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NRRI TECHNICAL REPORT

BENCH-SCALE EVALUATION OF HYDROMETALLURGICAL PROCESSING TO RECOVER VANADIUM FROM MINNESOTA TITANIUM RESOURCES

Submitted by:

G.J. Hudak, S. Monson Geerts,
J. Chen, A. Halim, R. Sridhar, V.I. Lakshmanan

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Collaborators:

Process Research Ortech, Mississauga, Ontario, Canada

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Website: www.nrri.umn.edu/

NRRI Duluth // Laboratories and Admin // 5013 5013 Miller Trunk Highway, Duluth, MN 55811 // (218) 788-2694

NRRI Coleraine // Laboratories // P.O. Box 188 // One Gayley Avenue, Coleraine, MN 55722 // (218) 667-4201

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Natural Resources Research Institute
University of Minnesota, Duluth
5013 Miller Trunk Highway
Duluth, MN 55811-1442
Telephone: 218.788.2694
e-mail: nrri-reports@umn.edu

Web site: <http://www.nrri.umn.edu>

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INTRODUCTION AND BACKGROUND

Introduction

Vanadium is the twenty-second most abundant element in the Earth’s crust and occurs as a major component (greater than 10% by weight) in 156 minerals that occur in a variety of mineral deposit types. These mineral deposit types are globally distributed and include vanadiferous titanomagnetite (VTM) deposits, sandstone hosted (SSV) deposits, shale-hosted vanadium deposits, and vanadate deposits (Kelley et al., 2017). The Duluth Complex of northeastern Minnesota contains a variety of base and precious metal resources (Fig. 1), including a number of Mesoproterozoic-age copper-nickel-cobalt-platinum group element (Cu-Ni-Co-PGE) resources as well as a series of younger, Mesoproterozoic-age oxide ultramafic intrusions (OUIs) that contain both titanium and vanadium resources (Minnesota Minerals Coordinating Committee, 2016; Table 1). Vanadium deposits within OUI deposits associated with the Duluth Complex are classified as vanadiferous titanomagnetite (VTM-type) vanadium deposits by the United States Geological Survey (USGS; Kelley et al., 2017).

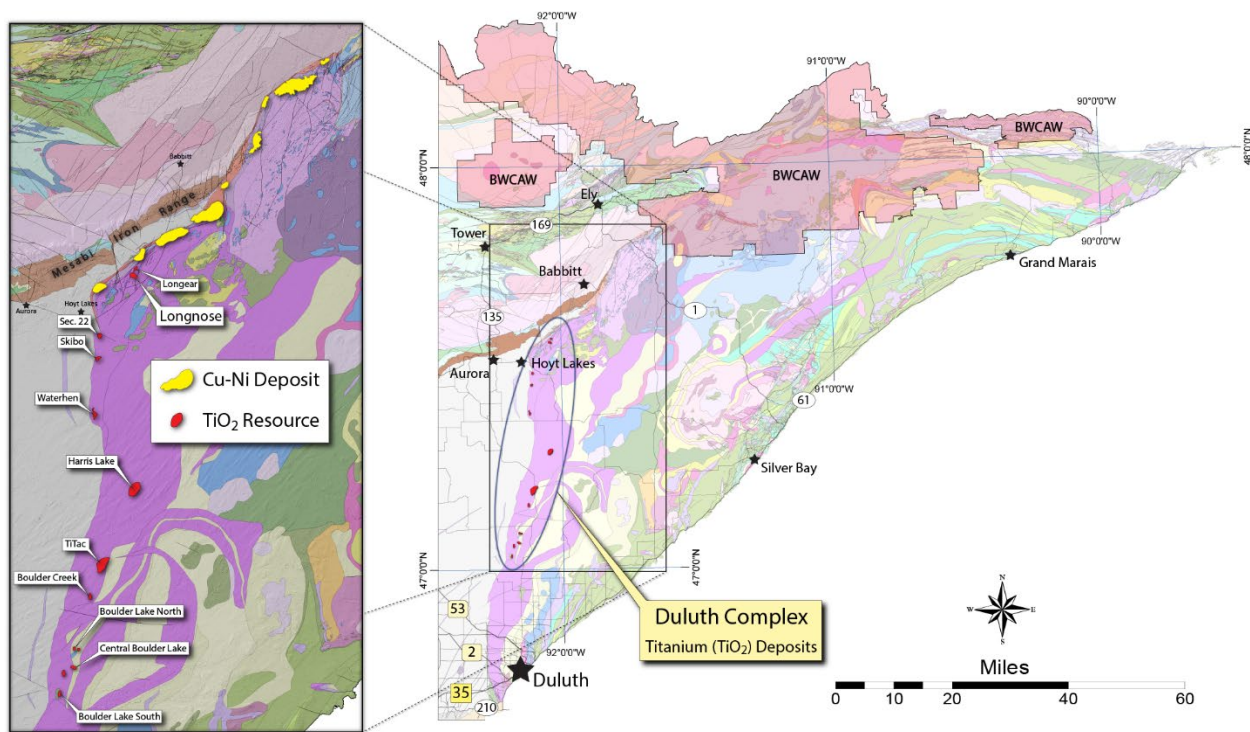


Figure 1. Location map of the Duluth Complex Cu-Ni and TiO₂ resources (after Hudak et al., 2021).

Table 1. Summary of TiO₂ and vanadium resources associated with Minnesota OUIs (modified from Minnesota Minerals Coordinating Committee, 2016).

Deposit	Drill Holes	Average TiO ₂ (wt. %)	Max. TiO ₂ (wt. %)	Avg. V (ppm)	Max. V (ppm)	Resources in Millions of Tons
Longnose	27	12.49	30.37	1,325	4,400	58 Mt @16.6% TiO ₂ (indicated)
Water Hen	37	11.15	29.30	1,065	2,285	62 Mt @ 14% TiO ₂ (not NI-43-101 compliant)
Longyear	3	18.06	50.50	580	3,590	?
Titac (Section 34)	32	15.66	26.74	2,610	4,035	45 Mt @ 15% TiO ₂ (inferred)
Section 17	6	33 analyses	14.66	790	950	?
Section 22	2	62 analyses	28.72	1,130	2,790	?
Skibo	9	18 analyses	25.28	165	220	?
Skibo South	1	3 analyses	12.60	1,100	1,346	?
Wyman Creek	4	10 analyses	28.65	?	540	?
Boulder Creek	2	8 analyses	19.09	4,630	8,125	?
Boulder Lake North	3	6 analyses	35.20	4,045	6,835	?
Central Boulder Lake	1	No analysis	?	?	?	?
Boulder Lake South	3	2 analyses	16.03	?	787	?

World resources of vanadium are greater than 63 million tons; however, vanadium concentrations generally constitute less than 2% of the deposit host rock (Polyak, 2021). In 2020, mine production of vanadium worldwide was approximately 94,800 tons, with the United States (0.2%), Brazil (7.7%), China (61.6%), Russia (21.0%) and South Africa (9.5%) being the major producers (Polyak, 2021).

Vanadium is utilized in a variety of applications. Its principal use is for the production of metal alloys such as high-strength steel and alloys utilized in the aerospace industry. It is also used for catalysts in the chemical industry, in ceramics, in glasses, and as a pigment (Schulz et al., 2017). Production of carbon-, full-alloy-, and high-strength low-alloy steels accounted for 18%, 45%, and 33% of domestic consumption in 2020, respectively (Polyak, 2021). The emerging need for large-scale “green” electrical energy storage associated with wind, solar, and other intermittent power sources may result in major utilization of vanadium in the form of vanadium redox-flow batteries (VFRB) which take advantage of the various electrical valencies of vanadium cations (<https://energystorage.org/why-energy-storage/technologies/vanadium-redox-vrb-flow-batteries/>). As well, vanadium is utilized in other battery applications, including lithium-vanadium-phosphate batteries and lithium ion batteries (Schulz et al., 2017). Commercial products resulting from processing of vanadium ores include ferrovandium (FeV, an iron-vanadium alloy), which is used in the production of steel alloys, vanadium pentoxide (V₂O₅), which is commonly utilized as a chemical catalyst, and ammonium metavanadate (NH₄VO₃), a precursor for the production of vanadium pentoxide, catalysts, and analytical reagents (Pérez-Benítez and Bernès, 2018).

In 2020, U.S. net import reliance for vanadium was 96%, with major import sources being Brazil, South Africa, Austria and Canada (United States Geological Survey, 2021). A large portion of domestic needs

could be met by domestic resources and secondary recovery processes (Polyak, 2021). As a result of this large net import reliance, vanadium is considered a critical mineral resource in the United States (Executive Order 13817 “Federal Strategy to Ensure Reliable Supplies of Critical Metals”; Schulz et al., 2017; Nassar and Fortier, 2021).

Results of recent hydrometallurgical experiments conducted by Process Research Ortech (PRO) and the Natural Resources Research Institute (NRRI) indicate that vanadium concentrations continue to increase within titanium raffinate as recycling of organics takes place in a closed-system hydrometallurgical circuit developed to produce TiO_2 and Fe_2O_3 products from the Longnose OUI mineral deposit (Hudak et al., 2021). The research described in this report discusses collaborative research conducted by PRO and NRRI to evaluate whether or not high-purity vanadium materials (specifically ammonium metavanadate and vanadium pentoxide) could be produced as by-products of hydrometallurgical processing of the titanium raffinate solutions resulting from continuous pilot-scale hydrometallurgical processing of Longnose mineral concentrates (Hudak et al., 2021).

This research was funded by research grants from the University of Minnesota Permanent University Trust Fund (PUTF) and an Enterprise for Strategic Resources Project Grant provided to the NRRI by the Minnesota Department of Iron Range Resources & Rehabilitation.

Previous Work

Geological Setting of the Longnose Deposit

Detailed descriptions of the geological setting of Duluth Complex-associated OUI deposits can be found in Mainwaring (1975), Mainwaring and Naldrett (1977), Severson and Hauck (1990), Linscheid (1991), Miner and Pasteris (1994), Miner (1995), Severson (1995), and SRK Consulting (2012). The geology of the Longnose deposit presented in Hudak et al. (2021) is summarized here. The Longnose OUI comprises one of thirteen Mesoproterozoic OUIs that intruded into the layered series troctolitic intrusions of the Mesoproterozoic Duluth Complex. The Longnose deposit contains disseminated, semi-massive, and massive oxides (ilmenite, titanomagnetite, magnetite) within a crudely-zoned ultramafic body comprising dunite, peridotite, feldspathic peridotite and oxide pyroxenite. Zones of semi-massive to massive oxide (labeled MX) occur primarily within the upper olivine-rich core of the intrusion, but can also occur in the lower pyroxenite zone (labeled PX; Fig. 2 and Fig. 3).

Electron microprobe analyses (EMPA) conducted by the NRRI on ilmenites and magnetites from the Titac, Water Hen, and Longnose deposits indicate that both magnetite and, to a lesser extent, ilmenite can contain vanadium in their atomic structures (Niles, 1996; Hudak et al., 2021). Mineral chemical concentrations obtained by EMPA indicate that the Longnose mineral concentrate that was hydrometallurgically processed to produce titanium raffinates in a closed-circuit hydrometallurgical process (Hudak et al., 2021) contains ilmenites that have between 0.14 weight percent (wt. %) and 0.34 wt. % (average 0.24 wt. %) V_2O_3 (Fig. 4), and magnetites/titanomagnetites have between 0.03 weight percent and 2.42 wt. % (average 0.80 wt. %) V_2O_3 (Fig. 5; Hudak et al., 2001).

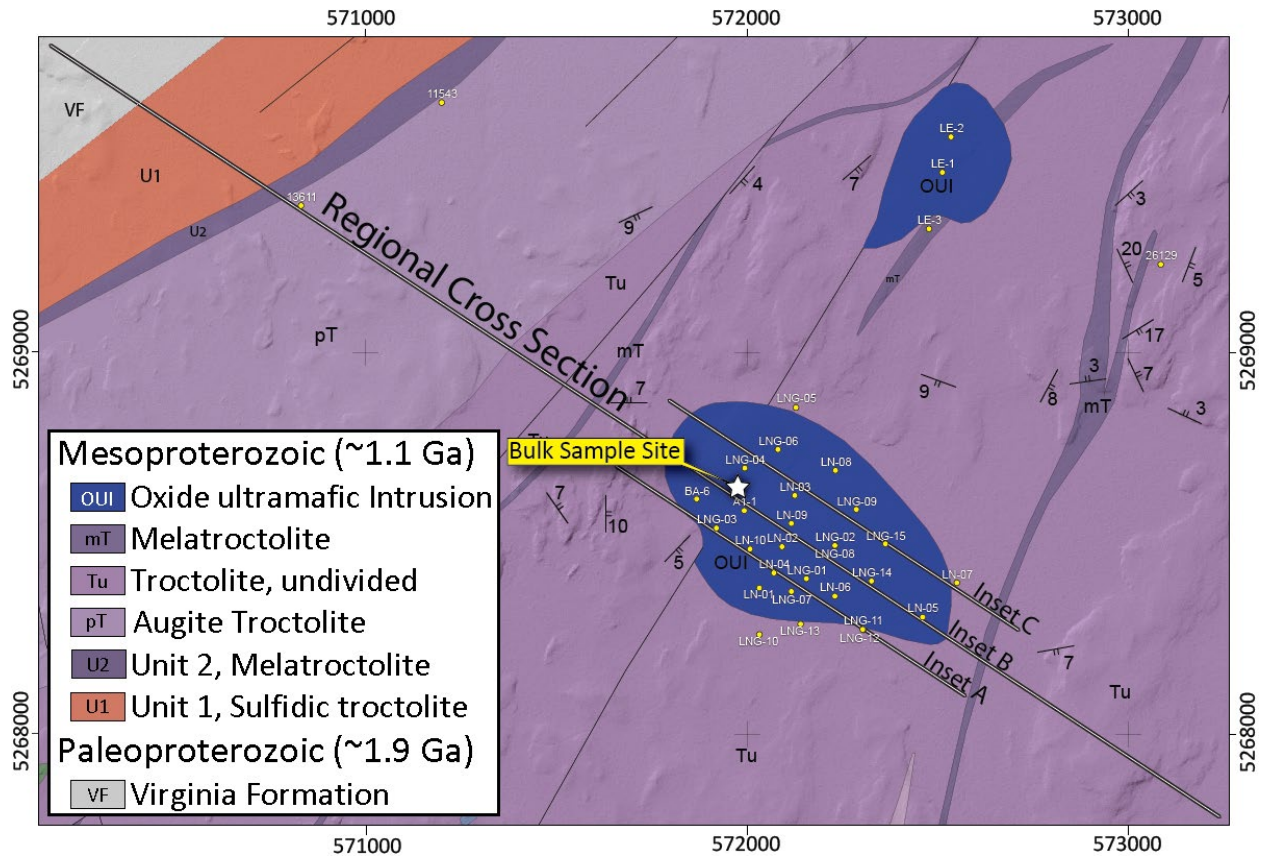


Figure 2. Geologic map of the Longnose Peridotite area with cross section lines illustrated in Figure 3 (after Hudak et al., 2021).

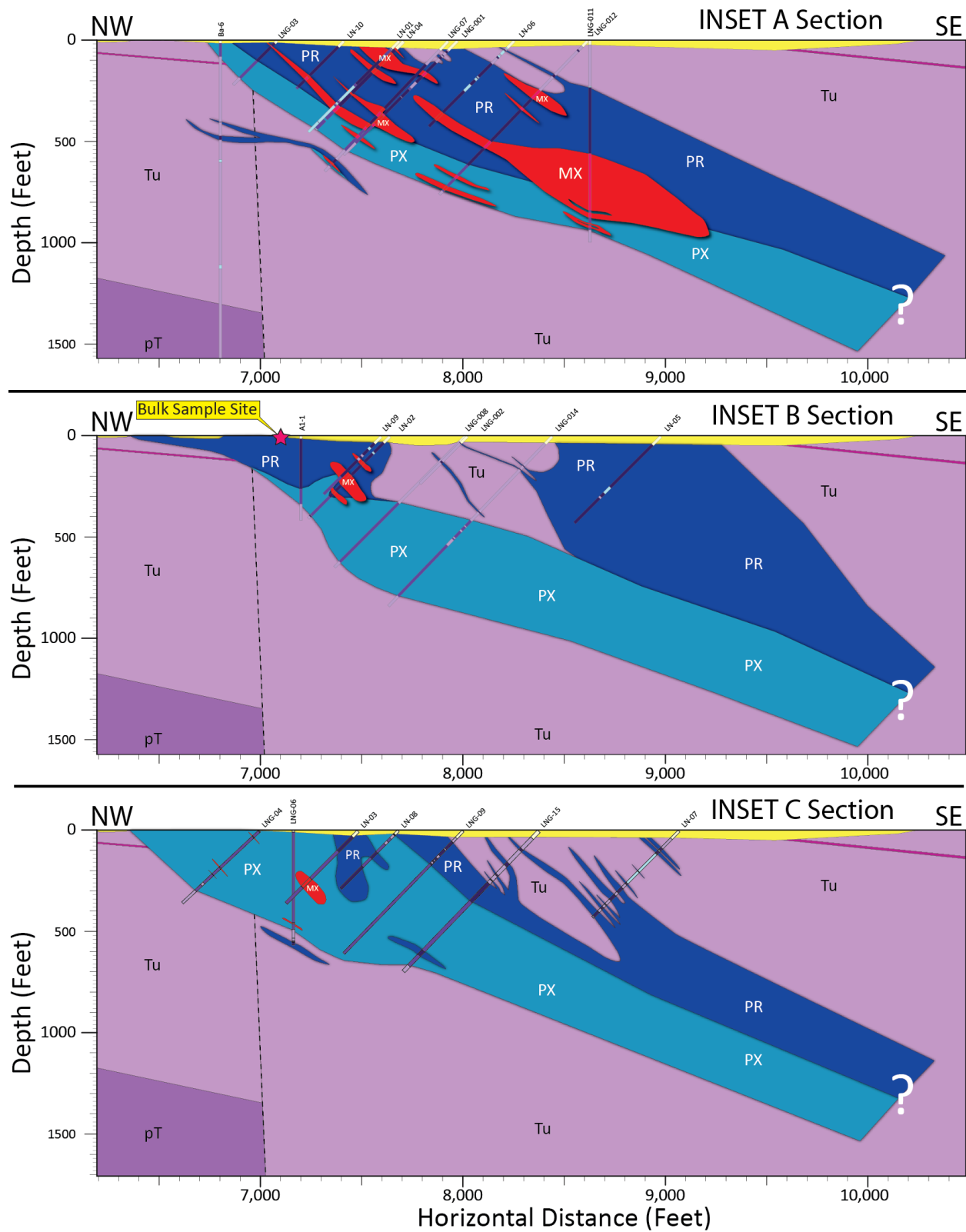


Figure 3. Geological cross sections through the Longnose deposit (after Hudak et al., 2021).

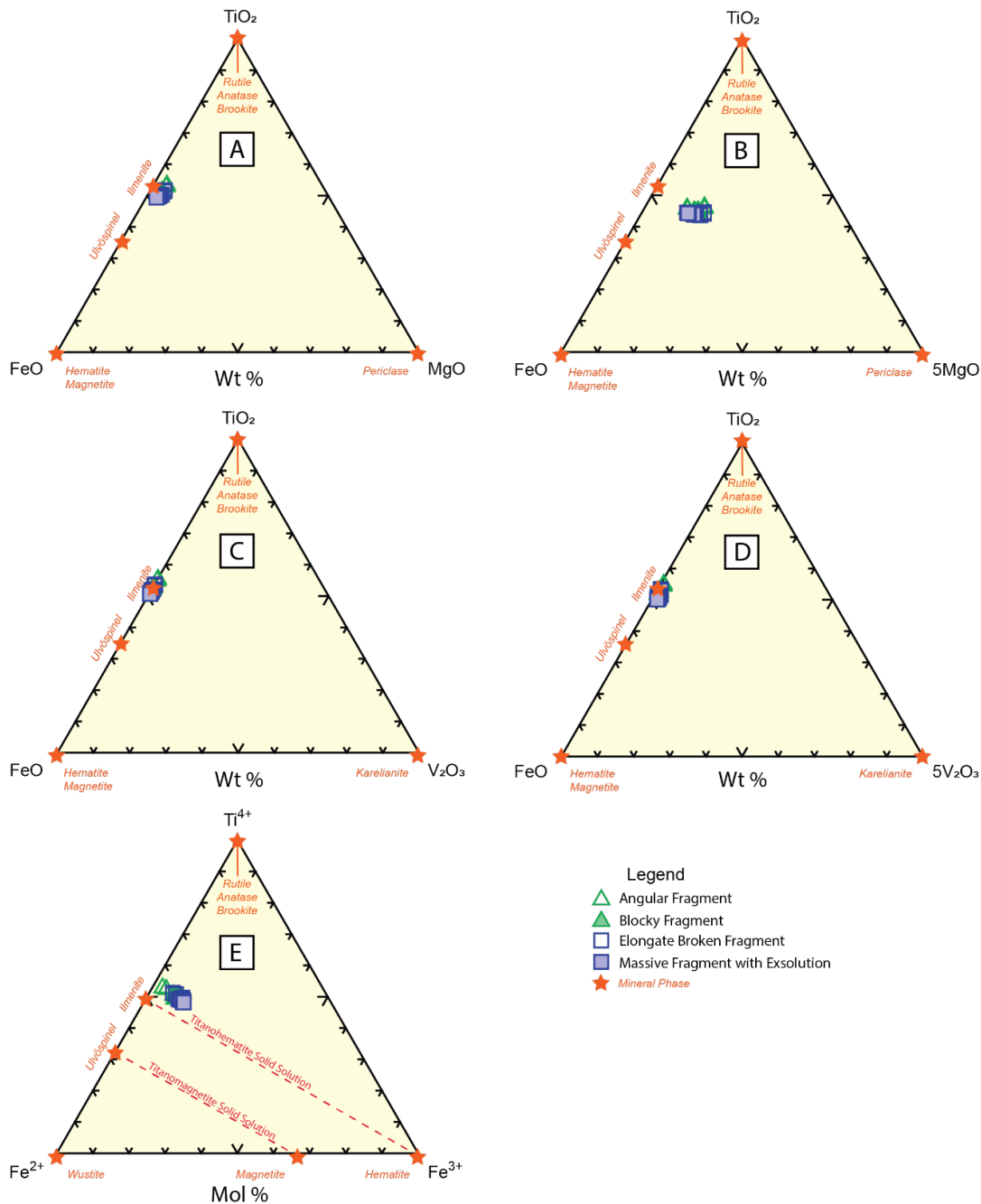


Figure 4. Ternary diagrams illustrating the chemical compositions of ilmenites from the Longnose ilmenite concentrate (from Hudak et al., 2021). A) FeO-TiO₂-MgO ternary diagram. Note that ilmenite composition plot off the FeO-TiO₂ compositional boundary in the direction of MgO. B) FeO-TiO₂-5MgO ternary diagram that emphasizes the magnesium contents of the Longnose ilmenite concentrate ilmenite compositions. C) FeO-TiO₂-V₂O₃ ternary diagram. Note that ilmenite compositions plot near the FeO-TiO₂ compositional boundary. D) FeO-TiO₂-5V₂O₃ ternary diagram that emphasizes the relatively low concentration of V₂O₃ in the Longnose ilmenite concentrate ilmenites. E) Fe²⁺-Ti⁴⁺-Fe³⁺ ternary diagram (modified after Klein and Hurlbut, 1999; Meinhold, 2010) based on stoichiometric calculations of ilmenite compositions utilizing ILMNCALC (Gabbrosoft.com). Note that massive fragments with exsolution contain more Fe³⁺ than other textures of ilmenite identified in the ilmenite concentrate samples. Wt % is weight percent, Mol % is molar percent.

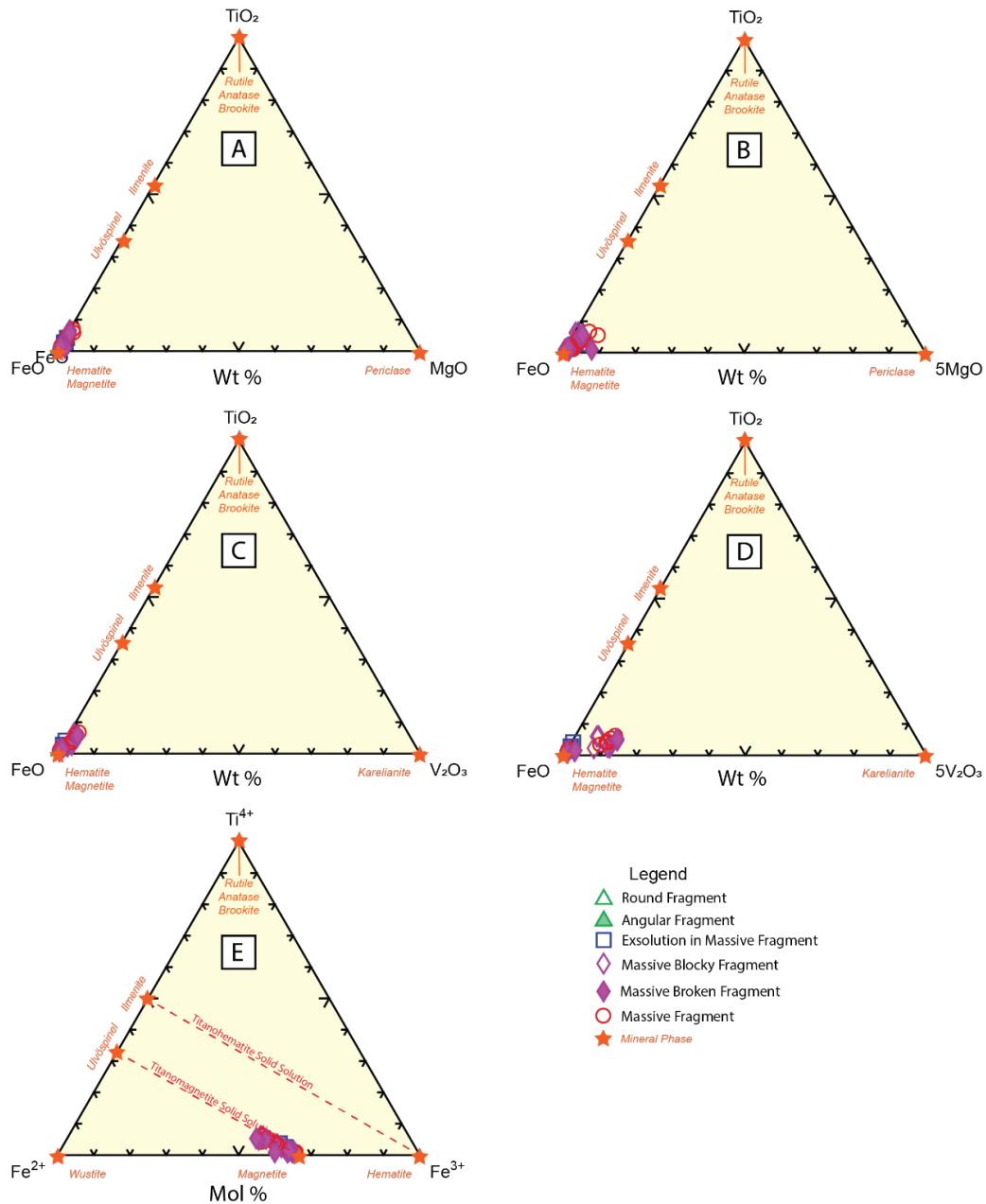


Figure 5. Ternary diagrams illustrating the chemical compositions of magnetites from the Longnose ilmenite concentrate (from Hudak et al., 2021). A) FeO-TiO₂-MgO ternary diagram illustrating that Longnose ilmenite concentrate magnetites are dominated by iron and titanium. B) FeO-TiO₂-5MgO ternary diagram that illustrates that massive broken fragments are slightly more Mg-enriched relative to other textures of magnetites analyzed. C) FeO-TiO₂-V₂O₃ ternary diagram. Note that magnetite compositions plot near the FeO-TiO₂ compositional boundary but are slightly offset in the direction of the V₂O₃ apex due to the presence of vanadium. D) FeO-TiO₂-5V₂O₃ ternary diagram. Note that exsolution lamellae in ilmenite are iron-enriched relative to other textures of magnetite analyzed. Also note that massive fragments and massive blocky fragments are generally more V₂O₃-enriched than other textures of magnetites analyzed. E) Fe²⁺-Ti⁴⁺-Fe³⁺ ternary diagram (modified after Klein and Hurlbut, 1999; Meinhold, 2010) based on stoichiometric calculations of magnetite compositions utilizing SPINCALC (Gabbrosoft.com). Note that Longnose ilmenite concentrate magnetites plot along the titanomagnetite solid solution tie line. Wt % is weight percent, Mol % is molar percent.

Previous Metallurgical Research on the Longnose Deposit

Previous research conducted by the NRRI suggests that vanadium (in the form of vanadium pentoxide, V_2O_5) may be a potential by-product from processing of oxide minerals from Minnesota OUI deposits (Coleraine Minerals Research Laboratory, 1992; Niles, 1996). A subsequent NRRI study (Engesser, 1997) to extract vanadium from a Minnesota OUI deposit using a combination of grinding, magnetic separation, flotation, salt roasting, leaching, precipitation solvent extraction, and ion exchange indicates that a 98% pure V_2O_5 product can be produced but that the vanadium recovery is limited to 16% from the ore and 48% from the magnetic cobber concentrate.

Over the past several years, the NRRI has partnered with PRO to conduct two (Mlinar et al., 2017; Hudak et al., 2021) hydrometallurgical processing experiments to understand the applicability of utilizing the proprietary PRO mixed chloride leach process and subsequent precipitation processes for obtaining high-purity titanium- and iron-oxide products from the Longnose OUI. Use of the PRO mixed chlorite leach process was required, as previous metallurgical processing of the Longnose mineral concentrate was unable to produce a high-purity TiO_2 product due to relatively high MgO contents (~2.6–4.0 weight percent) in the titanium mineral ilmenite within the Longnose deposit (Niles, 1996; Mlinar et al., 2017; Hudak et al., 2021).

During closed-circuit hydrometallurgical processing using the PRO process, vanadium concentrations continue to increase to concentrations up to 450 ppm within the titanium raffinate as recycling of organics takes place (Hudak et al., 2021). Discussions with PRO suggested that the PRO process may be capable of producing vanadium as vanadium pentoxide (V_2O_5) and as ammonium metavanadate (NH_4VO_3).

PROJECT GOALS AND OBJECTIVES

The objective of this research is to perform further bench-scale hydrometallurgical studies to evaluate the use of the PRO process to obtain high-purity V_2O_5 and NH_4VO_3 as by-products of hydrometallurgical processing that produces titanium dioxide and iron oxide products. The research has been conducted utilizing titanium raffinate produced during the recent continuous pilot-scale study (Hudak et al., 2021) as well as simulated solutions with vanadium concentrations similar to those produced in the pilot-scale study. Following production of the V_2O_5 and NH_4VO_3 products, NRRI is to independently perform EMPA analyses to evaluate the purity of these materials and validate the composition of the vanadium products produced.

Identification—and eventual successful production—of a high-purity vanadium product or products would increase the potential economic resources of this and (potentially) other northeastern Minnesota OUI-associated titanium-vanadium resources, decrease hydrometallurgical processing waste materials, and provide Minnesota and the United States with an additional possible domestic source of the critical mineral vanadium.

VANADIUM RECOVERY HYDROMETALLURGICAL RESEARCH

Introduction

PRO has developed an innovative process for the production of high-purity TiO_2 directly from ilmenite ore. PRO's process is protected by several patents in North America and abroad (US Patent No. 7,803,336 B2; Canadian Patent No. 2,513,309; Australian Patent No. 2004291568). The process consists of atmospheric chloride leach followed by solvent extraction of Fe, Ti, and V successively. A high-purity Ti-bearing strip solution is produced and can be used to produce Ti products dependent on the end market use such as high-purity TiO_2 for pigments, pharmaceutical, and food industries. Other products that can be obtained from the process are Fe_2O_3 , which is of high purity and can be used for pigment or iron production, and V_2O_5 , if the ore contains vanadium.

A pilot program for the recovery of Ti as TiO_2 from an oxide-rich bulk sample containing ilmenite and magnetite from the Longnose OUI located in northeastern Minnesota was performed to build on the information acquired from the previous study (Process Research Ortech, Inc., 2017) conducted in 2016 by performing additional steady-state piloting to incorporate the following:

- Examine variation in feed composition and effect on subsequent SX processes
- Incorporation of recycled streams such as SX process raffinates and filtrates from precipitation stages etc.
- Examine hydrohydrolysis process for the production of Fe_2O_3 and determination of the quality of regenerated acid
- Examine impurity build up in the circuit from integrated operation (i.e. recycling of raffinate) on the quality of Fe_2O_3 , TiO_2 product and potential bleed effluent.
- Evaluate TiO_2 quality from the integrated operation

The steady-state piloting conducted (Process Research Ortech, Inc., 2021) was successful in demonstrating the robustness of the process with respect to impurity buildup and was capable of producing a high-purity TiO_2 product. As a result of the recycling of reagents and process streams, a buildup of valuable impurities such as V takes place and can be a valuable by-product. From the continuous pilot operation, levels as high as 450 mg/L V were found in the Ti raffinate produced (Fig. 6). This is equivalent to ~\$78/t of V_2O_5 value per ton of ilmenite ore when using a cost of \$6/lb for V_2O_5 , which is significant considering the V has already been solubilized during the leach process and only requires separation process like a solvent extraction (SX) step to produce a high-purity V-bearing stream for subsequent processing to produce a V product such as V_2O_5 .

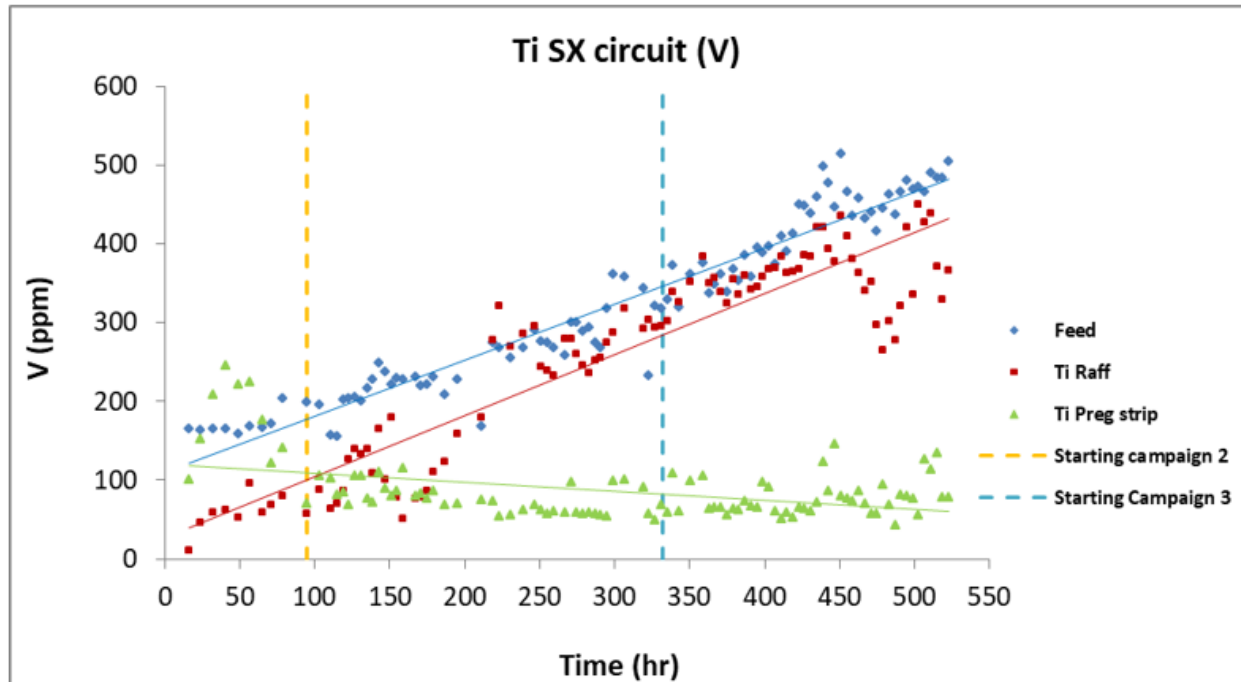


Figure 6. Vanadium content in Ti-raffinate produced in NRRI/PRO continuous pilot study (Hudak et al., 2021).

Vanadium exhibits a variety of complex species and oxidation states in aqueous solutions. In leach liquors at higher redox potentials, V(IV) and V(V) predominate in acidic medium. The potential–pH diagram for the V–H₂O system is shown in Figure 7. This diagram shows that at low pH and high redox potential, V(V) forms a pervanadyl cation VO₂⁺. The isoelectric point is between pH 1 and 2, above which the vanadium is changed into complex anions. At this point, the solubility of vanadium reaches a minimum, as is verified by solid V₂O₅ at pH 1.4–3.0. For V(IV), at low pH the ion in the solution is vanadyl ion VO²⁺, metavanadic acid, which will precipitate at about pH 3, converting into solid vanadium tetroxide (V₂O₄). At increasing pH, V₂O₄ will dissolve to form an anion HV₂O₅⁻. On contrary, trivalent vanadium dissolves in acid to form vanadic ion V³⁺ in solution at pH < 3. Then raising the pH value, vanadium trioxide (V₂O₃(s)) is formed, which is more stable than V(OH)₃.

The current program is an extension of the work done by Process Research Ortech, Inc. (2019) to increase the economics of the process by recovering the contained V in the Ti raffinate to produce a V product such as V₂O₅ or ammonium metavanadate (NH₄VO₃).

Objective

The objective of the project is to develop a sustainable process for the recovery of a valuable by-product of vanadium from titanium solvent extraction raffinate produced in the PRO TiO₂ process. The recovery of this metal is a part of the overall TiO₂ process flowsheet developed by PRO and can potentially increase the economic advantage of the PRO TiO₂ process in the treatment of ilmenite ores in Minnesota, USA.

Test Program

In this program, the following two process options were examined for the recovery of V from the Ti raffinate produced during the recovery of TiO₂ from ilmenite and are shown in Figure 8.

- Option A which is based on extracting the V directly from the process solution by SX, and
- Option B which involves precipitating the V and treating the concentrated solid.

Details of the test work conducted for each option are presented below.

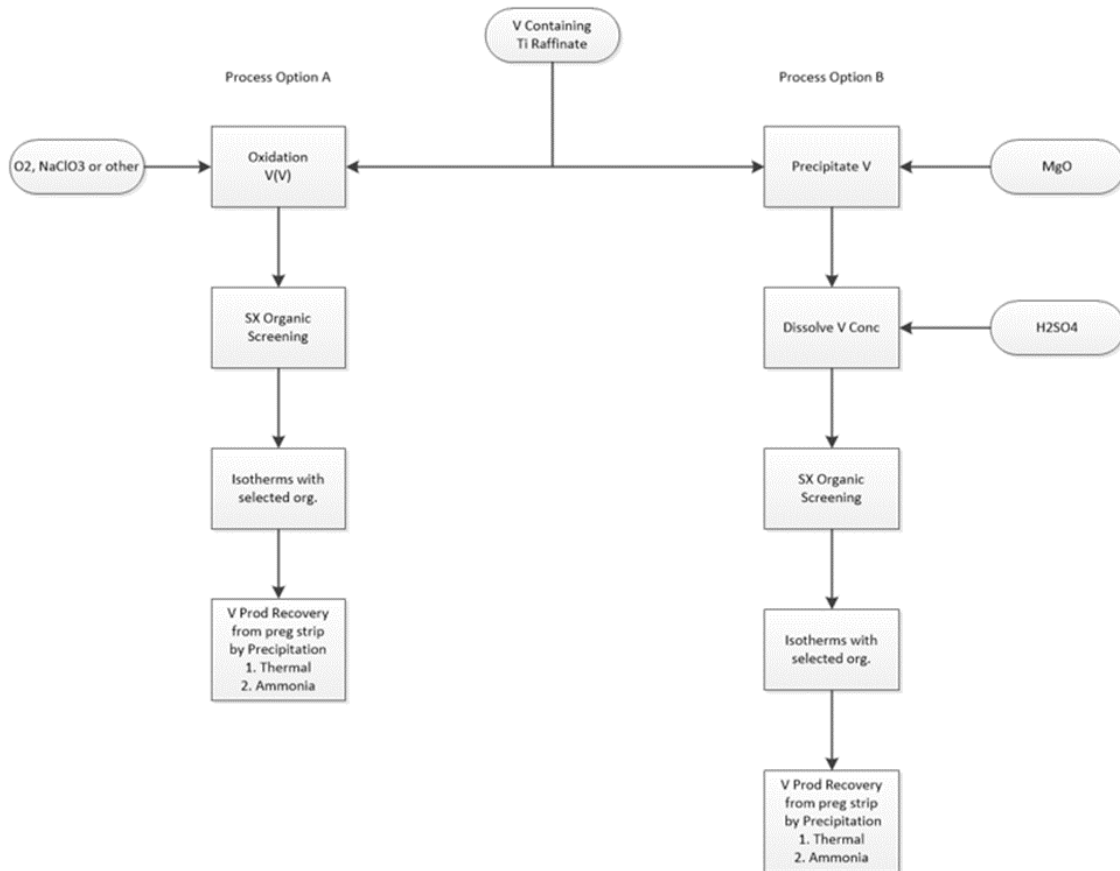


Figure 8. Vanadium recovery test program process options.

Option A – Direct Solvent Extraction

The following process steps were evaluated to separate and recover V from Ti pilot plant raffinate:

- Evaluated possible extractants to selectively extract V over other impurities such as Al and Cr from Ti raffinate at different redox potentials,
- Developed the McCabe-Thiele V extraction and stripping isotherms with a selected organic extractant for estimating the number of stages required for process design,
- Precipitated V as an NH_4VO_3 from a simulated pregnant strip solution, and
- Conducted calcination of NH_4VO_3 to produce vanadium pentoxide (V_2O_5).

Option B – Concentrate Process

The following process steps were evaluated to recover V from the Ti raffinate:

- Prepared feed by increasing V concentration in the Ti raffinate,
- Precipitated V from Ti raffinate to produce an intermediate V containing cake for increasing the concentration of V in the subsequent process solution,
- Evaluated leaching efficiency of sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions on intermediate V precipitate cake,
- Produced enough vanadium sulphate solution for subsequent V SX tests:
 - Screened organic extractants for V extraction,
 - Developed the McCabe-Thiele V extraction and stripping isotherms with an organic phase consisting of a selected extractant for estimating the number of stages required for process design,
- Precipitated V as a NH_4VO_3 from a simulated pregnant strip solution, and
- Calcined NH_4VO_3 to produce vanadium V_2O_5 .

Option A Results

Feed Preparation

As shown in Table 2, the concentration of V in the Ti SX raffinate has shown levels >400 mg/L by recycling of the Ti raffinate. From the prior pilot program, PRO had Ti raffinate that contained ~99 mg/L V. Based on the results of the pilot showing a buildup of V in the raffinate, the concentration of V was increased in the test solution from 99 mg/L to ~700 mg/L for subsequent testing by the following steps:

- Preparation of a synthetic vanadium chloride solution by dissolving commercially available V_2O_5 into concentrate HCl solution,
- Spiking of this vanadium chloride solution into the Ti raffinate to increase concentration to >700 mg/L V,
- Adjustment of pH to ~0.1 with MgO of V spiked Ti raffinate,
- Increasing the oxidation reduction potential (ORP) from <450 mV to >900 mV with H_2O_2 for oxidizing V from the lower oxidation state to higher state, and

- Preparation of enough this feed solution for V SX tests. Analysis of the test solution is presented in Table 2.

Table 2. ICP assay results, pH and ORP of prepared feed (Ti raffinate) for V solvent extraction tests.

	V	Al	As	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Sb	Ti	Zn	pH	ORP
	mg/L														mV
Feed	757	171	<5	675	47	<5	<5	65260	213	43	<5	40	<5	0	>900

Organic Extractant Screening

A total eight solvent extraction tests were conducted by contacting the aqueous feed solution with different organic phases consisting of 15%(v/v) extractant, 10(v/v) Exxal 13 (modifier) in ShelSol D80 (diluant). The extractants used in the V SX tests were Aliquat 336, Alamine 336, LIX 63, ACORGA M5774, Cyanex 923, LIX 984N, LIX 84-I and LIX 7950. Each screening SX test was carried out at the O/A phase ratio of 1 at ambient temperature (~22 OC) for 5 min at 400 rpm mixing. ICP-OES assay results are shown in Table 3. The concentration of V reduced from 757 mg/L to 76 mg/L, 75 mg/L, and 153 mg/L in the raffinates of the organic phases consisting of LIX 63, ACORGA M5774, and Cyanex 923, respectively. These results suggest that LIX 63, ACORGA M5774, and Cyanex 923 are much more effective extractants compared to others for V extraction. Furthermore, among these three extractants it was found that oxidation of the V species was not required with Cyanex 923, and V could be extracted without increasing ORP of the Ti raffinate (Table 4).

Table 3. Extractant screening test results for vanadium SX on the Ti raffinate.

ID	Organic Phase	Aqueous Phase	O/A	V	Al	As	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Sb	Ti	Zn
				mg/L												
		Feed-I		757	171	<5	675	47	<5	<5	65260	213	43	<5	40	<5
1	Aliquate 336 (15/10/75)	V Raffinate	1:1	601	173	<5	655	49	<5	<5	65500	155	44	<5	37	<5
2	Alamine 336 (15/10/75)	V Raffinate	1:1	626	176	<5	778	51	<5	<5	65320	146	46	<5	38	<5
3	LIX 63 (15/10/75)	V Raffinate	1:1	76	169	<5	714	47	<5	<5	63120	211	41	<5	37	<5
4	ACORGA M5774 (15/10/75)	V Raffinate	1:1	75	167	<5	707	46	<5	<5	69120	210	41	<5	37	<5
5	CYANEX 923 (15/10/75)	V Raffinate	1:1	153	173	<5	730	47	<5	<5	69360	179	45	<5	17	<5
ID	Organic Phase	Aqueous Phase	O/A	V	Al	As	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Sb	Ti	Zn
		Feed-II		706	166	<5	629	46	<5	<5	59460	210	40	<5	39	<5
6	LIX 984N (15/10/75)	V Raffinate	1:1	690	170	<5	684	44	<5	<5	60860	216	41	<5	38	<5
7	LIX 84-I (15/10/75)	V Raffinate	1:1	714	167	<5	691	43	<5	<5	60680	212	41	<5	37	<5
8	LIX 7950 (15/10/75)	V Raffinate	1:1	698	169	<5	643	45	<5	<5	59600	213	41	<5	37	<5

Table 4. Vanadium extraction with Cyanex 923 from the Ti raffinate at <450 mV.

ID	Organic Phase	Aqueous Phase	O/A	V	Al	As	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	Zn
				mg/L											
		Feed-III		616	127	<5	893	28	<5	<5	57600	148	32	38	<5
9	Cyanex 923 (15/10/75)	V Raffinate	1:1	81	122	<5	895	29	<5	<5	58420	140	33	19	<5

Based on these results, Cyanex 923 was chosen as the candidate extractant used for further testing in the program.

Vanadium SX Isotherms

The McCabe-Thiele V extraction isotherm was developed with an organic phase consisting of 15% (v/v) Cyanex 923 and 15% Exxal 13 in ShelSol D80. Cyanex 923 extractant was selected over LIX 63 and ACORGA M5774 due to the following potential advantages:

- Elimination of the requirement for increasing the ORP of the Ti raffinate as Cyanex 923 can extract V at lower redox potential (<450 mV) while LIX 63 and ACORGA M5774 requires >900 mV, and
- Elimination of cross-contamination of organic as Cyanex 923 is already used for the Ti solvent extraction step.

For the construction of the McCabe-Thiele extraction isotherm, a total of seven V SX tests were carried out at the organic to aqueous phase ratios of 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, and 1:10. Each test was completed at ~35°C for 5 min at 450 rpm. The McCabe-Thiele V extraction isotherm is shown in Figure 9, which suggests that V can be completely extracted from the Ti raffinate with 15%(v/v) Cyanex 923 by 6-stage extraction at the O/A phase ratio of 1:3.5. Under these conditions, about 1949 mg/L V can be loaded to the organic phase.

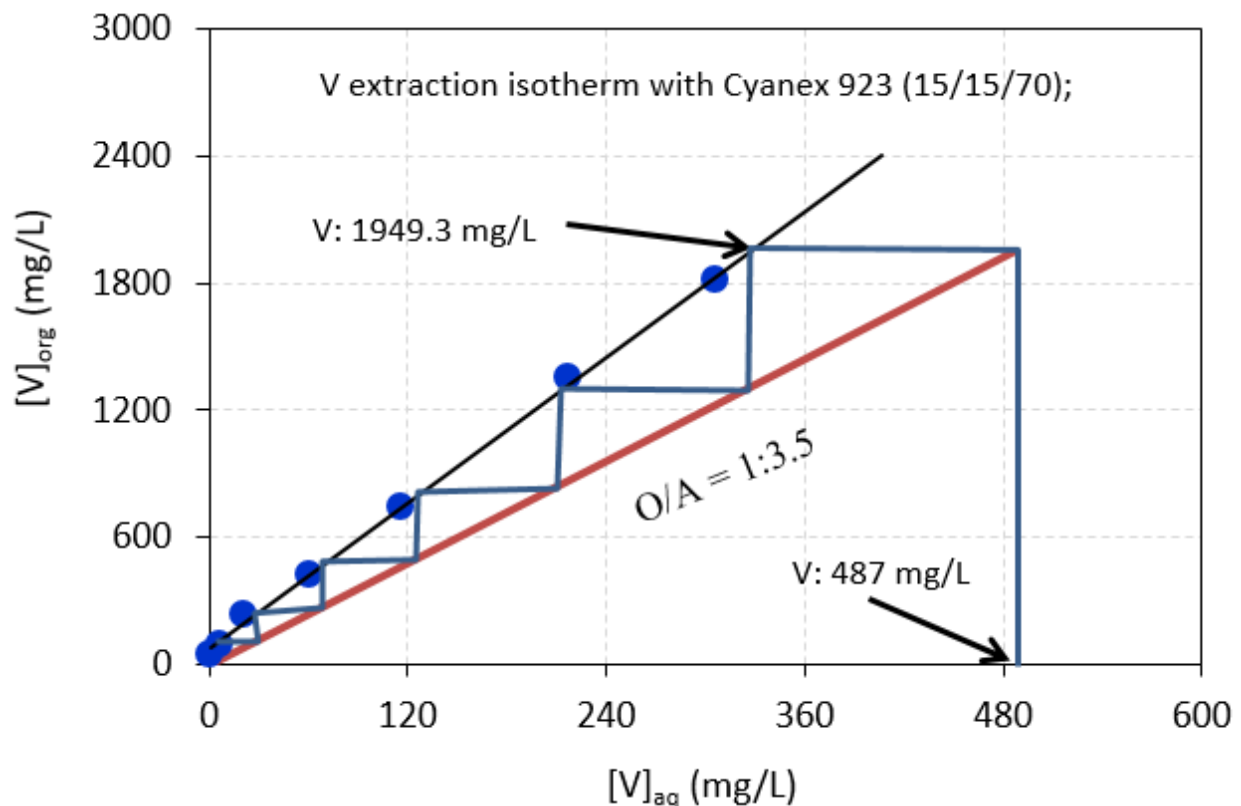


Figure 9. McCabe-Thiele V extraction isotherm with Cyanex 923 (15/15/70).

For the construction of the McCabe-Thiele stripping isotherm, a loaded organic was produced that contained approximately 2130 mg/L of V. This was done by contacting the organic phase (Cyanex 923 (15/15/70)) with an aqueous feed solution at the O/A phase ratio of 1:9 at ~35°C for 5 min (Fig. 10). The vanadium-loaded organic phase was contacted with 1.5 M H₂SO₄ solution at the O/A phase ratios of

10:1, 5:1, 2:1, 1:1, 1:2, and 1:5. For each SX test, the conditions used were a contact time of 15 min at 40-45°C and 450 rpm. Metals in the aqueous solutions were analyzed by ICP-OES. The developed McCabe-Thiele V stripping isotherm and ICP results on loading and stripping tests are shown in Figure 10, and Table 5 and Table 6, respectively. The stripping isotherm suggests that the loaded V can be completely stripped by 3-stage stripping at the O/A phase ratio of 6.1:1 with 1.5 M H₂SO₄. Moreover, about ~12995 mg/L V can be found in the pregnant strip solution by stripping at the O/A phase ratio of 10:1.

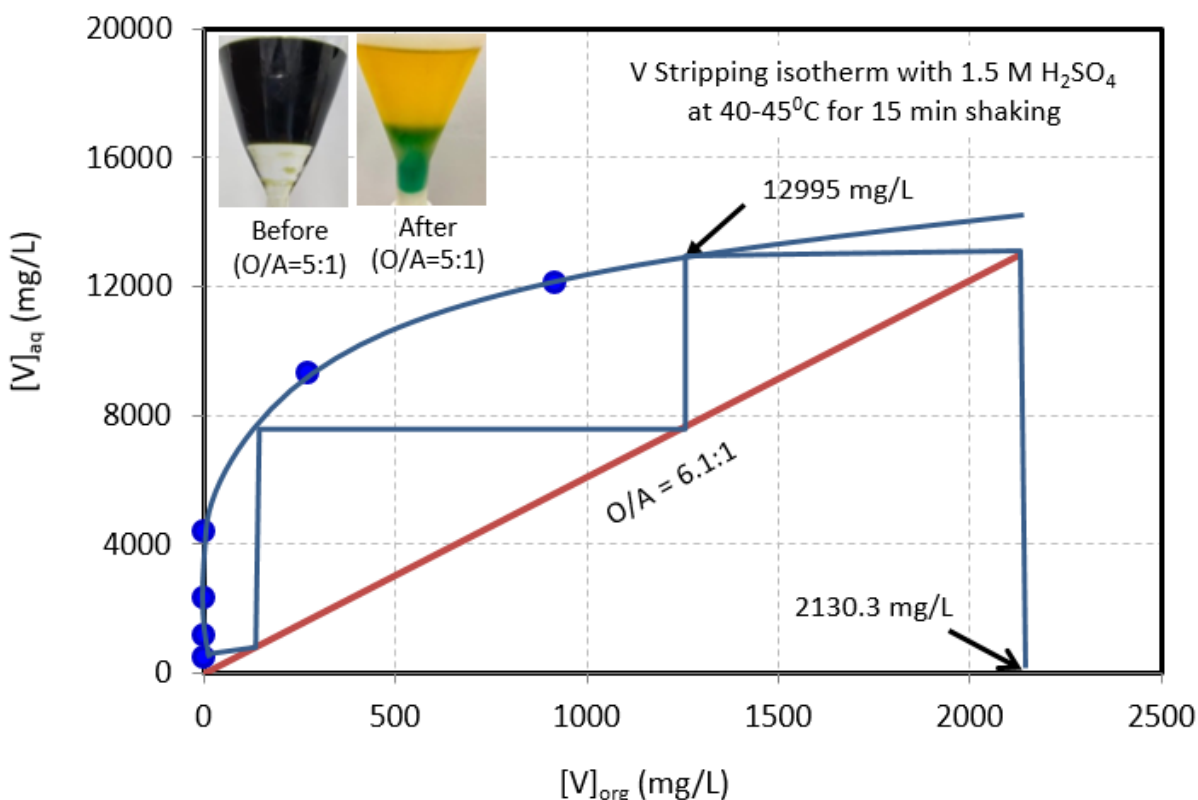


Figure 10. The McCabe-Thiele V stripping isotherm with 1.5M H₂SO₄ solution.

Table 5. ICP-Assay results for preparation of V loaded organic of Cyanex 923 (15/15/70) for McCabe-Thiele stripping isotherm test.

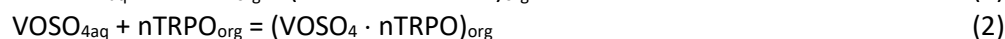
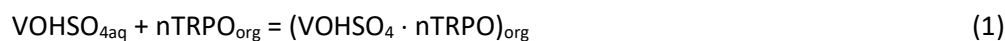
	O/A	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li
		mg/L										
Feed		475	147	<5	12058	<5	<5	36	<5	<5	1108	<5
V Raffinate	1:9	239	150	<5	12222	<5	<5	39	<5	<5	1110	<5
Loaded to organic:		2130	-32	<5	-1476	<5	<5	-22	<5	<5	-14	<5
	O/A	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Si	Ti	Zn
		mg/L										
Feed		57660	215	<5	775	39	<5	358	<5	<5	<5	<5
V Raffinate	1:9	58620	220	<5	807	40	<5	368	<5	<5	<5	<5
Loaded to organic:		-8640	-44	<5	-290	-9	<5	-90	<5	<5	<5	<5

Table 6. ICP-Assay results of the pregnant strip solutions produced for stripping isotherm.

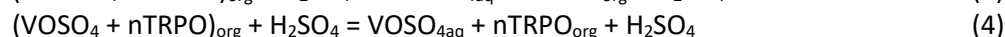
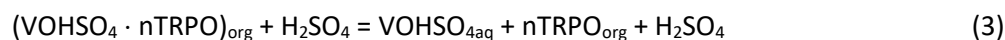
O/A	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li
	mg/L										
10:1	12108	28	<5	91	<5	<5	<5	<5	<5	<5	<5
5:1	9294	15	<5	41	<5	<5	<5	<5	<5	<5	<5
2:1	4366	5	<5	17	<5	<5	<5	<5	<5	<5	<5
1:1	2314	<5	<5	11	<5	<5	<5	<5	<5	<5	<5
1:2	1187	<5	<5	18	<5	<5	<5	<5	<5	<5	<5
1:5	476	<5	<5	9	<5	<5	<5	<5	<5	<5	<5
O/A	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Si	Ti	Zn
	mg/L										
10:1	191	<5	<5	43	<5	<5	39100	<5	<5	6	<5
5:1	79	<5	<5	41	<5	<5	44100	<5	<5	10	<5
2:1	29	<5	<5	20	<5	<5	42380	<5	<5	13	<5
1:1	20	<5	<5	22	<5	<5	42560	<5	<5	12	<5
1:2	18	<5	<5	61	<5	<5	43520	<5	<5	9	<5
1:5	6	<5	<5	63	<5	<5	43440	<5	<5	<5	<5

The possible V extraction and stripping mechanisms with Cyanex 923 can be shown by the following reactions:

- Vanadium Extraction (TRPO=Cyanex 923):



- Vanadium Stripping with H_2SO_4 :



Vanadium Precipitation

To examine the precipitation mechanism of V from a pregnant strip solution produced in the process being studied, testing was performed on a simulated pregnant strip solution with a composition similar to that achieved in the SX testing. The precipitation of V was then carried out on the simulated V pregnant strip solution with 18% ammonium hydroxide (NH_4OH) at ambient temperature. The following steps were followed to produce NH_4VO_3 :

- Preparation of a simulated V pregnant strip in 1.5 M H_2SO_4 solution by dissolving V_2O_5 ,
- Addition of 1.5 M NH_4Cl into the feed solution,
- Increase of ORP to ~850 mV with concentrate H_2O_2 ,
- Adjustment of pH to 7.0 -7.5 with 18% NH_3 solution,
- Mixing of the slurry for ~2.0 hrs at ambient temperature,

- Filtration and washing of the precipitate with D.I. water, and
- Drying of the filter cake at $\sim 65^\circ\text{C}$ for ~ 4 hrs.

Feed, filtrate and washed water were analyzed by ICP-OES. Solid samples were digested in multi-acid medium and finished by ICP-OES. About 97% V was precipitated under these conditions. Photos of the V precipitation process steps, mass balance and assay results of NH_4VO_3 are shown in Figure 11, Table 7 and Table 8, respectively. About 40% vanadium was assayed in the NH_4VO_3 product (Table 8), which was then calcined at 600°C for 3 hrs to produce V_2O_5 and resulted in about 52% vanadium in the final V_2O_5 product.

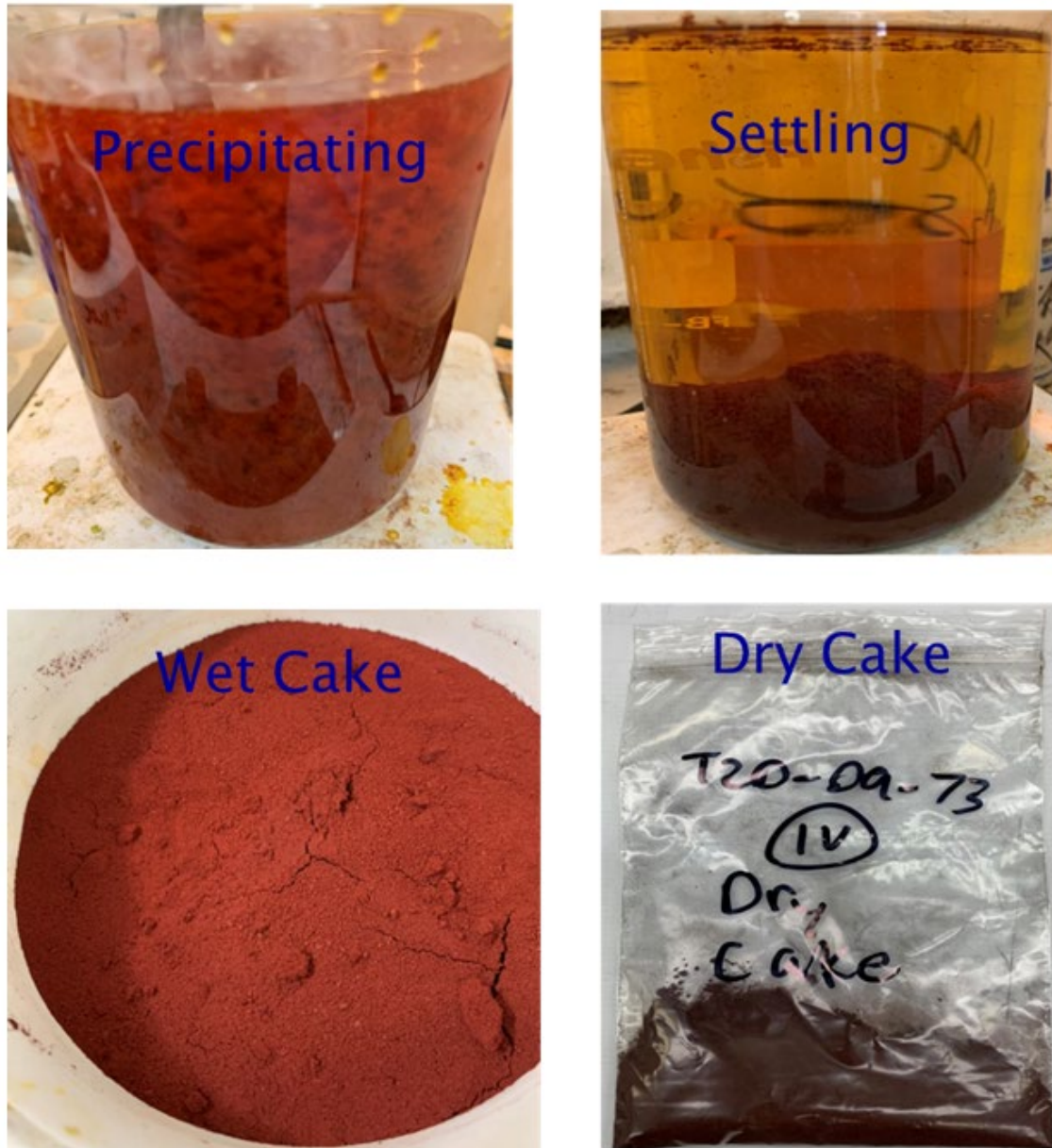


Figure 11. Photographs of vanadium precipitation process steps.

Table 7. Mass balance of vanadium precipitation test.

	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Ti	Zn
	mg/L																			
Feed	12030	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	15892	<5	<5	<5
Filtrate	151	<5	<5	7.7	<5	<5	<5	<5	<5	<5	9	<5	<5	5.1	<5	<5	14214	<5	<5	<5
WW	27.6	<5	<5	<5	<5	<5	<5	<5	<5	<5	31	<5	<5	<5	<5	<5	391	<5	<5	<5
	mg																			
Feed	601.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	794.6	-	-	-
Filtrate	13.0	-	-	0.7	-	-	-	-	-	-	0.7	-	-	0.4	-	-	1222.4	-	-	-
WW	5.5	-	-	-	-	-	-	-	-	-	0.0	-	-	-	-	-	0.0	-	-	-
	%																			
Precipitation	96.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-53.8	-	-	-

Table 8. Assay results of dried Option A ammonium metavanadate (NH₄VO₃) and vanadium pentoxide (V₂O₅) products.

	V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	S	Ti	Zn
	%															
Ammonium <u>Metavanadate</u>	40	<DL	<DL	0.01	<DL	<DL	0.05	<DL	<DL	<DL	<DL	<DL	<DL	0.08	<DL	<DL
Vanadium Pentoxide	52	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

Option B Results

Feed Preparation

Precipitation of V from the Ti raffinate was carried out by following the process steps outlined below:

- Filtration to produce aqueous feed for V precipitation,
- Precipitation of V with 35% (w/w) MgO at 60°C at pH 3.55,
- Filtration of the cake with vacuum filtration coupled with Buchner funnel, and
- Drying of a small portion of filter cake at 98°C and analyzed by multi-acid digestion followed by ICP-OES finish.

About 500 g of filter cake was produced from two batches of precipitation tests (Batch-I and Batch-II) for the subsequent V dissolution tests in H₂SO₄ and NaOH mediums. Analytical results of aqueous and solid samples, free HCl acid (FAT), and pH are shown in Table 9. Vanadium concentration in both filtrates was <5 mg/L, which suggests that >99.9% V was precipitated under these conditions. Moreover, concentrations of V in the Filter Cake-I and Filter Cake-II were ~5.5% and ~5.1%, respectively, which

were used in the subsequent dissolution tests. A significant amount of magnesium (Mg) were found in these cakes and is due to entrainment as the solid-liquid separation was difficult, taking more than 8 hrs to complete.

Table 9. Results on intermediate vanadium precipitation tests.

Batch-I																
	V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	Ti	Zn	FAT (HCl)	
	mg/L															N
Ti Raffinate	99	177	<5	674	49	<5	<5	1227	60320	236	<5	44	41	69	0.55	
V adjusted Ti raffinate	348	159	<5	654	51	<5	<5	1315	63820	226	<5	45	42	<5	0.50	
Filtrate	<5	<5	<5	668	<5	<5	<5	1371	75740	230	<5	37	<5	<5	pH: 3.55	
	%															
Filter Cake-I	5.5	3.5	<DL	0.1	0.6	0.0	0.0	0.3	10.1	0.1	<DL	0.1	0.5	0.0		
Batch-II																
	V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	Ti	Zn	FAT (HCl)	
	mg/L															N
Ti Raffinate	99	177	<5	674	49	<5	<5	1227	60320	236	<5	44	41	69	0.55	
V adjusted Ti raffinate	374	158	<5	639	45	<5	<5	1384	68380	223	<5	47	42	6	0.51	
Filtrate	<5	<5	<5	647	<5	<5	<5	1377	77860	<5	<5	39	<5	9	pH: 3.50	
	%															
Filter Cake-II	5.1	1.9	<DL	0.1	0.7	0.0	0.1	0.1	7.7	0.2	<DL	0.3	0.7	0.0		

Acid Leaching of V Precipitate

Leaching of the intermediate V cake was evaluated by varying the concentrations of H₂SO₄ and NaOH solutions. The following steps were followed for the H₂SO₄ leaching:

- Transferred target amount of V filter cake into a suitable Pyrex reactor fitted with impeller, condenser, thermocouple, pH and ORP probes,
- Maintained temperature ~60°C,
- Used pulp density of 10%,
- Maintained 30 min for stage sampling and acid addition,
- Filtered and returned the stage sample residues into the leaching reactor,
- Conducted the leaching test for a total of 3 hrs,
- Performed solid/liquid separation with vacuum filtration coupled with Buchner funnel, and
- Washed the residue two times with D.I. water.

After completion of leaching, aqueous and solid samples were analyzed. Analytical results are shown in Figure 12 and Table 10. The results suggest that based on concentration of V in the leach solutions which gradually increase with increase in H₂SO₄ content, the vanadium is completely dissolved after addition of 1.25M H₂SO₄, as no further increase in V is seen. Impurities such as Al, Mg, Cr, Mn, and Ti are also leached.

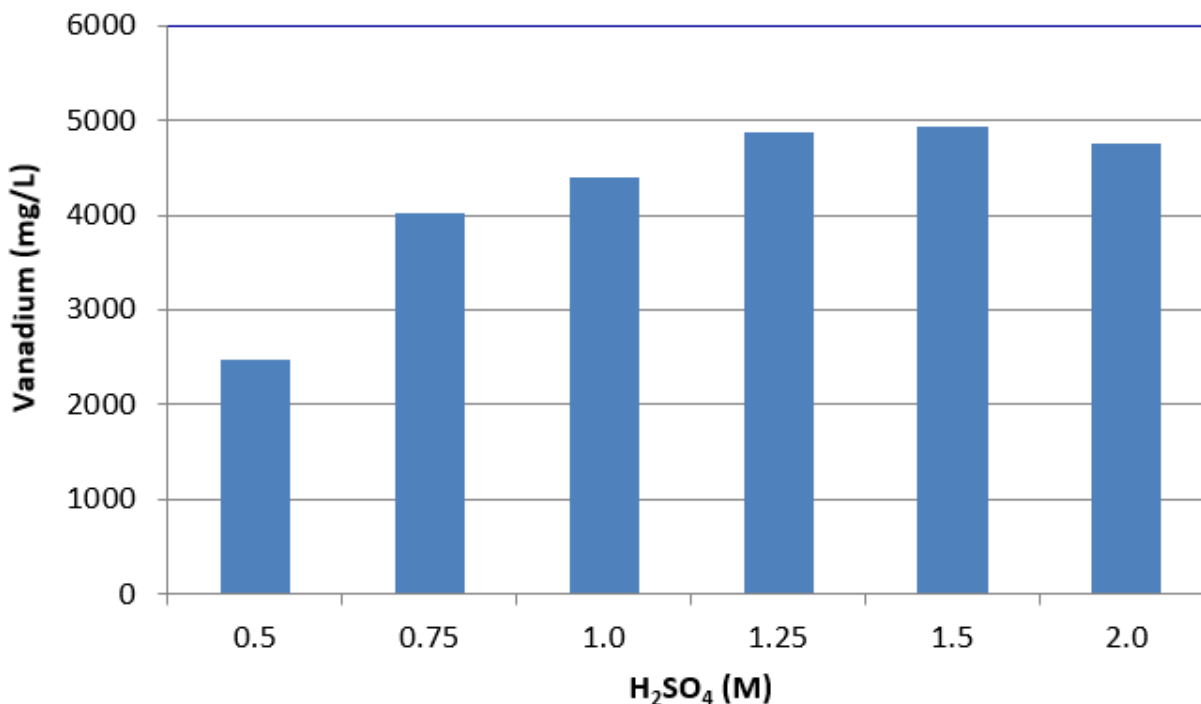


Figure 12. Concentration of vanadium in stage samples at different contents of H₂SO₄.

Table 10. Analytical results of leach solutions taken at different contents of H₂SO₄.

H ₂ SO ₄	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K
M	mg/L									
0.5	2470	2448	<5	160	<5	<5	728	64	38	299
0.75	4016	2582	<5	157	<5	<5	766	64	27	302
1.0	4406	2644	<5	158	<5	<5	728	66	17	303
1.25	4876	2632	<5	162	<5	<5	775	67	17	317
1.5	4930	2676	<5	167	<5	<5	814	70	16	322
2.0	4758	2554	<5	166	<5	<5	755	67	6	306
WW1	496.5	205	<5	18	<5	<5	53	5	20	19
WW2	39.8	<5	<5	10	<5	<5	<5	<5	23	<5
H ₂ SO ₄	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Ti	Zn
M	mg/L									
0.5	15154	209	<5	229	515	6	17584	<5	118	<5
0.75	15870	204	<5	227	509	8	26700	<5	319	<5
1.0	15022	205	<5	229	513	8	35300	<5	418	<5
1.25	15990	209	<5	232	523	8	46660	<5	483	<5
1.5	15860	216	<5	243	537	9	56400	<5	556	<5
2.0	15158	211	<5	247	523	<5	74680	<5	568	<5
WW1	1098	17	<5	<5	44	<5	5466	<5	43	<5
WW2	55	<5	<5	<5	<5	<5	286	<5	<5	<5

Following the procedure outlined above, another two leaching tests were completed with 1.0 M and 1.5 M of H₂SO₄ solutions to evaluate the mass balance. Vanadium leach recovery results are shown in Table 11 and Table 12 for 1.0 M H₂SO₄ and 1.5 M H₂SO₄, respectively. Leach recoveries of V were ~88% and ~100% for 1.0 M H₂SO₄ and 1.5 M H₂SO₄, respectively. Impurities were also completely dissolved with 1.5 M H₂SO₄.

Table 11. Mass balance on a leaching test completed with 1.0M H₂SO₄ solution.

H ₂ SO ₄	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K
M	mg/L									
0.5	2470	2448	<5	160	<5	<5	728	64	38	299
0.75	4016	2582	<5	157	<5	<5	766	64	27	302
1.0	4406	2644	<5	158	<5	<5	728	66	17	303
1.25	4876	2632	<5	162	<5	<5	775	67	17	317
1.5	4930	2676	<5	167	<5	<5	814	70	16	322
2.0	4758	2554	<5	166	<5	<5	755	67	6	306
WW1	496.5	205	<5	18	<5	<5	53	5	20	19
WW2	39.8	<5	<5	10	<5	<5	<5	<5	23	<5
H ₂ SO ₄	Mg	<u>Mn</u>	Mo	Na	Ni	<u>Pb</u>	S	Sb	<u>Ti</u>	Zn
M	mg/L									
0.5	15154	209	<5	229	515	6	17584	<5	118	<5
0.75	15870	204	<5	227	509	8	26700	<5	319	<5
1.0	15022	205	<5	229	513	8	35300	<5	418	<5
1.25	15990	209	<5	232	523	8	46660	<5	483	<5
1.5	15860	216	<5	243	537	9	56400	<5	556	<5
2.0	15158	211	<5	247	523	<5	74680	<5	568	<5
WW1	1098	17	<5	<5	44	<5	5466	<5	43	<5
WW2	55	<5	<5	<5	<5	<5	286	<5	<5	<5

Test Sample	Recovered (Residue/Head)						
	V	<u>Ti</u>	Ni	K	Ca	Al	Zn
	%						
Total recovered solution	87.8	72.2	99.8	99.8	99.2	99.2	100.0
Residue	12.2	27.8	0.2	0.2	0.8	0.8	0.0
Totals	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	Cu	Fe	Mg	<u>Mn</u>	<u>Pb</u>	Cu	
	%						
Total recovered solution	100.0	88.8	99.9	99.8	90.6	100.0	
Residue	0.0	11.2	0.1	0.2	9.4	0.0	
Totals	100.0	100.0	100.0	100.0	100.0	100.0	

Table 12. Mass balance on a leaching test completed with 1.5M H₂SO₄ solution.

H ₂ SO ₄	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K
M	mg/L									
0.5	2470	2448	<5	160	<5	<5	728	64	38	299
0.75	4016	2582	<5	157	<5	<5	766	64	27	302
1.0	4406	2644	<5	158	<5	<5	728	66	17	303
1.25	4876	2632	<5	162	<5	<5	775	67	17	317
1.5	4930	2676	<5	167	<5	<5	814	70	16	322
2.0	4758	2554	<5	166	<5	<5	755	67	6	306
WW1	496.5	205	<5	18	<5	<5	53	5	20	19
WW2	39.8	<5	<5	10	<5	<5	<5	<5	23	<5
H ₂ SO ₄	Mg	<u>Mn</u>	Mo	Na	Ni	<u>Pb</u>	S	Sb	<u>Ti</u>	Zn
M	mg/L									
0.5	15154	209	<5	229	515	6	17584	<5	118	<5
0.75	15870	204	<5	227	509	8	26700	<5	319	<5
1.0	15022	205	<5	229	513	8	35300	<5	418	<5
1.25	15990	209	<5	232	523	8	46660	<5	483	<5
1.5	15860	216	<5	243	537	9	56400	<5	556	<5
2.0	15158	211	<5	247	523	<5	74680	<5	568	<5
WW1	1098	17	<5	<5	44	<5	5466	<5	43	<5
WW2	55	<5	<5	<5	<5	<5	286	<5	<5	<5

Test Sample	Recovered (Residue/Head)						
	V	<u>Ti</u>	Ni	K	Ca	Al	Zn
	%						
Total recovered solution	100	100	100	100	100	100	100
Residue	0	0	0	0	0	0	0
Totals	100	100	100	100	100	100	100
Test Sample	Recovered (Residue/Head)						
	Cu	Fe	Mg	<u>Mn</u>	Mo	<u>Pb</u>	Cu
	%						
Total recovered solution	100	100	100	100	100	100	100
Residue	0	0	0	0	0	0	0
Totals	100	100	100	100	100	100	100

Caustic Leaching of V Precipitate

The following steps were followed for the leaching of intermediate V containing filter cake with NaOH solution:

- Transferred target amount of V filter cake into a suitable Pyrex reactor fitted with impeller, condenser, thermocouple, pH and ORP probes,
- Varied NaOH concentrations from 0.25 M to 1.0 M,
- Maintained temperature $\sim 70^{\circ}\text{C}$,
- Used pulp density of 10%,
- Maintained 30 min for stage sampling and NaOH addition,
- Filtered and returned the stage sample residues into the leaching reactor,
- Performed S/L separation with vacuum filtration coupled with Buchner funnel,
- Washed residue with D.I. water with two displacement volumes, and
- Analyzed aqueous samples by ICP-OES.

The effect of NaOH concentrations on the leaching of filter cake is shown in Figure 13 and Table 13. The results suggest that no leaching occurs with NaOH concentrations up to 0.75 M NaOH. Leaching only occurs after addition of 1M NaOH where ~ 1062 mg/L V is observed in the final filtrate.

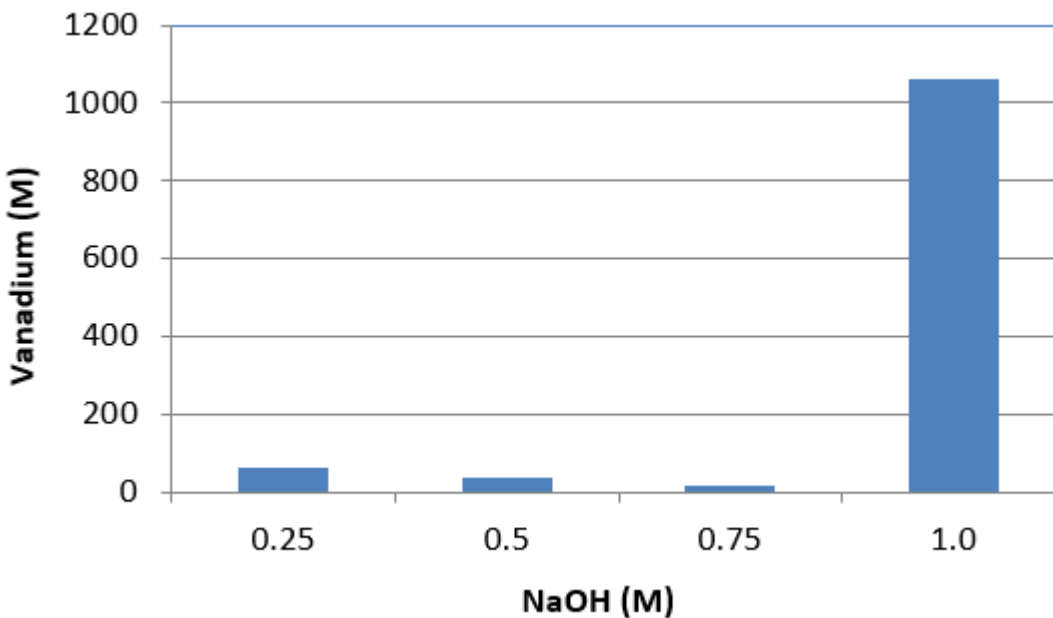


Figure 13. Concentrations of vanadium in stage samples a different contents of NaOH.

Table 13. Analytical results of aqueous samples taken after addition of NaOH solutions.

NaOH	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K
M	mg/L									
0.25	62	<5	<5	111	<5	<5	<5	<5	<5	271
0.5	37	<5	<5	98	<5	<5	<5	<5	<5	312
0.75	18	<5	<5	89	<5	<5	<5	<5	<5	367
1.0	1062	<5	<5	<5	<5	<5	<5	<5	<5	369
WW1	420	<5	<5	<5	<5	<5	<5	<5	<5	112
WW2	45	<5	<5	<5	<5	<5	<5	<5	<5	8
NaOH	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Ti	Zn
M	mg/L									
0.25	8206	<5	<5	5028	<5	<5	103	<5	<5	<5
0.5	5202	<5	<5	10882	<5	<5	96	<5	<5	<5
0.75	1816	<5	<5	17512	<5	<5	84	<5	<5	<5
1.0	<5	<5	<5	21040	<5	<5	303	<5	<5	<5
WW1	<5	<5	<5	8240	<5	<5	150	<5	<5	<5
WW2	<5	<5	<5	663	<5	<5	6	<5	<5	<5

Following the procedure outlined above, another aggressive leaching test was completed with 2.0 M NaOH solution at ~98°C for ~10 hrs to further evaluate the leaching efficiency of NaOH. The results of this test are shown in Table 14. About 80% V was recovered, which is ~20% lower than that observed in a leaching test that was completed with 1.5 % H₂SO₄. Based on these results, further testing was done on H₂SO₄ leach solutions in the subsequent Vanadium SX tests.

Table 14. Mass balance on a leaching test, which was carried out with 2.0 M NaOH solution.

Test Sample	Recovered (Residue/Head)						
	V	Ti	Ni	K	Ca	Al	Zn
	%						
Total recovered soln	80	-5	-119	84	-89	-146	-57
Residue	20	105	219	16	189	246	157
Totals	100	100	100	100	100	100	100
	Cu	Fe	Mg	Mn	Pb		
	%						
Total recovered soln	-71	-202	-92	-5	37		
Residue	171	302	192	105	63		
Totals	100	100	100	100	100		

Organic Extractant Screening

A number of vanadium solvent extraction tests were carried out by contacting aqueous feed solution obtained from H₂SO₄ leaching system with different organic phases consisting of an extractant, Exxal 13 (modifier), in ShelSol D80 (kerosene). The extractants used in this study were Aliquat 336, LIX 63, TBP, Cyanex 923, and Cyanex 272. Organic screening SX tests were carried out at ambient temperature (~22°C) for 5 min at 400 rpm and different O/A phase ratios. The pH values of the feed solutions ranged from 0.3 to 2.5. Metals in the aqueous phases were analyzed by ICP-OES. Observation and Vanadium SX test results are shown in Table 15, which suggests that LIX 63 is an excellent extractant for V. For other extractants tested, either precipitation or emulsion was observed in between the two phases (organic and aqueous) and therefore would not be viable. Furthermore, LIX 63 has very high selectivity for V over other metals, including Ti and Cr (Table 16). Therefore, LIX 63 was selected for developing V extraction and stripping isotherms in the subsequent stage.

Table 15. Organic screening test results for V extraction from H₂SO₄ leach solution.

Aqueous phase	Organic phase	O/A	V (mg/L)		pH	Observation
			Aqueous	Organic		
Feed			4212		2.5	
Raffinate	Aliquat 336 (15/10/75)	1:1	1335	2877	0.9	Precipitation observed
Raffinate	Aliquat 336 (15/10/75)	5:1	1332.8	576	0.9	Precipitation observed
Raffinate	Aliquat 336 (15/10/75)	1:5	1237.6	14872	2.0	Precipitation observed
Raffinate	LIX 63 (20/10/70)	1:1	3308	904	2.4	
Feed			6338		0.3	
Raffinate	TBP(35/25/40)	1:1	6652	-314	-0.3	Emulsion observed
Raffinate	Cyanex 923 (15/15/70)	1:1	4870	1468	-0.3	Emulsion observed
Raffinate	Cyanex 272 (15/10/75)	1:1	3958	2380	-0.3	Emulsion observed
Raffinate	LIX 63 (15/10/75)	1:1	2190	4148	-0.4	No Emulsion
Feed			7034		0.3	
Raffinate	LIX 63 (10/10/80)	1:1	2392	4642		No Emulsion
Raffinate	LIX 63 (15/10/75)	1:1	2202	4832	-0.2	No Emulsion
Raffinate	LIX 63 (20/10/70)	1:1	2144	4890		Emulsion observed

Table 16. Vanadium SX results for LIX 63 (10/10/80) at the O/A phase ratio of 1.

Aqueous	Organic	V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Ti	Zn	ORP	pH
		mg/L															
Feed		7034	4750	<5	273	1313	105	221	490	27900	370	380	964	455	16	830	0.3
Raffinate	LIX 63 (10/10/80)	2392	4828	<5	271	1323	96	233	493	28220	369	416	981	455	14.8	655	-0.2
Loading to the organic phase		4642	-78	<5	1.2	-10.6	8.7	-11.7	-3	-320	1.3	-36	-17	0.7	1.2		

Vanadium Extraction and Stripping Isotherms

The McCabe-Thiele V extraction and stripping isotherms were developed with an organic phase consisting of 10% (v/v) LIX 63 and 10%(v/v) Exxal 13 in ShelSol D80. Pregnant leach solution (PLS) obtained from leaching of intermediate V precipitate in H₂SO₄ medium was used as a feed. The pH and ORP of this PLS were adjusted to 0.3 and >900 mV, respectively to keep vanadium in solution as V(IV)/V(V).

A total of six V extraction tests were carried out by varying O/A phase ratios of 10:1, 5:1, 2:1, 1:1, 1:2, and 1:5. Each V SX test was completed at 35°C for 5 min at 450 rpm. Two phases were separated by a suitable separatory funnel, and aqueous phases were passed through a filter paper prior to submission for ICP-OES analysis. Analytical results of feed and raffinate are shown in Table 17. Based on this data, the McCabe-Thiele V extraction isotherm was developed (Fig. 14). The extraction isotherm suggests that about 2771 mg/L V can be loaded to the organic phase, and ~70% V can be extracted from the feed consisting of ~8940 mg/L V with 10%(v/v) LIX 63 by three stage extraction at the O/A phase ratio of 1:0.31. About 2148 mg/L V remained in the raffinate despite a high O/A phase ratio of 10:1. This remaining V may present in the raffinate at a lower oxidation stage, most likely as V(III), as the redox

potential decreased from ~900 mV (feed) to ~543 mV (raffinate). It further suggests that the LIX 63 can only extract V(IV)/V(V). To extract this remaining V, the ORP of the raffinate obtained from the test at the O/A phase of 10:1 was increased to ~900 mV with H₂O₂ and subsequently contacted with a fresh organic phase at the O/A phase ratio of 3:1. Results are shown Table 18, which further suggests that the vanadium can be completely extracted by maintaining higher ORP (~900 mV) during SX.

Table 17. Results of V extraction isotherm with LIX 63 (10/10/80).

O/A	V	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Ti	Zn	ORP
	mg/L														mV
	8940	4344	226	1199	89	179	411	23020	312	<5	303	834	912	11	902
10:1	2148	4608	236	1242	5	183	432	24220	321	<5	323	840	894	54	543
5:1	2724	4750	244	1274	12	192	442	24720	336	<5	339	867	901	37	
2:1	4490	4920	247	1304	51	195	458	25500	341	<5	350	918	986	24	
1:1	6208	4728	243	1262	91	191	446	24740	337	<5	335	901	944	18	
1:2	7250	4670	244	1249	94	187	444	24560	328	<5	336	894	939	15	
1:5	8208	4890	245	1299	95	188	446	25380	334	<5	384	924	974	13	

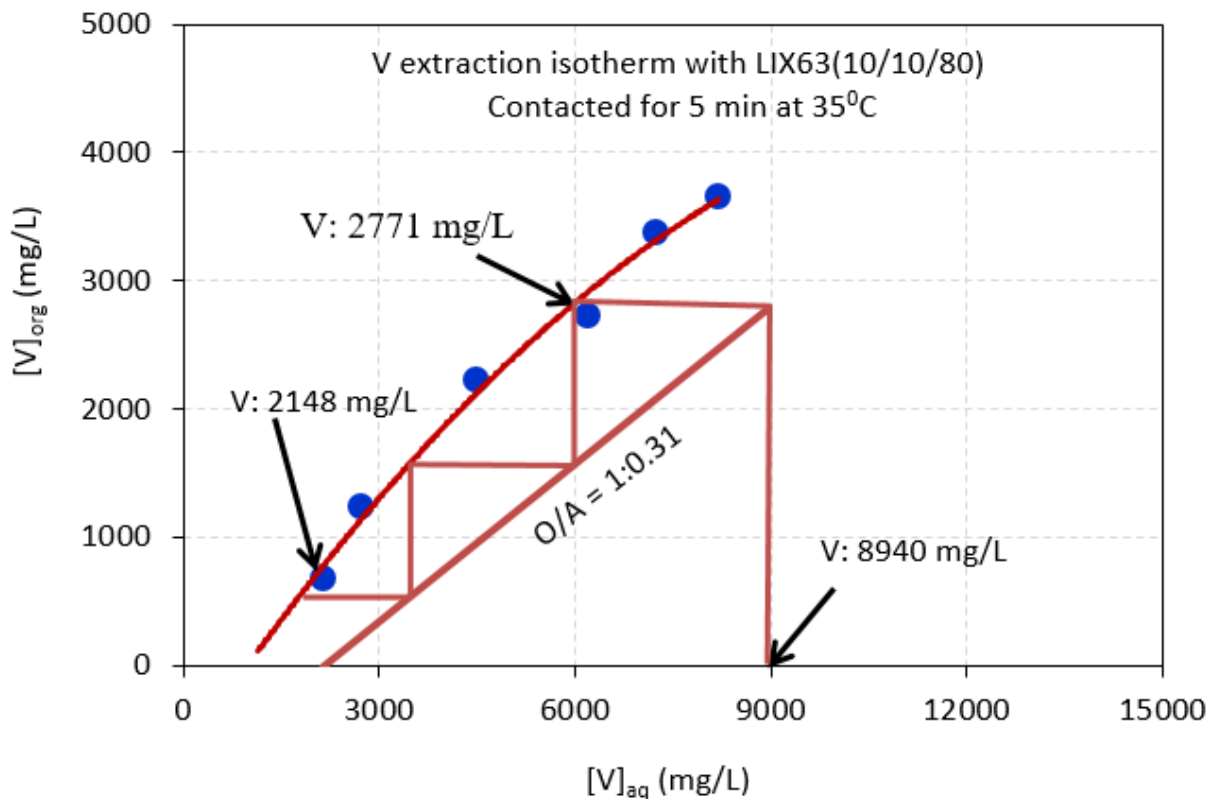


Figure 14. The McCabe-Thiele V extraction isotherm for LIX 63 (10/10/80).

Table 18. Results of V extraction on the raffinate obtained from O/A ratio of 10:1.

O/A	V	Al	Ca	Cr	Cu	Fe	K	Mg	<u>Mn</u>	Mo	Na	Ni	<u>Ti</u>	Zn	ORP
	mg/L														mV
	2186	4410	260	1232	17.6	252	486	26300	343	<5	373	849.5	998.5	12	900
3:1	34.5	4348	259	1211	<5	240	457	25620	332	<5	432	802.5	964.5	11	

The McCabe-Thiele V stripping isotherm was developed with an organic phase consisting of 10% (v/v) LIX 63 and 10% (v/v) Exxal 13 in Shelsol D80. About 2762 mg/L V was loaded to the organic phase by conducting this organic with an aqueous feed solution at the O/A phase ratio of 1:1 at ~35°C for 5 min (Table 19). Vanadium loaded organic phase was contacted with 1.5 M NaOH solution at the O/A phase ratios of 10:1, 5:1, 2:1, 1:1, 1:5 and 1:10. Each stripping SX test was carried out for 5 min at 35-40°C and 450 rpm. After the completion of each test, the aqueous phase was separated from the organic phase, passed through a filter paper and analyzed by ICP-OES. Assay results and the developed McCabe-Thiele V stripping isotherm are shown in Table 20 and Figure 15, respectively. These results suggest that V can be completely stripped with NaOH by two-stage stripping at the O/A phase ratio of 10:1. Moreover, over 27000 mg/L V can be found in the pregnant strip solution at the O/A phase ratio of 10:1.

Table 19. Results on the loading of vanadium to the LIX 63 (10/10/80) from H₂SO₄ leach solution.

	O/A	V	Al	Ca	Cr	Cu	Fe	K	Mg	<u>Mn</u>	Ni	<u>Ti</u>	Zn
		mg/l											
Feed		8934	4592	247	1334	95	204	459	25700	337	888	911	13
Raffinate	1:1	6172	4582	247	1328	88	209	458	25680	339	884	895	13
Loaded to organic		2762	10	-0.5	6.2	6.9	-5.3	0.9	20	-2.5	4.4	16	0.4

Table 20. Results of V stripping isotherm for LIX 63 (10/10/80) with 1.5 M NaOH solution.

O/A	V	Al	Ca	Cr	Cu	Fe	K	Mg	<u>Mn</u>	Ni	<u>Ti</u>	Zn
	mg/L											
10:1	27240	<5	<5	<5	<5	<5	<5	<5	<5	<5	15.7	<5
5:1	13478	<5	<5	<5	<5	<5	<5	<5	<5	<5	8.5	<5
2:1	5414	<5	<5	<5	<5	<5	<5	<5	<5	<5	6.3	<5
1:1	2764	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
1:5	559.5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
1:10	278	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

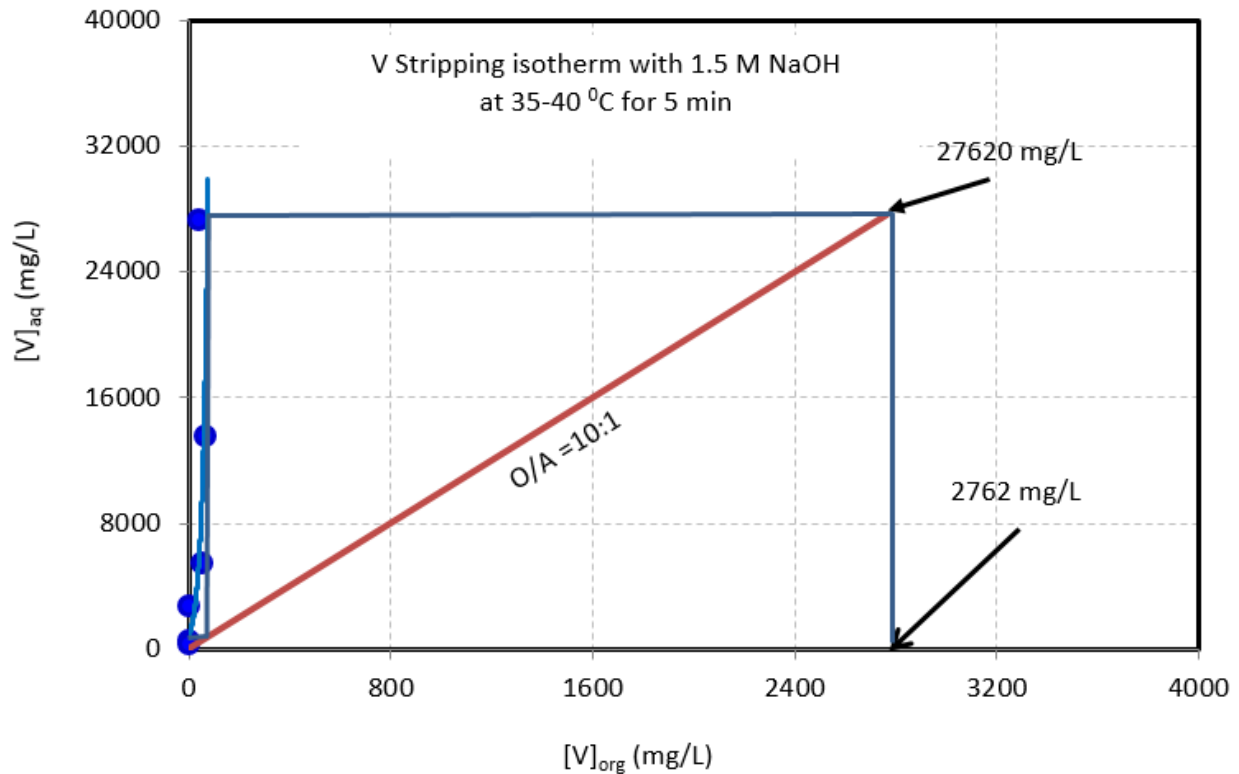


Figure 15. The McCabe-Thiele V stripping isotherm with 1.5M NaOH solution.

Vanadium Precipitation

A pH-dependent V precipitation test was carried out on a simulated V pregnant strip solution with 18% ammonium hydroxide (NH_4OH) at ambient temperature. The following steps were followed to precipitate V as an ammonium metavanadate:

- Preparation of a simulated V pregnant strip solution by dissolving V_2O_5 into 1.5 M NaOH solution,
- Transferred a target amount of feed solution to a suitable glass beaker, which was placed on a magnetic plate,
- Added 1.5 M NH_4Cl into this solution,
- Decreased the pH of the feed solution from 13.6 to 5.5 with 1.0–1.5 M H_2SO_4 solution,
- Maintained ~30 minutes residence time between each pH range for stage sampling and acid addition/pH adjustment,
- Mixed the slurry at ambient temperature,
- Filtered the intermediate samples and returned the residues to beaker,
- Filtered and washed the final precipitate with D.I. water, and
- Dried a portion of the filter cake at ~65 °C for ~3 hrs for assaying.

Aqueous samples were analyzed by ICP-OES. The solid sample was digested in multi-acid medium and finished by ICP-OES. The results and photos of the V precipitation test are shown in Table 21 and Table 22, and Figure 16. These results suggest that >99% vanadium was precipitated at pH 7.0 as an ammonium metavanadate under these conditions, and ~39.6% V found in the dried cake. About 4.2 % Na was also found in the dried product (NH₄VO₃). The remaining wet filter cake was further washed with a two volume displacements with D.I. water to reduce Na content. The final wet cake was initially dried at 85°C for 4 hours and then calcined at 600°C for 3 hours to produce a V₂O₅. About 39.1% V and 56.8%V were found in the NH₄VO₃ and V₂O₅, respectively, while the content of Na was reduced to 2.3% from 4.2% in the washed NH₄VO₃ (Table 23).

Table 21. Results of V precipitation test.

	pH	V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Si	Ti	Zn
	mg/L															
Feed	13.6	26240	<5	<5	8	<5	<5	<5	<5	<5	<5	20980	<5	<5	<5	<5
Filtrate	9.8	9218	<5	<5	8	<5	<5	<5	<5	<5	<5	16748	<5	<5	<5	<5
Filtrate	8.0	246	<5	<5	7	<5	<5	<5	<5	<5	<5	14814	<5	<5	<5	<5
Filtrate	7.5	163	<5	<5	5	<5	<5	<5	<5	<5	<5	14394	<5	<5	<5	<5
Filtrate	7.0	129	<5	<5	9	<5	<5	<5	<5	<5	<5	14066	<5	<5	<5	<5
Filtrate	6.5	109	<5	<5	12	<5	<5	<5	<5	<5	<5	14688	<5	<5	<5	<5
Filtrate	6.0	106	<5	<5	<5	<5	<5	<5	<5	<5	<5	14584	<5	<5	<5	<5
Filtrate	5.5	102	<5	<5	7	<5	<5	<5	<5	<5	<5	14724	<5	<5	<5	<5
Filtrate	5.5	110	<5	<5	<5	<5	<5	<5	<5	<5	<5	13664	<5	<5	<5	<5
Wash Water		28	<5	<5	<5	<5	<5	<5	<5	<5	<5	327	<5	<5	<5	<5

Table 22. Mass balance of V precipitation test and dried cake assay results.

	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	Si	Ti	Zn
	mg/L																			
Feed	26240	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	20980	<5	<5	<5	<5	<5	<5
Filtrate	110	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	13664	<5	<5	<5	<5	<5	<5
Wash Water	28	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	327	<5	<5	<5	<5	<5	<5
	mg																			
Feed	9840													7868						
Filtrate	58													7242						
Wash Water	20													238						
	%																			
Precipitation	99.2													4.9						
	V	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Ti	Zn
	%																			
Dry Cake	39.6	<DL	<DL	0.02	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	4.2	<DL	<DL	<DL	<DL	<DL	<DL



Figure 16. Photographs of V precipitation test and dried product.

Table 23. Assay results of Option B ammonium metavanadate (NH_4VO_3) and vanadium pentoxide (V_2O_5) products.

	Heating conditions		V	Al	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	S	Ti	Zn
			%															
Option-B	Dried at 85 °C for 4 hrs	NH_4VO_3	39.1	<DL	<DL	0.01	<DL	<DL	0.02	0.08	<DL	<DL	<DL	2.30	<DL	<DL	<DL	<DL
	Dried at 600 °C for 3 hrs	V_2O_5	56.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL		<DL	<DL	<DL	<DL

VANADIUM PRODUCT CHARACTERIZATION

Introduction

Following hydrometallurgical processing, four powdered precipitates produced by PRO were sent to NRRI for further mineralogical (x-ray diffraction (XRD)) and mineral chemistry analysis (electron microprobe analysis (EMPA)). The four powdered precipitate samples included:

- Option A ammonium metavanadate
- Option A vanadium pentoxide
- Option B ammonium metavanadate
- Option B vanadium pentoxide

The purpose of these analyses was to independently verify the mineralogical compositions of the precipitates and to obtain both mineral chemistry and textural information about the precipitates.

Methods

X-Ray Diffraction (XRD) Analysis

XRD analyses were performed at the NRRI Coleraine Laboratory in Coleraine, Minnesota. Four process precipitate samples (Option A ammonium metavanadate, Option A vanadium pentoxide, Option B ammonium metavanadate, Option B vanadium pentoxide) were analyzed for their mineralogy using a Bruker D2 Phaser x-ray diffractometer. Mineral phase identification utilized Bruker AXS-Diffrac.EVA

V4.3.1.2 phase identification software, the ICCD-PDF-4+ 20129 powder diffraction database, with Reitfeld refinement using Sietronics PTY – Siroquant V4.0 software.

Electron Microprobe Analysis (EMPA)

The four powdered samples were prepared as separate polished pucks for subsequent electron microprobe analysis (EMPA). EMPA was carried out utilizing a field emission JOEL JXA-8350fPlus electron microprobe analyzer located at the Electron Microscopy Laboratory (EML) in the Department of Earth and Environmental Sciences at the University of Minnesota Twin Cities (UMTC). This instrument is equipped with a soft x-ray emission spectrometer (SXES) detector, five automated wave-dispersive spectrometers (WDS), and an energy dispersive spectrometer (EDS) for rapid mineral chemical analysis. Elemental analyses of precipitates were performed on polished puck samples. Dr. Anette von der Handt (EML-UMTC Lab Manager) performed all analyses and provided all mineral chemical analyses and stoichiometric calculation results. Dr. George Hudak (Professional Geologist, State of Minnesota) assisted with selection of individual precipitate particles that were evaluated during the analysis.

Electron microprobe standards for the suite of elements analyzed included (Dr. Anette von der Handt, UMTC Electron Microprobe Lab Director, and personal communication 2021):

- Si: Orthoclase, Taylor, KAlSi_3O_8 ,
- Ti: Ilmenite, NMNH 96189,
- Pb: Lead Telluride, MAC, PbTe ,
- Al: Aluminum Oxide, MM, Al_2O_3 ,
- V: V-metal, MM, V,
- Fe: Ilmenite, NMNH 96189,
- Ca: Fluorapatite, NMHH 104021,
- Na: Albite, Taylor, $\text{NaAlSi}_3\text{O}_8$,
- K: Orthoclase, Taylor, KAlSi_3O_8 ,
- P: Fluorapatite, NMNH 104021, and
- N: Si_3N_4 .

Results

X-Ray Diffraction Results

XRD results utilizing Reitfeld refinement are summarized in Table 24. The Option A ammonium metavanadate precipitate is composed of 69.9 weight percent (wt. %) ammonium vanadium oxide and 31.1 wt. % shcherbinaite (V_2O_5). The option A vanadium pentoxide is composed of 100 wt. % shcherbinaite. The Option B ammonium metavanadate precipitate is composed of 57.9 wt. % ammonium vanadium oxide and 42.1 wt. % ammonium sodium vanadium oxide. The Option B vanadium pentoxide is composed of 68.2 wt. % shcherbinaite and 31.8 wt. % sodium vanadium oxide. These results will be discussed in the Summary and Discussion section of this report.

Table 24. X-ray diffraction mineral identification of PRO hydrometallurgical precipitates.

X-Ray Diffraction Results – Vanadium-Bearing Hydrometallurgical Processing Precipitates				
Sample	Material	Phase	Weight Percentage/ Modal Analysis	Error of Fit
ML21-280	Option A Ammonium Metavanadate	Ammonium Vanadium Oxide	68.9	6.42
		Shcherbinaite	31.1	6.42
ML21-290	Option A Vanadium Pentoxide	Shcherbinaite	100.0	0.00
ML21-300	Option B Ammonium Metavanadate	Ammonium Vanadium Oxide	57.9	0.19
		Ammonium Sodium Vanadium Oxide	42.1	0.19
ML21-310	Option B Vanadium Pentoxide	Shcherbinaite	68.2	0.83
		Sodium Vanadium Oxide	31.8	0.83

Electron Microprobe Analysis Results

Option A ammonium metavanadate was morphologically and chemically evaluated via EMPA. Figure 17 illustrates the morphologies of these precipitates. Option A ammonium metavanadate occurs in four morphologies: 1) subhedral columnar grains up to ~50µm in length and 20-30µm in width; 2) anhedral to subhedral elongate or acicular grains up to ~300µm in length and ~25-35µm in width; 3) coarser-grained, anhedral to subhedral equant to stubby columnar, porous grains ranging from ~120µm-130 µm in length and ~30µm-80µm in width; and 4) finer-grained, anhedral porous to “sponge-like” porous grains ranging from ~5µm-125µm in length and <5µm-~75µm in width (Fig. 17).

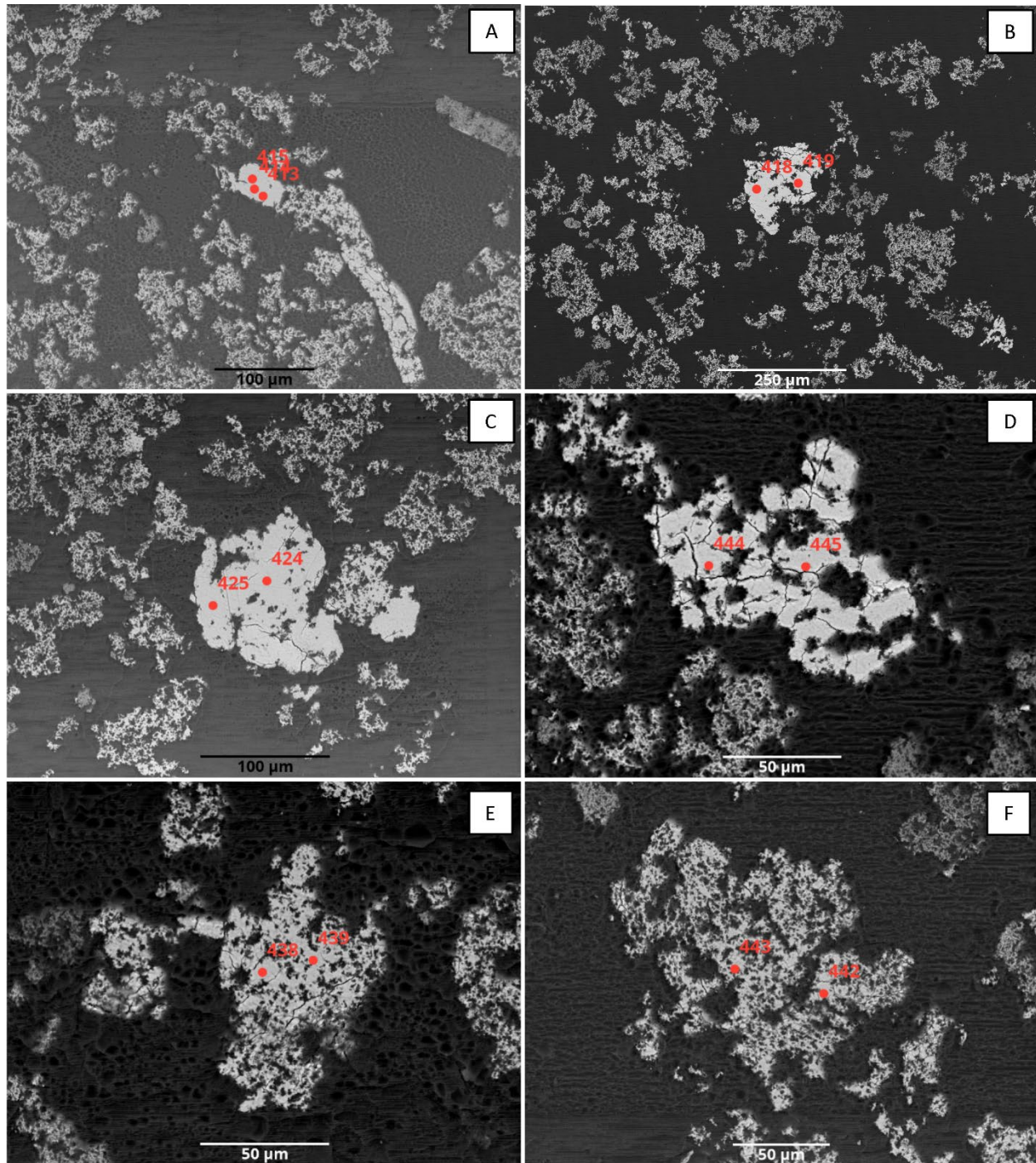


Figure 17. Electron microprobe backscatter images showing morphologies of Option A ammonium metavanadate. Bar scales for each image are in micrometers (μm). Red numbers and circles in images are EMPA analysis locations.

Thirty-two chemical analyses of Option A ammonium metavanadate obtained via EMPA are contained in Table 25. For the 32 analyses performed, analytical totals ranged from 56.807% to 102.368%, with average and median analytical totals being 92.076% and 95.785%, respectively.

Table 25. EMPA chemical analysis of Option A ammonium metavanadate.

SAMPLE	NUMBER	LINE	SiO2	TiO2	PbO	Al2O3	V2O5	Fe2O3	CaO	Na2O	K2O	P2O5	N	O	H	TOTAL
AAM_B-01	7	413	0.015	0.013	0.000	0.005	92.786	0.014	0.004	0.476	0.028	0.000	3.444	0.000	0.991	97.796
AAM_B-01	9	414	0.010	0.000	0.000	0.001	90.771	0.000	0.012	0.436	0.024	0.000	3.494	0.000	1.006	95.754
AAM_B-01	9	415	0.047	0.007	0.000	0.003	90.903	0.006	0.018	0.427	0.030	0.008	3.366	0.000	0.969	95.785
AAM_B-02	10	416	0.005	0.000	0.000	0.012	90.984	0.000	0.032	0.180	0.014	0.000	3.407	0.000	0.981	95.616
AAM_B-02	10	417	0.072	0.011	0.000	0.013	89.292	0.018	0.047	0.511	0.028	0.000	2.826	0.000	0.814	93.632
AAM_B-03	11	418	0.051	0.000	0.011	0.014	90.366	0.008	0.027	0.220	0.010	0.004	3.471	0.000	0.999	95.181
AAM_B-03	11	419	0.025	0.000	0.000	0.005	91.606	0.002	0.023	0.212	0.014	0.011	3.603	0.000	1.037	96.538
AAM_B-04	12	420	0.011	0.000	0.000	0.000	90.748	0.038	0.032	0.151	0.007	0.000	2.918	0.000	0.840	94.744
AAM_B-04	12	421	0.045	0.012	0.000	0.015	91.553	0.031	0.029	0.155	0.009	0.000	3.142	0.000	0.905	95.897
AAM_B-04	12	422	0.010	0.036	0.000	0.017	93.019	0.011	0.031	0.974	0.065	0.000	3.046	0.000	0.877	98.085
AAM_B-04	12	423	0.056	0.000	0.011	0.013	96.969	0.016	0.060	1.236	0.084	0.000	3.047	0.000	0.877	102.368
AAM_B-05	13	424	0.008	0.000	0.000	0.001	90.292	0.000	0.047	0.117	0.013	0.003	3.164	0.000	0.911	94.558
AAM_B-05	13	425	0.004	0.006	0.009	0.001	90.941	0.006	0.029	0.103	0.002	0.003	3.065	0.000	0.882	95.051
AAM_E-01	16	428	0.027	0.032	0.000	0.008	91.729	0.005	0.029	0.221	0.015	0.000	3.756	0.000	1.021	96.970
AAM_E-01	16	429	0.071	0.009	0.015	0.014	91.363	0.000	0.096	0.227	0.013	0.000	3.567	0.000	1.027	96.341
AAM_E-02	17	430	0.072	0.022	0.000	0.008	93.546	0.000	0.041	0.276	0.011	0.010	3.301	0.000	0.950	96.235
AAM_E-02	17	431	0.029	0.022	0.000	0.007	92.130	0.000	0.030	0.401	0.029	0.000	3.167	0.000	0.912	95.727
AAM_E-03	18	432	0.041	0.000	0.002	0.013	91.470	0.012	0.028	0.443	0.022	0.000	3.718	0.000	1.070	96.819
AAM_E-03	18	433	0.038	0.000	0.005	0.000	93.403	0.031	0.046	1.102	0.047	0.003	2.787	0.000	0.802	98.266
AAM_E-04	19	434	0.013	0.015	0.000	0.007	93.364	0.019	0.035	0.229	0.007	0.006	3.662	0.000	1.054	98.411
AAM_E-04	19	435	0.116	0.023	0.000	0.012	91.610	0.023	0.030	0.362	0.016	0.000	3.513	0.000	1.011	96.717
AAM_E-05	20	437	0.045	0.002	0.000	0.004	92.229	0.000	0.035	0.359	0.018	0.000	3.543	0.000	1.020	97.254
AAM_S-01	21	438	0.075	0.000	0.026	0.014	87.249	0.030	0.098	0.331	0.022	0.000	3.140	0.000	0.934	91.830
AAM_S-01	21	439	0.042	0.000	0.008	0.007	84.022	0.012	0.040	0.271	0.017	0.000	2.819	0.000	0.812	88.049
AAM_S-02	22	440	0.038	0.024	0.016	0.005	88.666	0.004	0.047	0.203	0.012	0.003	3.201	0.000	0.921	93.141
AAM_S-02	22	441	0.105	0.000	0.000	0.031	82.860	0.000	0.041	0.295	0.015	0.007	2.749	0.000	0.791	86.835
AAM_S-03	23	442	0.214	0.000	0.000	0.026	77.664	0.000	0.052	0.385	0.030	0.003	2.413	0.000	0.635	81.421
AAM_S-03	23	443	0.187	0.000	0.000	0.026	61.106	0.000	0.049	0.342	0.029	0.000	1.715	0.000	0.494	63.966
AAM_S-04	24	444	0.112	0.010	0.000	0.013	82.287	0.003	0.037	0.963	0.051	0.002	2.739	0.000	0.788	87.007
AAM_S-04	24	445	0.140	0.000	0.000	0.013	91.370	0.009	0.041	0.314	0.021	0.000	3.488	0.000	1.004	96.400
AAM_S-05	25	446	0.039	0.000	0.002	0.007	70.090	0.003	0.033	0.217	0.009	0.000	2.886	0.000	0.831	74.107
AAM_S-05	25	447	0.114	0.006	0.007	0.014	53.462	0.002	0.029	0.530	0.035	0.002	2.008	0.000	0.578	56.807
		<i>Minimum</i>	0.004	0.000	0.000	0.000	53.462	0.000	0.012	0.103	0.002	0.000	1.715	0.000	0.494	56.807
		<i>Maximum</i>	0.214	0.038	0.026	0.031	96.969	0.038	0.060	1.236	0.084	0.011	3.756	0.000	1.081	102.368
		<i>Average</i>	0.059	0.008	0.003	0.010	87.497	0.011	0.035	0.396	0.023	0.002	3.130	0.000	0.901	92.076
		<i>Median</i>	0.042	0.000	0.000	0.008	90.984	0.006	0.035	0.314	0.017	0.000	3.167	0.000	0.912	95.785
		<i>Stan. Dev.</i>	0.051	0.011	0.006	0.007	9.364	0.011	0.010	0.280	0.017	0.003	0.464	0.000	0.134	9.830

In summary (all values in wt. %):

- SiO₂ ranged from 0.004% to 0.214% (average = 0.059%, median = 0.042%),
- TiO₂ ranged from 0.000% - 0.038% (average = 0.008%, median = 0.000%),
- PbO ranged from 0.000% - 0.026% (average = 0.003%, median = 0.000%),
- Al₂O₃ ranged from 0.000% - 0.031% (average = 0.010%, median = 0.008%),
- V₂O₅ ranged from 53.462% - 96.969% (average = 87.497%, median = 90.984%),
- Fe₂O₃ ranged from 0.000% - 0.038% (average = 0.011%, median = 0.006%),
- CaO ranged from 0.012% - 0.060% (average = 0.035%, median = 0.035%),
- Na₂O ranged from 0.103% - 1.236% (average = 0.396%, median = 0.314%),
- K₂O ranged from 0.002% - 0.084% (average = 0.023%, median = 0.017%),
- P₂O₅ ranged from 0.000% - 0.011% (average = 0.002%, median = 0.000%),
- N ranged from 1.715% - 3.756% (average = 3.130%, median = 3.167%),
- O was not identified during the analyses, and
- H ranged from 0.494% - 1.081% (average = 0.901%, median = 0.912%).

Stoichiometrically pure ammonium metavanadate has a chemical composition of NH₄VO₃. Therefore, stoichiometric calculations of Option A ammonium metavanadate were completed on the basis of 3 oxygens in the molecular formula.

Table 26 contains stoichiometric calculations of the composition of Option A ammonium metavanadate. The average chemical composition of Option A ammonium metavanadate from the 32 EMPA analyses was found to be N_{0.277}H_{1.109}V_{1.195}O₃, and the median chemical composition of Option A ammonium metavanadate was found to be N_{0.280}H_{1.120}V_{1.196}O₃. The presence of minor amounts of sodium in this material was observed. Relative to stoichiometric ammonium metavanadate, the Option A ammonium metavanadate appears to be deficient in both nitrogen and hydrogen. This will be discussed in the Discussion and Summary section.

Option A vanadium pentoxide was also morphologically and chemically evaluated via EMPA. Figure 18 illustrates the morphologies of these precipitates. Option A vanadium pentoxide occurs in four morphologies: 1) subhedral to euhedral columnar to tabular grains ranging from ~20µm-100µm in length and 15µm-40µm in width that commonly display two cleavages at 90°; 2) subhedral elongate or acicular particles ranging from ~30µm-150µm in length and ~25-35µm in width that also commonly display two cleavages at 90°; 3) elongate, porous aggregates up to ~120µm in length and ~20µ-30µm in width that comprise agglomerations of finer-grained tabular to acicular grains ranging from ~2-5µm in length and 1µm-3µm in width; and 4) anhedral to subhedral columnar to acicular grains that range from 5-25µm in length and up to 10µm in width (Fig. 18).

Table 26. Stoichiometric calculations for Option A ammonium metavanadate.

SAMPLE	FORMULA	BASIS	Si FORMULA	Ti FORMULA	Pb FORMULA	Al FORMULA	V FORMULA	Fe FORMULA	Ca FORMULA	Na FORMULA	K FORMULA	P FORMULA	N FORMULA	O FORMULA	H FORMULA
AAM_B-01	3	O	0.000	0.000	0.000	0.000	1.195	0.000	0.001	0.018	0.001	0.000	0.288	3.000	1.152
AAM_B-01	3	O	0.000	0.000	0.000	0.000	1.196	0.000	0.000	0.017	0.001	0.000	0.299	3.000	1.196
AAM_B-01	3	O	0.001	0.000	0.000	0.000	1.195	0.000	0.000	0.016	0.001	0.000	0.287	3.000	1.149
AAM_B-02	3	O	0.000	0.000	0.000	0.000	1.198	0.000	0.001	0.007	0.000	0.000	0.291	3.000	1.165
AAM_B-02	3	O	0.001	0.000	0.000	0.000	1.194	0.000	0.001	0.020	0.001	0.000	0.245	3.000	0.981
AAM_B-03	3	O	0.001	0.000	0.000	0.000	1.197	0.000	0.001	0.009	0.000	0.000	0.298	3.000	1.194
AAM_B-03	3	O	0.001	0.000	0.000	0.000	1.197	0.000	0.000	0.008	0.000	0.000	0.306	3.000	1.223
AAM_B-04	3	O	0.000	0.000	0.000	0.000	1.198	0.001	0.001	0.006	0.000	0.000	0.250	3.000	1.000
AAM_B-04	3	O	0.001	0.000	0.000	0.000	1.197	0.000	0.001	0.006	0.000	0.000	0.267	3.000	1.067
AAM_B-04	3	O	0.000	0.001	0.000	0.000	1.191	0.000	0.001	0.037	0.002	0.000	0.253	3.000	1.013
AAM_B-04	3	O	0.001	0.000	0.000	0.000	1.189	0.000	0.001	0.044	0.002	0.000	0.243	3.000	0.970
AAM_B-05	3	O	0.000	0.000	0.000	0.000	1.198	0.000	0.001	0.005	0.000	0.000	0.273	3.000	1.091
AAM_B-05	3	O	0.000	0.000	0.000	0.000	1.199	0.000	0.001	0.004	0.000	0.000	0.262	3.000	1.049
AAM_E-01	3	O	0.001	0.001	0.000	0.000	1.197	0.000	0.001	0.008	0.000	0.000	0.318	3.000	1.272
AAM_E-01	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.009	0.000	0.000	0.303	3.000	1.213
AAM_E-02	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.010	0.000	0.000	0.274	3.000	1.096
AAM_E-02	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.015	0.001	0.000	0.267	3.000	1.067
AAM_E-03	3	O	0.001	0.000	0.000	0.000	1.195	0.000	0.001	0.017	0.001	0.000	0.315	3.000	1.262
AAM_E-03	3	O	0.001	0.000	0.000	0.000	1.190	0.000	0.001	0.041	0.001	0.000	0.231	3.000	0.922
AAM_E-04	3	O	0.000	0.000	0.000	0.000	1.197	0.000	0.001	0.009	0.000	0.000	0.305	3.000	1.219
AAM_E-04	3	O	0.002	0.000	0.000	0.000	1.194	0.000	0.001	0.014	0.000	0.000	0.297	3.000	1.190
AAM_E-05	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.014	0.000	0.000	0.298	3.000	1.193
AAM_S-01	3	O	0.002	0.000	0.000	0.000	1.195	0.000	0.001	0.013	0.001	0.000	0.279	3.000	1.117
AAM_S-01	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.011	0.000	0.000	0.261	3.000	1.042
AAM_S-02	3	O	0.001	0.000	0.000	0.000	1.197	0.000	0.001	0.008	0.000	0.000	0.281	3.000	1.122
AAM_S-02	3	O	0.002	0.000	0.000	0.001	1.195	0.000	0.001	0.012	0.000	0.000	0.257	3.000	1.029
AAM_S-03	3	O	0.005	0.000	0.000	0.001	1.191	0.000	0.001	0.017	0.001	0.000	0.240	3.000	0.961
AAM_S-03	3	O	0.006	0.000	0.000	0.001	1.190	0.000	0.002	0.020	0.001	0.000	0.217	3.000	0.867
AAM_S-04	3	O	0.002	0.000	0.000	0.000	1.189	0.000	0.001	0.041	0.001	0.000	0.257	3.000	1.028
AAM_S-04	3	O	0.003	0.000	0.000	0.000	1.195	0.000	0.001	0.012	0.001	0.000	0.296	3.000	1.185
AAM_S-05	3	O	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.011	0.000	0.000	0.320	3.000	1.280
AAM_S-05	3	O	0.004	0.000	0.000	0.001	1.188	0.001	0.001	0.035	0.002	0.000	0.290	3.000	1.159
		<i>Minimum</i>	0.000	0.000	0.000	0.000	1.188	0.000	0.000	0.004	0.000	0.000	0.217	3.000	0.867
		<i>Maximum</i>	0.006	0.001	0.000	0.001	1.199	0.001	0.002	0.044	0.002	0.000	0.320	3.000	1.280
		<i>Average</i>	0.001	0.000	0.000	0.000	1.195	0.000	0.001	0.016	0.001	0.000	0.277	3.000	1.109
		<i>Median</i>	0.001	0.000	0.000	0.000	1.196	0.000	0.001	0.013	0.000	0.000	0.280	3.000	1.120
		<i>Stan. Dev.</i>	0.001	0.000	0.000	0.000	0.003	0.000	0.000	0.011	0.000	0.000	0.026	0.000	0.105

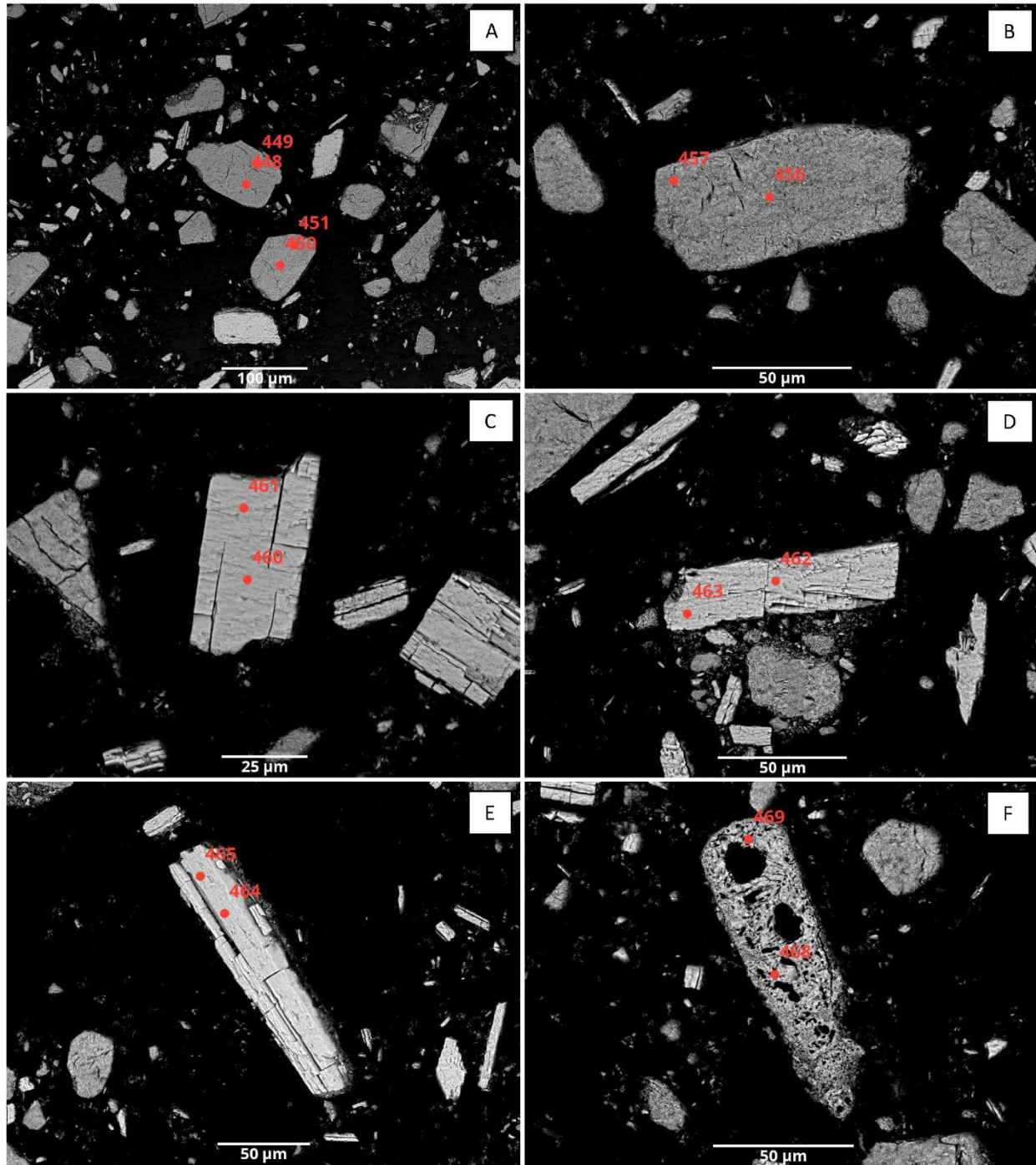


Figure 18. Electron microprobe backscatter images showing morphologies of Option A vanadium pentoxide. Bar scales for each image are in micrometers (μm). Red numbers and circles in images are EMPA analysis locations.

Twenty-four chemical analyses of Option A vanadium pentoxide obtained via EMPA are contained in Table 27. For the 24 analyses performed, analytical totals ranged from 36.696% to 99.522.368%, with average and median analytical totals being 84.705% and 86.607%, respectively.

Table 27. EMPA chemical analysis of Option A vanadium pentoxide.

SAMPLE	NUMBER	LINE	SiO2	TiO2	PbO	Al2O3	V2O5	FeO	CaO	Na2O	K2O	P2O5	N	O	H2O	TOTAL
AVP_B-01	26	448	0.142	0.001	0.018	0.016	84.162	0.027	0.019	0.039	0.016	0.006	0.729	0.000	0.000	85.175
AVP_B-01	26	449	0.441	0.011	0.029	0.033	84.353	0.014	0.035	0.069	0.014	0.000	0.460	0.000	0.000	85.458
AVP_B-02	27	450	0.223	0.000	0.000	0.017	84.057	0.002	0.035	0.072	0.012	0.005	0.508	0.000	0.000	84.932
AVP_B-02	27	451	0.232	0.002	0.002	0.026	82.829	0.033	0.029	0.074	0.011	0.000	0.587	0.000	0.000	83.824
AVP_B-03	28	452	0.474	0.000	0.000	0.051	85.514	0.007	0.027	0.065	0.016	0.003	0.589	0.000	0.000	86.745
AVP_B-03	28	453	0.163	0.000	0.000	0.022	87.232	0.005	0.032	0.063	0.017	0.004	0.663	0.000	0.000	88.202
AVP_B-04	29	454	0.287	0.000	0.000	0.014	85.542	0.009	0.033	0.074	0.012	0.000	0.499	0.000	0.000	86.469
AVP_B-04	29	455	0.530	0.000	0.000	0.055	40.738	0.031	0.044	0.051	0.017	0.000	0.401	0.000	0.000	41.866
AVP_B-05	30	456	0.432	0.000	0.015	0.034	82.297	0.000	0.031	0.081	0.013	0.000	0.458	0.000	0.000	83.362
AVP_B-05	30	457	0.328	0.000	0.030	0.034	85.200	0.000	0.038	0.072	0.012	0.002	0.379	0.000	0.000	86.095
AVP_E-01	31	458	1.405	0.108	0.000	0.263	94.482	0.018	0.032	0.086	0.028	0.000	0.121	0.000	0.000	96.543
AVP_E-01	31	459	1.852	0.064	0.000	0.274	72.294	0.034	0.062	0.065	0.037	0.002	0.281	0.000	0.000	74.966
AVP_E-02	32	460	1.518	0.111	0.000	0.242	97.309	0.000	0.028	0.041	0.012	0.000	0.054	0.000	0.000	99.316
AVP_E-02	32	461	1.518	0.132	0.000	0.223	91.577	0.052	0.043	0.040	0.012	0.006	0.070	0.000	0.000	93.672
AVP_E-03	33	462	3.236	0.005	0.010	0.184	92.672	0.018	0.076	0.106	0.226	0.000	0.110	0.000	0.000	96.643
AVP_E-03	33	463	1.468	0.074	0.000	0.235	85.857	0.013	0.051	0.081	0.096	0.012	0.165	0.000	0.000	88.050
AVP_E-04	34	464	1.951	0.088	0.000	0.368	96.922	0.026	0.039	0.043	0.014	0.008	0.062	0.000	0.000	99.522
AVP_E-04	34	465	1.749	0.067	0.000	0.323	96.415	0.026	0.031	0.027	0.015	0.007	0.000	0.000	0.000	98.660
AVP_E-05	35	466	2.630	0.073	0.000	0.348	90.478	0.028	0.065	0.074	0.023	0.000	0.000	0.000	0.000	93.719
AVP_E-05	35	467	1.874	0.087	0.000	0.322	94.517	0.008	0.033	0.095	0.018	0.000	0.104	0.000	0.000	97.060
AVP_S-01	36	468	0.291	0.000	0.000	0.031	87.643	0.007	0.039	0.078	0.009	0.012	0.238	0.000	0.000	88.347
AVP_S-01	36	469	0.448	0.011	0.003	0.030	70.686	0.014	0.040	0.048	0.006	0.006	0.644	0.000	0.000	71.937
AVP_S-02	37	470	0.598	0.000	0.011	0.042	35.248	0.023	0.045	0.038	0.006	0.000	0.684	0.000	0.000	36.696
AVP_S-02	37	471	0.369	0.000	0.002	0.034	84.728	0.004	0.036	0.090	0.012	0.007	0.381	0.000	0.000	85.663
		<i>Minimum</i>	0.142	0.000	0.000	0.014	35.248	0.000	0.019	0.027	0.006	0.000	0.000	0.000	0.000	36.696
		<i>Maximum</i>	3.236	0.132	0.030	0.368	97.309	0.052	0.076	0.106	0.226	0.012	0.729	0.000	0.000	99.522
		<i>Average</i>	1.007	0.035	0.005	0.134	83.031	0.017	0.039	0.066	0.027	0.003	0.341	0.000	0.000	84.705
		<i>Median</i>	0.502	0.004	0.000	0.046	85.528	0.014	0.036	0.071	0.014	0.002	0.380	0.000	0.000	86.607
		<i>Stan. Dev.</i>	0.857	0.044	0.009	0.127	15.099	0.013	0.013	0.020	0.045	0.004	0.236	0.000	0.000	15.374

In summary (all values in wt. %):

- SiO₂ ranged from 0.142% to 3.236% (average = 1.007%, median = 0.502%),
- TiO₂ ranged from 0.000% - 0.132% (average = 0.035%, median = 0.004%),
- PbO ranged from 0.000% - 0.030% (average = 0.005%, median = 0.000%),
- Al₂O₃ ranged from 0.014% - 0.368% (average = 0.134%, median = 0.046%),
- V₂O₅ ranged from 35.248% - 97.309% (average = 83.031%, median = 85.528%),
- FeO ranged from 0.000% - 0.052% (average = 0.017%, median = 0.014%),
- CaO ranged from 0.019% - 0.076% (average = 0.039%, median = 0.036%),
- Na₂O ranged from 0.027% - 0.106% (average = 0.066%, median = 0.071%),
- K₂O ranged from 0.006% - 0.226% (average = 0.027%, median = 0.014%),
- P₂O₅ ranged from 0.000% - 0.012% (average = 0.003%, median = 0.002%),
- N ranged from 0.000% - 0.729% (average=0.341%, median = 0.380%),
- O was not identified during the analyses, and
- H₂O was not identified during the analysis.

Stoichiometrically pure vanadium pentoxide has a chemical composition of V₂O₅. Therefore, stoichiometric calculations of Option A vanadium pentoxide were completed on the basis of the presence of five oxygens in the molecular formula.

Table 28 contains stoichiometric calculations of the composition of Option A vanadium pentoxide. The average chemical composition of Option A vanadium pentoxide from the 24 EMPA analyses was found to be V_{1.966}O₅, and the median chemical composition of Option A vanadium pentoxide was found to be V_{1.972}O₅. Minor amounts of Si, Al, Na, and N in this material were also observed. Based on these results, nearly stoichiometric vanadium pentoxide was produced using processing Option A, although trace amounts of Option A ammonium metavanadate may also be indicated by the presence of minor amounts of nitrogen.

Figure 19 illustrates the appearance of Option B ammonium metavanadate that was morphologically and chemically evaluated using EMPA. Option B ammonium metavanadate primarily occurs as rounded to oval aggregates ~30µm-125µm in diameter that comprise one or more rounded to sub-rounded agglomerations ranging from ~20µm-50µm in diameter. These smaller agglomerations are composed of semi-radially to radially-oriented acicular to columnar particles that range from ~3µm-20µm in length and 2µm-10µm in width (Fig. 19).

Table 28. Stoichiometric calculations for Option A vanadium pentoxide.

SAMPLE	FORMULA	BASIS	Si FORMULA	Ti FORMULA	Pb FORMULA	Al FORMULA	V FORMULA	Fe FORMULA	Ca FORMULA	Na FORMULA	K FORMULA	P FORMULA	N FORMULA	O FORMULA	H FORMULA
AVP_B-01	5	O	0.005	0.000	0.000	0.001	1.994	0.001	0.001	0.003	0.001	0.000	0.112	5.000	0.000
AVP_B-01	5	O	0.016	0.000	0.000	0.001	1.985	0.000	0.001	0.005	0.001	0.000	0.070	5.000	0.000
AVP_B-02	5	O	0.008	0.000	0.000	0.001	1.991	0.000	0.001	0.005	0.001	0.000	0.078	5.000	0.000
AVP_B-02	5	O	0.008	0.000	0.000	0.001	1.991	0.001	0.001	0.005	0.001	0.000	0.092	5.000	0.000
AVP_B-03	5	O	0.017	0.000	0.000	0.002	1.984	0.000	0.001	0.004	0.001	0.000	0.089	5.000	0.000
AVP_B-03	5	O	0.006	0.000	0.000	0.001	1.993	0.000	0.001	0.004	0.001	0.000	0.098	5.000	0.000
AVP_B-04	5	O	0.010	0.000	0.000	0.001	1.990	0.000	0.001	0.005	0.001	0.000	0.075	5.000	0.000
AVP_B-04	5	O	0.039	0.000	0.000	0.005	1.962	0.002	0.003	0.007	0.002	0.000	0.125	5.000	0.000
AVP_B-05	5	O	0.016	0.000	0.000	0.001	1.985	0.000	0.001	0.006	0.001	0.000	0.072	5.000	0.000
AVP_B-05	5	O	0.012	0.000	0.000	0.001	1.988	0.000	0.001	0.005	0.001	0.000	0.057	5.000	0.000
AVP_E-01	5	O	0.044	0.003	0.000	0.010	1.955	0.000	0.001	0.005	0.001	0.000	0.016	5.000	0.000
AVP_E-01	5	O	0.075	0.002	0.000	0.013	1.928	0.001	0.003	0.005	0.002	0.000	0.049	5.000	0.000
AVP_E-02	5	O	0.046	0.003	0.000	0.009	1.955	0.000	0.001	0.002	0.000	0.000	0.007	5.000	0.000
AVP_E-02	5	O	0.049	0.003	0.000	0.008	1.951	0.001	0.001	0.002	0.000	0.000	0.010	5.000	0.000
AVP_E-03	5	O	0.101	0.000	0.000	0.007	1.911	0.000	0.003	0.006	0.009	0.000	0.015	5.000	0.000
AVP_E-03	5	O	0.050	0.002	0.000	0.009	1.949	0.000	0.002	0.005	0.004	0.000	0.024	5.000	0.000
AVP_E-04	5	O	0.059	0.002	0.000	0.013	1.942	0.001	0.001	0.003	0.001	0.000	0.008	5.000	0.000
AVP_E-04	5	O	0.053	0.002	0.000	0.012	1.948	0.001	0.001	0.002	0.001	0.000	0.000	5.000	0.000
AVP_E-05	5	O	0.084	0.002	0.000	0.013	1.921	0.001	0.002	0.005	0.001	0.000	0.000	5.000	0.000
AVP_E-05	5	O	0.058	0.002	0.000	0.012	1.943	0.000	0.001	0.006	0.001	0.000	0.014	5.000	0.000
AVP_S-01	5	O	0.010	0.000	0.000	0.001	1.989	0.000	0.001	0.005	0.000	0.000	0.035	5.000	0.000
AVP_S-01	5	O	0.019	0.000	0.000	0.002	1.982	0.000	0.002	0.004	0.000	0.000	0.117	5.000	0.000
AVP_S-02	5	O	0.050	0.000	0.000	0.004	1.954	0.002	0.004	0.006	0.001	0.000	0.246	5.000	0.000
AVP_S-02	5	O	0.013	0.000	0.000	0.001	1.987	0.000	0.001	0.006	0.001	0.000	0.058	5.000	0.000
		<i>Minimum</i>	<i>0.005</i>	<i>0.000</i>	<i>0.000</i>	<i>0.001</i>	<i>1.911</i>	<i>0.000</i>	<i>0.001</i>	<i>0.002</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>	<i>5.000</i>	<i>0.000</i>
		<i>Maximum</i>	<i>0.101</i>	<i>0.003</i>	<i>0.000</i>	<i>0.013</i>	<i>1.994</i>	<i>0.002</i>	<i>0.004</i>	<i>0.007</i>	<i>0.009</i>	<i>0.000</i>	<i>0.246</i>	<i>5.000</i>	<i>0.000</i>
		<i>Average</i>	<i>0.035</i>	<i>0.001</i>	<i>0.000</i>	<i>0.005</i>	<i>1.966</i>	<i>0.001</i>	<i>0.002</i>	<i>0.005</i>	<i>0.001</i>	<i>0.000</i>	<i>0.061</i>	<i>5.000</i>	<i>0.000</i>
		<i>Median</i>	<i>0.029</i>	<i>0.000</i>	<i>0.000</i>	<i>0.003</i>	<i>1.972</i>	<i>0.000</i>	<i>0.001</i>	<i>0.005</i>	<i>0.001</i>	<i>0.000</i>	<i>0.058</i>	<i>5.000</i>	<i>0.000</i>
		<i>Stan. Dev.</i>	<i>0.027</i>	<i>0.001</i>	<i>0.000</i>	<i>0.005</i>	<i>0.025</i>	<i>0.001</i>	<i>0.001</i>	<i>0.001</i>	<i>0.002</i>	<i>0.000</i>	<i>0.055</i>	<i>0.000</i>	<i>0.000</i>

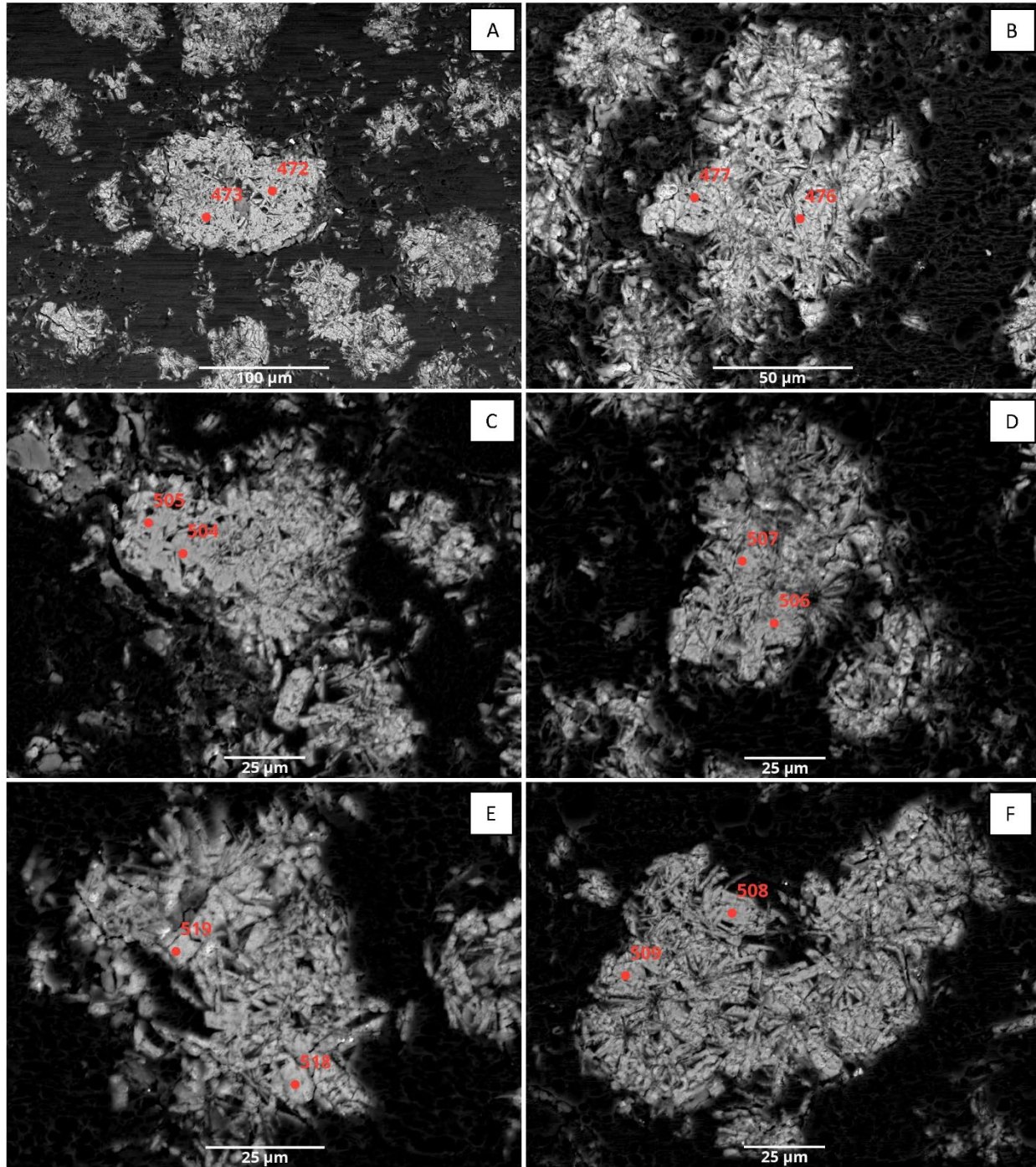


Figure 19. Electron microprobe backscatter images showing morphologies of Option B ammonium metavanadate. Bar scales for each image are in micrometers (μm). Red numbers and circles in images are EMPA analysis locations.

Thirty-two chemical analyses of Option B ammonium metavanadate obtained via EMPA are contained in Table 29. For the 32 analyses performed, analytical totals ranged from 70.393% to 101.732%, with average and median analytical totals being 91.676% and 93.984%, respectively.

Table 29. EMPA chemical analysis of Option B ammonium metavanadate.

SAMPLE	NUMBER	LINE	SiO2	TiO2	PbO	Al2O3	V2O5	Fe2O3	CaO	Na2O	K2O	P2O5	N	O	H	TOTAL
BAM_A-01	38	472	2.245	0.002	0.000	0.359	72.065	0.047	0.050	0.089	0.006	0.000	6.285	0.000	1.809	82.958
BAM_A-01	38	473	0.403	0.000	0.000	0.045	82.286	0.045	0.032	0.083	0.005	0.000	8.535	0.000	2.474	93.968
BAM_A-02	39	474	0.780	0.003	0.000	0.097	82.170	0.035	0.055	0.181	0.015	0.000	8.545	0.000	2.460	94.340
BAM_A-02	39	475	0.937	0.000	0.006	0.110	71.671	0.039	0.053	0.144	0.007	0.008	6.649	0.000	1.914	81.539
BAM_A-03	40	476	0.629	0.002	0.002	0.092	73.750	0.078	0.040	0.334	0.019	0.022	6.204	0.000	1.786	82.958
BAM_A-03	40	477	2.872	0.000	0.000	0.411	81.636	0.048	0.093	0.213	0.021	0.005	7.533	0.000	2.169	95.001
BAM_A-04	41	478	1.616	0.000	0.000	0.169	82.422	0.000	0.060	0.147	0.011	0.008	7.430	0.000	2.139	94.000
BAM_A-04	41	479	6.437	0.008	0.000	0.826	69.074	0.058	0.096	0.290	0.017	0.001	5.411	0.000	1.557	83.774
BAM_A-05	42	480	0.258	0.000	0.021	0.022	76.783	0.017	0.043	0.324	0.017	0.000	8.545	0.000	2.460	88.489
BAM_A-05	42	481	0.467	0.000	0.000	0.063	80.980	0.181	0.049	0.354	0.022	0.014	6.665	0.000	1.919	90.713
BAM_A-06	54	504	0.066	0.000	0.000	0.005	82.660	0.061	0.027	0.051	0.004	0.000	10.684	0.000	3.075	96.634
BAM_A-06	54	505	0.127	0.000	0.000	0.015	83.384	0.015	0.032	0.153	0.001	0.011	10.251	0.000	2.951	96.940
BAM_A-07	55	506	0.147	0.000	0.008	0.015	82.743	0.034	0.018	0.013	0.001	0.000	9.486	0.000	2.731	95.196
BAM_A-07	55	507	0.346	0.001	0.000	0.048	88.525	0.055	0.036	0.035	0.004	0.000	6.799	0.000	1.957	97.806
BAM_A-08	56	508	0.091	0.000	0.000	0.016	84.198	0.066	0.016	0.009	0.002	0.005	10.907	0.000	3.140	98.450
BAM_A-08	56	509	0.213	0.000	0.000	0.024	83.876	0.061	0.018	0.009	0.008	0.000	9.660	0.000	2.781	96.648
BAM_A-09	57	510	0.307	0.000	0.000	0.036	82.937	0.092	0.027	0.019	0.005	0.000	9.309	0.000	2.680	95.412
BAM_A-09	57	511	0.469	0.000	0.000	0.032	85.791	0.043	0.041	0.188	0.019	0.000	7.954	0.000	2.290	96.827
BAM_A-10	58	512	0.641	0.011	0.000	0.061	78.374	0.080	0.050	0.050	0.004	0.007	8.097	0.000	2.331	89.707
BAM_A-10	58	513	0.169	0.000	0.001	0.016	81.928	0.042	0.029	0.033	0.004	0.007	11.159	0.000	3.212	96.600
BAM_A-10	58	514	0.519	0.000	0.000	0.058	89.671	0.196	0.050	0.079	0.009	0.006	8.653	0.000	2.491	101.732
BAM_A-11	59	515	0.501	0.015	0.000	0.064	80.238	0.151	0.042	0.665	0.028	0.000	9.433	0.000	2.715	93.853
BAM_A-11	59	516	0.569	0.018	0.000	0.060	79.404	0.064	0.047	1.349	0.033	0.000	7.927	0.000	2.282	91.754
BAM_A-12	60	517	0.409	0.000	0.006	0.073	81.623	0.337	0.040	0.762	0.090	0.000	10.316	0.000	2.970	96.625
BAM_A-13	61	518	0.450	0.000	0.000	0.062	83.457	0.065	0.031	0.056	0.007	0.000	8.894	0.000	2.560	95.582
BAM_A-13	61	519	1.418	0.000	0.011	0.151	80.651	0.116	0.056	0.106	0.007	0.000	8.013	0.000	2.307	92.837
BAM_A-14	62	520	0.652	0.000	0.008	0.103	81.835	0.155	0.035	0.329	0.033	0.000	11.933	0.000	3.435	98.517
BAM_A-14	62	521	0.744	0.008	0.000	0.103	71.614	0.111	0.028	0.066	0.011	0.000	8.122	0.000	2.338	83.145
BAM_A-14	62	522	0.411	0.000	0.010	0.037	62.364	0.017	0.022	0.034	0.004	0.000	5.819	0.000	1.675	70.393
BAM_A-14	62	523	2.395	0.000	0.000	0.370	76.433	3.691	0.046	0.075	0.015	0.006	6.610	0.000	1.903	91.543
BAM_A-15	63	524	0.328	0.000	0.000	0.033	72.706	0.083	0.061	0.025	0.003	0.016	8.375	0.000	2.411	84.040
BAM_A-15	63	525	0.796	0.007	0.000	0.088	74.859	0.324	0.060	0.169	0.016	0.003	7.255	0.000	2.088	85.664
		<i>Minimum</i>	0.066	0.000	0.000	0.005	62.364	0.000	0.016	0.009	0.001	0.000	5.411	0.000	1.557	70.393
		<i>Maximum</i>	6.437	0.018	0.021	0.826	89.671	3.691	0.096	1.349	0.090	0.022	11.933	0.000	3.435	101.732
		<i>Average</i>	0.888	0.002	0.002	0.114	79.441	0.200	0.043	0.201	0.014	0.004	8.360	0.000	2.406	91.676
		<i>Median</i>	0.485	0.000	0.000	0.061	81.629	0.063	0.042	0.097	0.008	0.000	8.249	0.000	2.374	93.984
		<i>Stan. Dev.</i>	1.202	0.005	0.005	0.163	5.800	0.632	0.018	0.271	0.016	0.005	1.622	0.000	0.467	6.644

In summary (all values in wt. %):

- SiO₂ ranged from 0.066% to 6.437% (average = 0.888%, median = 0.485%),
- TiO₂ ranged from 0.000% - 0.018% (average = 0.002%, median = 0.000%),
- PbO ranged from 0.000% - 0.021% (average = 0.002%, median = 0.000%),
- Al₂O₃ ranged from 0.005% - 0.826% (average = 0.114%, median = 0.061%),
- V₂O₅ ranged from 62.364% - 89.671% (average = 79.441%, median = 81.629%),
- Fe₂O₃ ranged from 0.000% - 3.691% (average = 0.200%, median = 0.063%),
- CaO ranged from 0.016% - 0.096% (average = 0.043%, median = 0.042%),
- Na₂O ranged from 0.009% - 1.349% (average = 0.201%, median = 0.097%),
- K₂O ranged from 0.001% - 0.090% (average = 0.014%, median = 0.008%),
- P₂O₅ ranged from 0.000% - 0.022% (average = 0.004%, median = 0.000%),
- N ranged from 5.411% - 11.933% (average = 8.360%, median = 8.249%),
- O was not identified during the analyses, and
- H ranged from 1.557% - 3.435% (average = 2.406%, median = 2.374%).

Stoichiometrically pure ammonium metavanadate has a chemical composition of NH₄VO₃. Therefore, stoichiometric calculations of Option B ammonium metavanadate were completed on the basis of three oxygens in the molecular formula.

Table 30 contains stoichiometric calculations of the composition of Option B ammonium metavanadate. The average chemical composition of Option B ammonium metavanadate from the 32 EMPA analyses was found to be N_{0.721}H_{2.884}V_{1.119}O₃, and the median chemical composition of Option B ammonium metavanadate was found to be N_{0.698}H_{2.793}V_{1.183}O₃. The presence of trace amounts of sodium, aluminum, and iron were also observed. Relative to stoichiometric ammonium metavanadate, the Option B ammonium metavanadate appears to be deficient in both nitrogen and hydrogen. This will be discussed in the Discussion and Summary section.

Option B vanadium pentoxide was also morphologically and chemically evaluated via EMPA. Figure 20 illustrates the morphologies of these precipitates. Option B vanadium pentoxide occurs in two primary morphologies: 1) blocky subhedral columnar particles ranging from ~40µm-75µm in length and 25µm-50µm in width that commonly display two cleavages at 90°; and 2) subhedral elongate or acicular particles ranging from ~10µm-80µm in length and ~2µm-25µm in width that locally display two cleavages at 90°. Locally, bent subhedral elongate or acicular particles are observed.

Table 30. Stoichiometric calculations for Option B ammonium metavanadate.

SAMPLE	FORMULA	BASIS	Si FORMULA	Ti FORMULA	Pb FORMULA	Al FORMULA	V FORMULA	Fe FORMULA	Ca FORMULA	Na FORMULA	K FORMULA	P FORMULA	N FORMULA	O FORMULA	H FORMULA
BAM_A-01	3	O	0.045	0.000	0.000	0.009	0.964	0.001	0.001	0.003	0.000	0.000	0.546	3.000	2.183
BAM_A-01	3	O	0.007	0.000	0.000	0.001	0.994	0.001	0.001	0.003	0.000	0.000	0.674	3.000	2.695
BAM_A-02	3	O	0.014	0.000	0.000	0.002	0.988	0.000	0.001	0.006	0.000	0.000	0.667	3.000	2.667
BAM_A-02	3	O	0.019	0.000	0.000	0.003	0.984	0.001	0.001	0.006	0.000	0.000	0.593	3.000	2.370
BAM_A-03	3	O	0.013	0.000	0.000	0.002	0.987	0.001	0.001	0.013	0.001	0.000	0.539	3.000	2.156
BAM_A-03	3	O	0.051	0.000	0.000	0.009	0.959	0.001	0.002	0.007	0.000	0.000	0.575	3.000	2.299
BAM_A-04	3	O	0.029	0.000	0.000	0.004	0.978	0.000	0.001	0.005	0.000	0.000	0.572	3.000	2.288
BAM_A-04	3	O	0.127	0.000	0.000	0.019	0.902	0.001	0.002	0.011	0.000	0.000	0.459	3.000	1.835
BAM_A-05	3	O	0.005	0.000	0.000	0.001	0.994	0.000	0.001	0.012	0.000	0.000	0.718	3.000	2.872
BAM_A-05	3	O	0.009	0.000	0.000	0.001	0.990	0.003	0.001	0.013	0.001	0.000	0.529	3.000	2.115
BAM_A-06	3	O	0.001	0.000	0.000	0.000	1.198	0.001	0.001	0.002	0.000	0.000	0.924	3.000	3.694
BAM_A-06	3	O	0.003	0.000	0.000	0.000	1.196	0.000	0.001	0.006	0.000	0.000	0.877	3.000	3.509
BAM_A-07	3	O	0.003	0.000	0.000	0.000	1.197	0.001	0.000	0.001	0.000	0.000	0.819	3.000	3.275
BAM_A-07	3	O	0.006	0.000	0.000	0.001	1.193	0.001	0.001	0.001	0.000	0.000	0.547	3.000	2.187
BAM_A-08	3	O	0.002	0.000	0.000	0.000	1.197	0.001	0.000	0.000	0.000	0.000	0.926	3.000	3.702
BAM_A-08	3	O	0.004	0.000	0.000	0.001	1.195	0.001	0.000	0.000	0.000	0.000	0.821	3.000	3.286
BAM_A-09	3	O	0.006	0.000	0.000	0.001	1.193	0.001	0.001	0.001	0.000	0.000	0.799	3.000	3.197
BAM_A-09	3	O	0.009	0.000	0.000	0.001	1.190	0.001	0.001	0.007	0.000	0.000	0.658	3.000	2.633
BAM_A-10	3	O	0.013	0.000	0.000	0.002	1.186	0.001	0.001	0.002	0.000	0.000	0.731	3.000	2.925
BAM_A-10	3	O	0.003	0.000	0.000	0.000	1.196	0.001	0.001	0.001	0.000	0.000	0.972	3.000	3.888
BAM_A-10	3	O	0.010	0.000	0.000	0.001	1.189	0.003	0.001	0.003	0.000	0.000	0.685	3.000	2.738
BAM_A-11	3	O	0.010	0.000	0.000	0.002	1.183	0.002	0.001	0.026	0.001	0.000	0.830	3.000	3.321
BAM_A-11	3	O	0.012	0.000	0.000	0.001	1.178	0.001	0.001	0.054	0.001	0.000	0.701	3.000	2.806
BAM_A-12	3	O	0.008	0.000	0.000	0.002	1.183	0.005	0.001	0.030	0.002	0.000	0.892	3.000	3.567
BAM_A-13	3	O	0.009	0.000	0.000	0.001	1.191	0.001	0.001	0.002	0.000	0.000	0.757	3.000	3.028
BAM_A-13	3	O	0.029	0.000	0.000	0.004	1.172	0.002	0.001	0.004	0.000	0.000	0.695	3.000	2.780
BAM_A-14	3	O	0.013	0.000	0.000	0.002	1.184	0.002	0.001	0.013	0.001	0.000	1.030	3.000	4.119
BAM_A-14	3	O	0.017	0.000	0.000	0.003	1.182	0.002	0.001	0.003	0.000	0.000	0.800	3.000	3.201
BAM_A-14	3	O	0.011	0.000	0.000	0.001	1.190	0.000	0.001	0.002	0.000	0.000	0.662	3.000	2.649
BAM_A-14	3	O	0.049	0.000	0.000	0.009	1.120	0.057	0.001	0.003	0.000	0.000	0.578	3.000	2.312
BAM_A-15	3	O	0.007	0.000	0.000	0.001	1.191	0.001	0.001	0.001	0.000	0.000	0.819	3.000	3.276
BAM_A-15	3	O	0.017	0.000	0.000	0.002	1.179	0.005	0.001	0.007	0.000	0.000	0.682	3.000	2.728
		<i>Minimum</i>	0.001	0.000	0.000	0.000	0.902	0.000	0.000	0.000	0.000	0.000	0.459	3.000	1.835
		<i>Maximum</i>	0.127	0.000	0.000	0.019	1.198	0.057	0.002	0.054	0.002	0.000	1.030	3.000	4.119
		<i>Average</i>	0.018	0.000	0.000	0.003	1.119	0.003	0.001	0.008	0.000	0.000	0.721	3.000	2.884
		<i>Median</i>	0.010	0.000	0.000	0.001	1.183	0.001	0.001	0.004	0.000	0.000	0.698	3.000	2.793
		<i>Stan. Dev.</i>	0.024	0.000	0.000	0.004	0.100	0.010	0.000	0.011	0.000	0.000	0.142	0.000	0.569

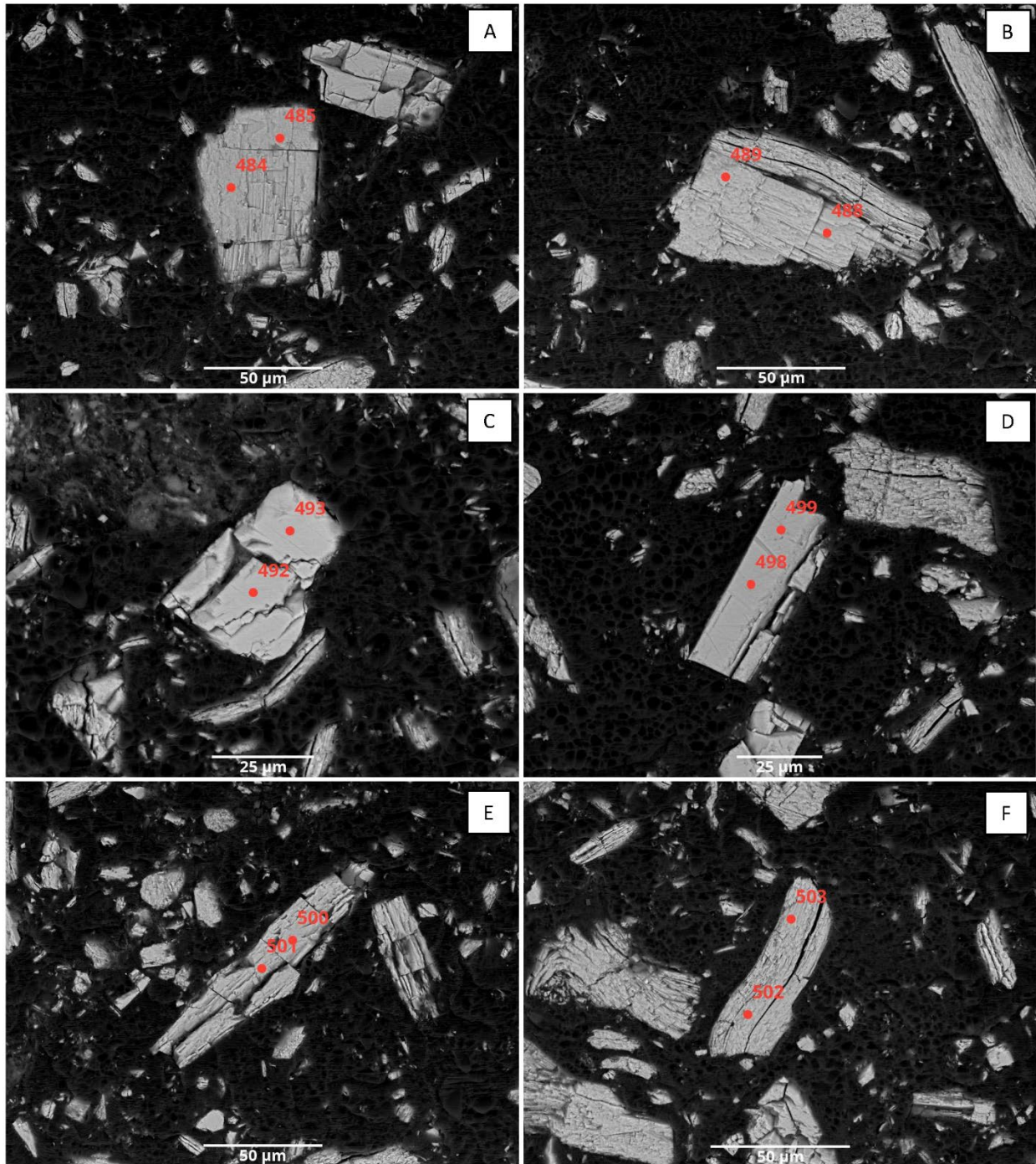


Figure 20. Electron microprobe backscatter images showing morphologies of Option B vanadium pentoxide. Bar scales for each image are in micrometers (μm). Red numbers and circles in images are EMPA analysis locations.

Twenty chemical analyses of Option B vanadium pentoxide obtained via EMPA are contained in Table 31. For the 20 analyses performed, analytical totals ranged from 92.024% to 107.851%, with average and median analytical totals being 99.513% and 99.027%, respectively.

Table 31. EMPA chemical analysis of Option B vanadium pentoxide.

SAMPLE	NUMBER	LINE	SiO2	TiO2	PbO	Al2O3	V2O5	Fe2O3	CaO	Na2O	K2O	P2O5	N	O	H	TOTAL
BVP_B-01	44	484	0.040	0.000	0.000	0.001	100.175	0.000	0.024	0.294	0.003	0.000	0.010	0.000	0.000	100.547
BVP_B-01	44	485	0.268	0.004	0.055	0.022	99.388	0.000	0.034	0.283	0.008	0.000	0.000	0.000	0.000	100.063
BVP_B-02	45	486	2.252	0.019	0.000	4.184	89.169	0.142	0.098	3.354	1.310	0.027	0.000	0.000	0.000	100.554
BVP_B-02	45	487	2.264	0.080	0.009	2.758	89.861	0.199	0.081	3.663	0.569	0.019	0.025	0.000	0.000	99.529
BVP_B-03	46	488	0.059	0.011	0.000	0.019	98.118	0.014	0.053	0.283	0.012	0.004	0.048	0.000	0.000	98.621
BVP_B-03	46	489	0.026	0.018	0.000	0.008	98.609	0.000	0.035	0.245	0.004	0.000	0.065	0.000	0.000	99.009
BVP_B-04	47	490	0.346	0.000	0.000	0.034	89.262	0.011	0.033	2.282	0.023	0.009	0.024	0.000	0.000	92.024
BVP_B-04	47	491	0.232	0.000	0.012	0.016	94.108	0.000	0.035	1.994	0.049	0.000	0.000	0.000	0.000	96.445
BVP_B-05	48	492	0.479	0.015	0.000	0.033	105.360	0.040	0.039	0.003	0.000	0.005	0.000	0.000	0.000	105.973
BVP_B-05	48	493	0.013	0.030	0.005	0.008	107.752	0.031	0.007	0.000	0.005	0.000	0.000	0.000	0.000	107.851
BVP_E-01	49	494	1.376	0.018	0.000	0.234	94.961	0.021	0.076	0.292	0.021	0.003	0.159	0.000	0.000	97.160
BVP_E-01	49	495	1.124	0.025	0.000	0.121	96.577	0.015	0.055	0.262	0.014	0.013	0.113	0.000	0.000	98.318
BVP_E-02	50	496	3.837	0.000	0.002	0.263	93.047	0.016	0.111	0.339	0.029	0.005	0.001	0.000	0.000	97.650
BVP_E-02	50	497	2.904	0.051	0.000	0.184	94.763	0.030	0.100	0.310	0.025	0.010	0.084	0.000	0.000	98.460
BVP_E-03	51	498	0.026	0.001	0.000	0.013	100.066	0.019	0.025	1.800	0.007	0.000	0.000	0.000	0.000	101.958
BVP_E-03	51	499	0.048	0.007	0.000	0.018	100.154	0.000	0.029	1.919	0.019	0.000	0.000	0.000	0.000	102.194
BVP_E-04	52	500	0.107	0.001	0.000	0.030	95.257	0.010	0.032	3.734	0.014	0.000	0.000	0.000	0.000	99.184
BVP_E-04	52	501	1.766	0.000	0.000	0.102	92.176	0.003	0.059	3.198	0.014	0.010	0.000	0.000	0.000	97.327
BVP_E-05	53	502	0.102	0.003	0.000	0.020	99.128	0.022	0.038	0.214	0.008	0.000	0.067	0.000	0.000	99.603
BVP_E-05	53	503	0.496	0.024	0.008	0.046	96.849	0.030	0.061	0.269	0.014	0.000	0.000	0.000	0.000	97.797
		Minimum	0.013	0.000	0.000	0.001	89.169	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	92.024
		Maximum	3.837	0.080	0.055	4.184	107.752	0.199	0.111	3.734	1.310	0.027	0.159	0.000	0.000	107.851
		Average	0.888	0.015	0.005	0.406	96.739	0.030	0.051	1.237	0.107	0.005	0.030	0.000	0.000	99.513
		Median	0.307	0.009	0.000	0.031	96.713	0.015	0.039	0.302	0.014	0.001	0.000	0.000	0.000	99.097
		Stan. Dev.	1.109	0.020	0.012	1.049	4.793	0.049	0.028	1.325	0.301	0.007	0.045	0.000	0.000	3.262

In summary (all values in wt. %):

- SiO_2 ranged from 0.013% to 3.837% (average = 0.888%, median = 0.307%),
- TiO_2 ranged from 0.000% - 0.080% (average = 0.015%, median = 0.009%),
- PbO ranged from 0.000% - 0.055% (average = 0.005%, median = 0.000%),
- Al_2O_3 ranged from 0.001% - 4.184% (average = 0.406%, median = 0.031%),
- V_2O_5 ranged from 89.169% - 107.752% (average = 96.739%, median = 96.713%),
- Fe_2O_3 ranged from 0.000% - 0.199% (average = 0.030%, median = 0.015%),
- CaO ranged from 0.007% - 0.111% (average = 0.051%, median = 0.039%),
- Na_2O ranged from 0.000% - 3.734% (average = 1.237%, median = 0.302%),
- K_2O ranged from 0.000% - 1.310% (average = 0.107%, median = 0.014%),
- P_2O_5 ranged from 0.000% - 0.027% (average = 0.005%, median = 0.001%),
- N ranged from 0.000% - 0.159% (average=0.030%, median = 0.000%),
- O was not identified during the analyses, and
- H_2O was not identified during the analysis.

Stoichiometrically, pure vanadium pentoxide has a chemical composition of V_2O_5 . Therefore, stoichiometric calculations of Option B vanadium pentoxide were completed on the basis of five oxygens in the molecular formula.

Table 32 contains stoichiometric calculations of the composition of Option B vanadium pentoxide. The average chemical composition of Option B vanadium pentoxide from the 20 EMPA analyses was found to be $\text{V}_{1.952}\text{O}_5$, and the median chemical composition of Option B vanadium pentoxide was found to be $\text{V}_{1.972}\text{O}_5$. Minor amounts of Si, Al, Na, Fe, Ca, and N were observed. Based on these results, nearly stoichiometric vanadium pentoxide was produced using processing Option B, although trace amounts of Option B ammonium metavanadate may also be indicated by the presence of minor amounts of nitrogen.

Table 32. Stoichiometric calculations for Option B vanadium pentoxide.

SAMPLE	FORMULA	BASIS	Si FORMULA	Ti FORMULA	Pb FORMULA	Al FORMULA	V FORMULA	Fe FORMULA	Ca FORMULA	Na FORMULA	K FORMULA	P FORMULA	N FORMULA	O FORMULA	H FORMULA
BVP_B-01	5	O	0.001	0.000	0.000	0.000	1.995	0.000	0.001	0.017	0.000	0.000	0.001	5.000	0.000
BVP_B-01	5	O	0.008	0.000	0.000	0.001	1.989	0.000	0.001	0.017	0.000	0.000	0.000	5.000	0.000
BVP_B-02	5	O	0.069	0.000	0.000	0.151	1.800	0.003	0.003	0.199	0.051	0.001	0.000	5.000	0.000
BVP_B-02	5	O	0.070	0.002	0.000	0.100	1.830	0.005	0.003	0.219	0.022	0.000	0.003	5.000	0.000
BVP_B-03	5	O	0.002	0.000	0.000	0.001	1.993	0.000	0.002	0.017	0.000	0.000	0.006	5.000	0.000
BVP_B-03	5	O	0.001	0.000	0.000	0.000	1.995	0.000	0.001	0.015	0.000	0.000	0.009	5.000	0.000
BVP_B-04	5	O	0.011	0.000	0.000	0.001	1.960	0.000	0.001	0.147	0.001	0.000	0.003	5.000	0.000
BVP_B-04	5	O	0.007	0.000	0.000	0.001	1.968	0.000	0.001	0.122	0.002	0.000	0.000	5.000	0.000
BVP_B-05	5	O	0.014	0.000	0.000	0.001	1.987	0.001	0.001	0.000	0.000	0.000	0.000	5.000	0.000
BVP_B-05	5	O	0.000	0.001	0.000	0.000	1.999	0.001	0.000	0.000	0.000	0.000	0.000	5.000	0.000
BVP_E-01	5	O	0.043	0.000	0.000	0.009	1.955	0.001	0.003	0.018	0.001	0.000	0.021	5.000	0.000
BVP_E-01	5	O	0.035	0.001	0.000	0.004	1.965	0.000	0.002	0.016	0.001	0.000	0.015	5.000	0.000
BVP_E-02	5	O	0.118	0.000	0.000	0.010	1.894	0.000	0.004	0.020	0.001	0.000	0.000	5.000	0.000
BVP_E-02	5	O	0.089	0.001	0.000	0.007	1.918	0.001	0.003	0.018	0.001	0.000	0.011	5.000	0.000
BVP_E-03	5	O	0.001	0.000	0.000	0.000	1.978	0.000	0.001	0.104	0.000	0.000	0.000	5.000	0.000
BVP_E-03	5	O	0.001	0.000	0.000	0.001	1.976	0.000	0.001	0.111	0.001	0.000	0.000	5.000	0.000
BVP_E-04	5	O	0.003	0.000	0.000	0.001	1.951	0.000	0.001	0.224	0.001	0.000	0.000	5.000	0.000
BVP_E-04	5	O	0.055	0.000	0.000	0.004	1.913	0.000	0.002	0.195	0.001	0.000	0.000	5.000	0.000
BVP_E-05	5	O	0.003	0.000	0.000	0.001	1.994	0.001	0.001	0.013	0.000	0.000	0.009	5.000	0.000
BVP_E-05	5	O	0.015	0.001	0.000	0.002	1.982	0.001	0.002	0.016	0.001	0.000	0.000	5.000	0.000
		<i>Minimum</i>	0.000	0.000	0.000	0.000	1.800	0.000	0.000	0.000	0.000	0.000	0.000	5.000	0.000
		<i>Maximum</i>	0.118	0.002	0.000	0.151	1.999	0.005	0.004	0.224	0.051	0.001	0.021	5.000	0.000
		<i>Average</i>	0.027	0.000	0.000	0.015	1.952	0.001	0.002	0.074	0.004	0.000	0.004	5.000	0.000
		<i>Median</i>	0.010	0.000	0.000	0.001	1.972	0.000	0.001	0.018	0.001	0.000	0.000	5.000	0.000
		<i>Stan. Dev.</i>	0.034	0.000	0.000	0.038	0.054	0.001	0.001	0.080	0.012	0.000	0.006	0.000	0.000

DISCUSSION AND SUMMARY

Recovery of vanadium from Ti SX raffinate obtained from previous pilot plant testing was carried by the following two process routes:

- Option A – Direct V solvent extraction, and
- Option B – Intermediate V precipitation.

The following tasks were completed to evaluate the process Option A:

- Increased V concentration from 99 mg/L to ~700 mg/L in the Ti raffinate by spiking a synthetic vanadium chloride solution,
- Adjusted pH to ~0.3 with MgO prior to conducting the Vanadium SX extractant screening,
- Conducted Vanadium SX tests with different extractants (Aliquat 336, Alamine 336, LIX 63, ACORGA M5774, Cyanex 923, LIX 984N, LIX 84-I and LIX 7950) by varying the process parameters to select a suitable extractant for subsequent V extraction and stripping isotherm development,
- Developed McCabe-Thiele V SX isotherms to evaluate the number of stages required for extracting and stripping of V,
- Evaluated V precipitation conditions to produce NH_4VO_3 , and
- Produced NH_4VO_3 and V_2O_5 for product characterization.

Among the examined extractants, Cyanex 923 showed an excellent behavior in extracting V with and without oxidation. The use of Cyanex 923 can also mitigate the cross-contamination, as it is used in the Ti solvent extraction process steps. The McCabe-Thiele V extraction and stripping isotherms were developed with an organic phase consisting of 15%(v/v) Cyanex 923 and 15%(v/v) Exxal 13 in Shelsol D80. Stripping of V from the loaded organic phase was carried with 1.5 M H_2SO_4 solution. About ~12995 mg/L V was found in the pregnant strip solution at the O/A phase ratio of 10:1. The design parameters of Vanadium SX for Option A are summarized in Table 33. Over >97% V was precipitated with ammonia solution at pH of 7.0 -7.5 at ambient temperature within 2 hrs. About 40% vanadium was found in the NH_4VO_3 , which was then calcined at 600°C for 3 hrs to produce V_2O_5 . About 52% vanadium was found in the V_2O_5 product.

Table 33. The design parameters for Option A – direct Vanadium SX from the Ti raffinate.

	O:A	# of Stage	Temp., °C	Time, min	RPM
Extraction	1:3.5	6	35	5	500
Stripping	6.1:1	3	35–40	15	500

The following steps were completed to evaluate the process Option B:

- Prepared feed solution by dissolving V_2O_5 into the Ti raffinate at 60°C,
- Precipitated V from Ti raffinate with 35% (w/w) MgO at 60°C at pH 3.55,

- (iii) Evaluated dissolution efficiency of H_2SO_4 (0.5 M – 2.0 M) and NaOH (0.25 M – 2.0 M) on this intermediate V precipitate,
- (iv) Conducted Vanadium SX screening tests with different extractants (Aliquat 336, LIX 63, TBP, Cyanex 923, and Cyanex 272) by varying the process parameters to select a suitable extractant for subsequent V extraction and stripping isotherm development,
- (v) Developed McCabe-Thiele V SX isotherms to evaluate the number of stages required for extraction and stripping of V,
- (vi) Evaluated V precipitation conditions to produce NH_4VO_3 , and
- (vii) Produced NH_4VO_3 and V_2O_5 for characterization.

Ti raffinate was spiked with V_2O_5 to increase V concentration from 99 mg/L to ~350 mg/L with V_2O_5 . A precipitate was produced recovering over 99% V at pH 3.6 with the addition of MgO. Solid-liquid separation was challenging with the vacuum filtration unit and it took >8 hrs to filter the sample and resulted entrainment of a significant amount of Mg in the filter cake. The filter cake concentrated V and contained over 5% V. In the subsequent step this cake was completely leached with 1.5 M H_2SO_4 at 60°C for subsequent V solvent extraction process steps. Caustic soda was also evaluated as a leaching reagent. About 80% V was dissolved with 2.0 M NaOH at ~98°C for 10 hrs and demonstrated more selectivity compared to H_2SO_4 for V over other metals including Al, Cr, Mg, Mn, Cu, and Ti extraction (refer to Table 10 and Table 14). However, due to the lower recovery and long residence time for NaOH leaching, the H_2SO_4 dissolution route was selected for further Vanadium SX tests.

It was found that LIX 63 is an excellent organic for selective extraction of V over Al, Cr, and Mg compared to the other extractants tested (Aliquat 336, TBP, Cyanex 923, and Cyanex 272). The McCabe-Thiele V extraction and stripping isotherms were developed with an organic phase consisting of 10%(v/v) LIX 63 and 10%(v/v) Exxal 13 in Shelsol D80. About 2771 mg/L V was loaded to this organic phase by three-stage extraction at the O/A ratio of 1:0.31 at 35°C and was able to extract most of the vanadium from feed solution by maintaining ORP of ~900 mV. Moreover, 1.5 M NaOH was able to completely strip V from the loaded organic phase by two-stage stripping at the O/A phase ratio of 10:1. Under these conditions, >28000 mg/L V can be produced in the pregnant strip solution. The design parameters of Vanadium SX for Option B are summarized in Table 34.

Table 34. The design parameters for Option B – intermediate V precipitation from the Ti raffinate.

	O:A	# of Stage	Temp., °C	Time, min	RPM
Extraction	1:0.31	3	35	5	500
Stripping	10:1	2	35-40	5	500

Over 99% V was precipitated as NH_4VO_3 from a simulated strip solution at pH of 7.0 -7.5 at ambient temperature. Over 39% vanadium was found in NH_4VO_3 . This product was calcined at 600°C to produce V_2O_5 in which the concentration of V was ~56%. This product also contained >2.3% Na.

Ammonium metavanadate and vanadium pentoxide powders produced from Option A and Option B processing schemes were provided to NRRI by PRO for further morphological and mineral chemical

analysis by means of EMPA. The morphologies of the ammonium metavanadate produced during Option A and Option B were different: Option A ammonium metavanadate occurred as anhedral, commonly porous particles with local, less porous, anhedral to subhedral columnar to acicular, less porous particles, whereas Option B ammonium metavanadate occurred as subrounded to oval, commonly radially-oriented aggregations of columnar to acicular particles up to 20 μm in length and up to 10 μm in width (refer to Fig. 17 and Fig. 19). The genetic cause of the differences between these morphologies remains poorly understood; however, the columnar to acicular crystalline forms identified via EMPA analysis in both Option A and Option B ammonium metavanadate samples are consistent with the orthorhombic symmetry that occurs in crystalline ammonium metavanadate (space group *Pbcm*; Pérez-Benítez and Bernés, 2018).

The stoichiometries of both Option A and Option B ammonium metavanadates deviate from the generalized chemical formula for ammonium metavanadate (NH_4VO_3). As indicated above, EMPA analysis indicates that the average and median chemical compositions of Option A ammonium metavanadate are $\text{N}_{0.277}\text{H}_{1.109}\text{V}_{1.195}\text{O}_3$ and $\text{N}_{0.280}\text{H}_{1.120}\text{V}_{1.196}\text{O}_3$, whereas the average and median chemical compositions of Option B ammonium metavanadate are $\text{N}_{0.721}\text{H}_{2.884}\text{V}_{1.119}\text{O}_3$, and $\text{N}_{0.698}\text{H}_{2.793}\text{V}_{1.183}\text{O}_3$, respectively. These results indicate that both the average and mean stoichiometric compositions for Option A and Option B ammonium metavanadate are deficient in nitrogen (N) and hydrogen (H) relative to vanadium, assuming three oxygens in the stoichiometric formula. Range and Zintl (1988) indicate that the thermal decomposition of ammonium metavanadate will eventually yield vanadium pentoxide plus ammonia gas plus water vapor, with many intermediate N, H, V, O, and H compounds being formed during the process. Therefore, we initially interpret the stoichiometric results of the Option A and Option B ammonium metavanadate materials produced during this study to be indicative of decomposition of ammonium metavanadate via loss of NH_3 and H_2O via a decrease in the ratio of ammonia and water to vanadium and oxygen (Brown and Stewart, 1970).

The morphologies of vanadium pentoxide produced during Option A and Option B were similar: both occurred as columnar to acicular particles that are consistent with the orthorhombic symmetry (space group *Pmmm*; Chakrabarti et al., 1999; Singh et al., 2017) consistent with the mineral shcherbinaite (Nickel and Nichols, 1991). The two cleavages observed at 90° represent orthogonal cleavages present in shcherbinaite (see <https://www.mindat.org/min-3636.html>), the crystalline mineral variety of V_2O_5 that was identified via x-ray diffraction analysis in this study (refer back to Fig. 18 and Fig. 20 as well as Table 24).

The stoichiometries of Option A and Option B vanadium pentoxide produced during this study were found to be nearly stoichiometric V_2O_5 . As indicated above, EMPA analysis indicates that the average and median chemical compositions of Option A vanadium pentoxide are $\text{V}_{1.966}\text{O}_5$ and $\text{V}_{1.972}\text{O}_5$, whereas the average and median chemical compositions of Option B vanadium pentoxide are $\text{V}_{1.952}\text{O}_5$, and $\text{V}_{1.972}\text{O}_5$, respectively. Minor amounts of Si, Al, Na, Fe, Ca, and N were also identified.

CONCLUSIONS AND RECOMMENDATIONS

The bench-scale study successfully demonstrated two potential processes for the recovery of V from Ti raffinate produced during the treatment of ilmenite ores from Minnesota. Ammonium metavanadate produced during this study that was subsequently analyzed via EMPA analysis was found to be deficient in both N and H, relative to V and O. The degradation of this material is believed to be due to volatilization of NH_2 and/or H_2O components of the material. The exact nature of this devolatilization of this material remains poorly understood. Vanadium pentoxide produced during these bench-scale experiments approached stoichiometric vanadium pentoxide.

Preliminary process criteria have been established for the two process options however further testing involving detailed bench scale and pilot plant test programs are highly recommended to examine the following:

- to mitigate the challenges faced in this study which include solid liquid separation of V precipitate in Option B,
- reduction of Na content in the final products and evaluation of product quality,
- to optimize the design parameters in steady state continuous operation for demonstration and/or commercial plant design, and
- to understand the effects of steady state continuous operation on the qualities of the ammonium metavanadate and vanadium pentoxide products.

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