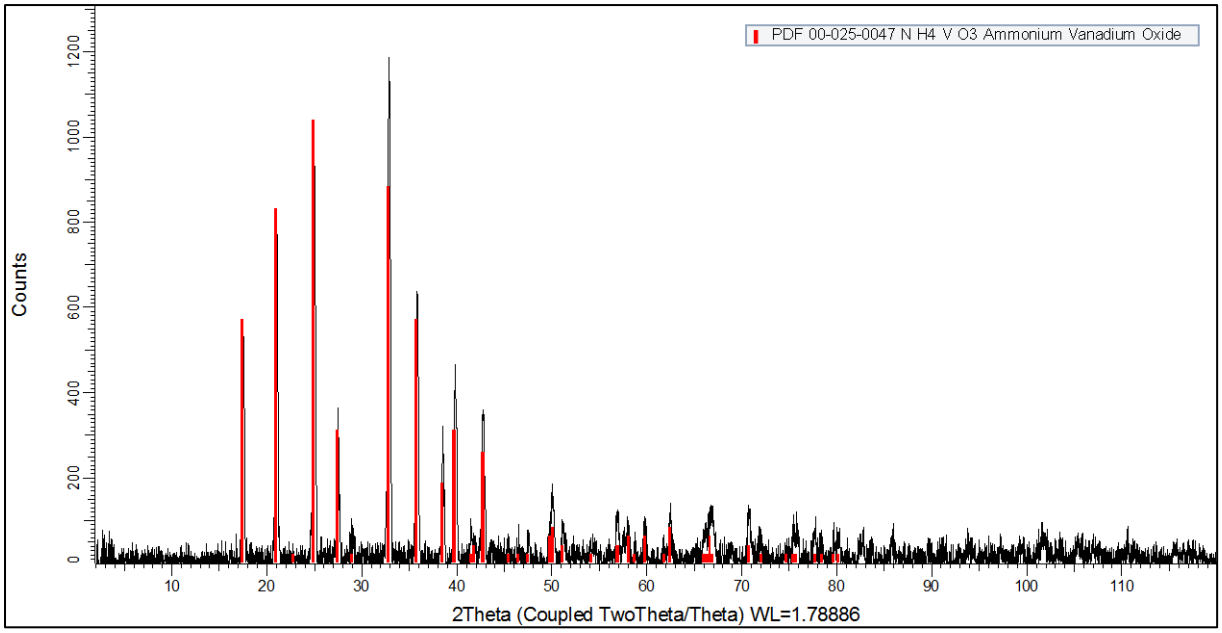

Figure 11 XRD scan of the AMV intermediate product

4. SHE RISKS

A preliminary risk assessment of the entire project revealed that the hazardous materials included dust/ fumes from handling: raw materials, Na_2CO_3, ammonium metavanadate powder, ammonium sulphate. Other potential risks included the handling of solutions: vanadium bearing solutions, NaOH and H_2SO_4. In addition, operations at high temperatures presented other safety risks.

4.1.1. In case of particulate and powder material

These materials were considered very hazardous. The exposure effects were expected to become significant through the eye or skin contact and inhalation. Exposure to eyes could result in irritation, pain and redness. Skin contact could result in irritation, itching and delayed dermatitis. Inhalation could result to delayed organ failures and/ or death.

The following personal protective equipment (PPE) was therefore worn all the times when working with these materials: Safety goggles, latex gloves (where there is no heat), respirator or dust mask, safety boots and coveralls. Other than that, appropriate equipment available for use in emergencies was always on standby.

4.1.2. In case of hazardous solutions

Handling of hazardous solutions was also done with proper PPE. The general PPE included safety goggles, latex gloves (where there is no heat), respirator if deemed necessary, safety boots and coveralls. Other than that, appropriate equipment available for use in emergencies was always on standby.

4.1.3. High temperature operations

The most common risk associated with high temperatures was that of burns. Hence specialised high temperature PPE was always worn when working on the induction, DC tilting bench plant and horizontal tube furnaces and accessing the contents of the furnaces. The PPE included high temperature gloves, face shield, heat resistant overalls and dark glasses for easy viewing of tests in progress.

In case of emissions (CO, CO_2, H_2O) during roasting testwork, the extraction system was always switched on.

Kindly note that all safety, health and environmental ("SHE") risk information is given for information purposes only and does not constitute a risk assessment for any SHE purposes, nor does it substitute any statutory risk assessment that the client is required to undertake. Mintek assumes no risk or liability on behalf of the client or any of its officers or employees in respect of SHE legislative requirements.

5. CONCLUSION AND RECOMMENDATIONS

Preliminary investigations were conducted to study the technical feasibility of the extraction of vanadium from selected by-product samples from the defunct EHSV waste dumps using un-optimised roast-leach conditions. Samples labelled 1A, 1B, 1D-S/N and 1E performed the worst as only 2% to 5% vanadium extraction efficiencies were achieved. Hence, for any chance of the extraction of vanadium from these materials, a systematic study incorporating mineralogical characterization and intense roasting conditions may be required.

Red dust material was different to the other samples: it had higher V_2O_5 and Fe concentrations and low titania concentrations. Though, the vanadium extraction efficiencies from the red dust using the un-optimised roast-leach conditions were also low at about 11%, the relatively higher V_2O_5 concentration compared to other samples and relatively low roasting temperature requirement (to avoid sintering) made the processing of red dust more attractive. The vanadium extraction from the red dust material after roasting at 800°C was generally sensitive to roasting time. The best vanadium extraction efficiency of about 69% was achieved after roasting for 240 minutes – the extraction efficiency had not reached the saturation point.

The vanadium pregnant leachate was subjected to impurity rejection, and subsequently vanadium precipitation as AMV, which would be used by the client for marketing purposes. XRD analysis only detected the existence of AMV phase in the vanadium precipitate – thus, the concentrations of other phases would be less than 3%, which is the limit of detection of the XRD instrument employed in the current study.

When the vanadium is in solution, the processes for impurity rejection, concentration of vanadium to facilitate the efficient precipitation, and AMV precipitation are well established. The impurity rejection and vanadium concentration stages typically do not result in vanadium losses. The vanadium precipitation or recovery efficiency to AMV is typically 95%. Thus, the cumulative vanadium extraction from the red dust material to AMV through the roast-leach vanadium primary production process would be 66%. It is thus estimated that for a 100 kg red dust material processed through the conventional roast-leach process, about 3.1 kg AMV would be precipitated.

Optimization testwork is recommended for the maximization of the vanadium extraction from the red dust material. Techno-economic evaluation of the proposed roast-leach process flowsheet of the red dust material for the determination of the economies of scale is also recommended. The techno-economic study will take into consideration the mass and energy balance throughout the flowsheet. The minimum production scale for reasonable net present value (NPV), internal rate of return (IRR) and payback period (PP) or return of investment will be established.

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