

Article

Extraction of Vanadium from Ammonia Slag under Near-Atmospheric Conditions

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Abstract: A process for extracting vanadium from ammonia slag is proposed in this work, taking advantage of the nature of V^{5+} vanadate ions condensing into a solid phase around a pH of 2. The slag is a mixture of oxides of Ca (36.0 mass %), Si (28.4 mass %), Al (9.3 mass %), Fe (7.1 mass %), V (6.9 mass %), S (3.9 mass %), Na (2.7 mass %), Ni (2.5 mass %), Mg (1.3 mass %), and other (K, P, and Ti) (1.9 mass %). The difficulty with extraction originates from the oxyanionic character of the vanadate ions, leading to the formation of vanadate salts with the concomitant cations. In contrast, a stepwise-pH-control process that is proposed in this work is effective for separating vanadium from the slag, as (1) the Si component in the slag is filtered off as the residue at the initial leaching step; (2) Fe, Al, and other cations are precipitated as the vanadate salts at pH 6, leaving $Ca^{2+}(aq)$ in the solution; (3) the vanadate component is transferred to the liquid phase by dissolving the precipitate in a NaOH(aq) solution of pH 13, leaving Fe, Ti, and Ni ions in the solid phase; and finally, (4) the pH of the solution is adjusted to 2. The vanadium component is solidified as sodium vanadate and V_2O_5 . The maximum yield of vanadium from the slag is evaluated as 80.7%, obtaining for NaV_6O_{15} and V_2O_5 with a purity of 97 mass %.

Keywords: vanadium extraction; pH control; ammonia slag; aqueous solution; sodium vanadate

1. Introduction

Vanadium is an important element in the steel and chemical industries as it has been used to strengthen steels or as catalysts to produce sulfuric acid [1]. A high-strength alloy of aluminum, vanadium, and titanium is emerging in the aerospace field [1,2], and vanadium-redox-flow batteries have attracted much attention due to their potential applications for large-scale energy storages [3].

Since no high-vanadium-content ore is commercially available, vanadium has usually been produced from secondary sources and industrial wastes, such as titaniferrous magnetites, concentrates, slags, fly ashes, and petroleum residues [1,4,5]. The salt-roasting technique is a major process for extracting vanadium from those sources, by which a vanadium source is heated with a sodium salt to form sodium metavanadate. This material is typically converted into ammonium metavanadate in an aqueous solution by adding ammonium ions to collect it as the precipitate. This technique is quite effective for mass production of vanadium, especially in a large facility, but it is not suitable for small-to-middle-scale plants, because it requires kilns that can bear high-temperature treatment (e.g., 800–1230 °C) [2,6]. Energy consumption and toxic-gas emission during high-temperature treatments are also problematic [7,8].

Direct-leaching techniques have been investigated to collect vanadium under moderate conditions. The primary problem with direct leaching is the existence of concomitant cations, which makes the selective collection of vanadium difficult. The secondary sources and industrial wastes contain a range

of metals such as Fe, Al, Ca, and Mg and they are usually extracted in the leachant, together with vanadium. The effectiveness of using organic extractants [9–15] and ion-exchanging resins [16–21] to collect vanadium from the extracted solutions has been examined.

A Japanese ammonia manufacture, for example, discharges a few thousand tons of ammonia slag every year. The slag typically contains up to 5–10 mass % vanadium as oxides, although it has not been used as a vanadium source because this content is relatively low. The concentration does not merit the costs that are involved in conventional vanadium-extraction processes, and therefore, the slag is wasted by solidifying it in cement.

This work proposes a technique for collecting vanadium from ammonia slag. The process was based on an aqueous solution, which is beneficial from the environmental and economic points of view. The concept is explained with Figure 1, which shows an equilibrium diagram of V^{5+} vanadate ions in an aqueous solution [22]. The key points are as follows: (1) several types of vanadate ions are formed in an aqueous solution depending on the pH and the concentration; (2) they are stably soluble over a wide pH region; and, (3) solid-state V_2O_5 is condensed around pH 2 at relatively higher concentrations. The latter two points are contrasted with the nature of a typical cation being dissolved in an acidic solution and precipitating as hydroxide in the higher-pH region. One might suppose that the concomitant cations can be separated by raising the pH once to precipitate hydroxides and then lowering it to pH 2 to solidify the vanadate compounds simply lead to separation of vanadium from a solution containing several cations; however, in our previous paper [23], we reported that the oxyanionic character of the vanadate ions leads to the formation of vanadate salts, interfering with the selective collection of vanadium through a simple pH change. This paper builds upon [23] to establish a process for extracting vanadium from the slag by revealing the effects of the concomitant cations crucially influencing the formation behaviors of vanadate salts and the role of the each step in separating those cations.

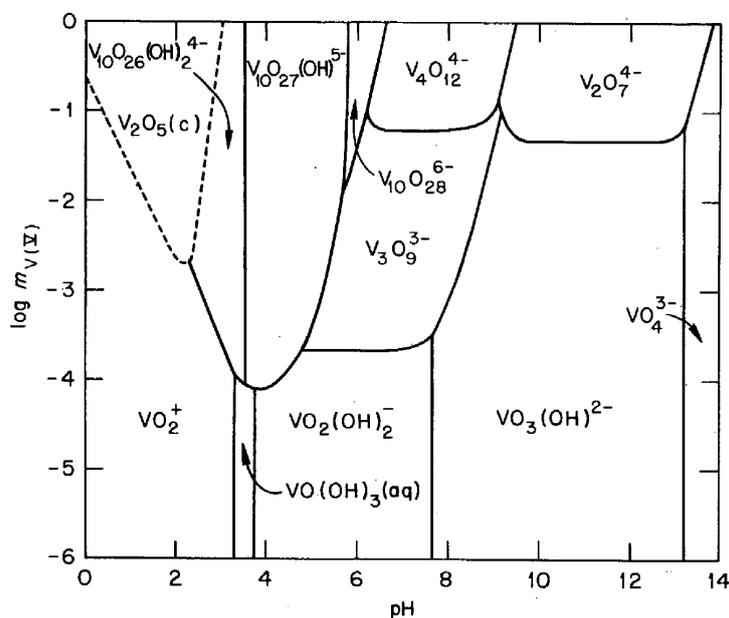


Figure 1. Predominance diagram for V^{5+} - OH^- species at 25 °C [22]. The solid lines represent conditions under which the predominant species in adjacent regions contain equal amounts of V^{5+} . The dashed lines represent the solubility of V_2O_5 in terms of the V^{5+} concentration. $m_{V(V)}$: moles of V^{5+} per kg of water. (Reprinted with permission from “The Hydrolysis of Cations”, Copyright (1976) John Wiley & Sons).

2. Experimental Section

2.1. Chemical Composition of the Ammonia Slag

The ammonia slag was offered from a Japanese ammonia manufacturer in Yamaguchi Prefecture. The slag is a mixture of oxides (and probably sulfides) of several metals. The chemical composition of the ash content excluding oxygen is shown in Table 1. The concentrations were evaluated by X-ray fluorescence spectroscopy (XRF) (EDXL 300, Rigaku, Tokyo, Japan), and they are shown as mass-percentages in elemental form. The examined slag contained Ca (36.0 mass %), Si (28.4 mass %), Al (9.3 mass %), Fe (7.1 mass %), V (6.9 mass %), S (3.9 mass %), Na (2.7 mass %), Ni (2.5 mass %), Mg (1.3 mass %), and other (K, P, and Ti) (1.9 mass %). Ca originated in CaCO_3 , which is an additive that acted as a melting-point depressant for coke ash. The other components were from the coke used to produce hydrogen for ammonia production via the water gas reaction. The composition of the slag was somewhat different from that used in our previous paper, and this difference was due to deviation of the usual nonuniformity of the composition of the industrial-waste mixture.

Table 1. Chemical composition of the ash content of ammonia slag.

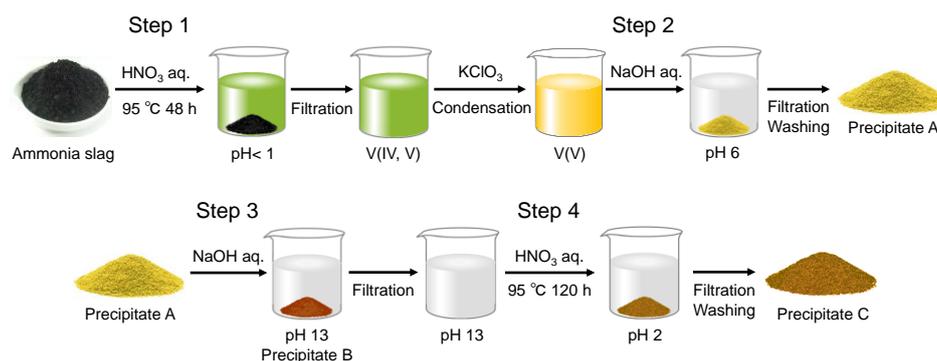
Element	Concentration (mass %)
Ca	36.0
Si	28.4
Al	9.3
Fe	7.1
V	6.9
S	3.9
Na	2.7
Ni	2.5
Mg	1.3
Other (K, P, and Ti)	1.9

2.2. Extraction Procedure

The optimized extraction process for collecting vanadium is shown in Scheme 1. The ammonia slag was dried at 95 °C on a hot plate and ground in an alumina mortar. A given amount of the slag was weighed for the extraction experiment. Typically, 2.0 g of the ammonia slag was treated in 50 mL $\text{HNO}_3(\text{aq})$ (1.3 mol/L) in an autoclave at 95 °C for 48 h. After the insoluble residue was filtered off, 0.10 g of KClO_3 was added to the filtrate to oxidize V^{4+} to V^{5+} [23], which led the solution to change the color from green to yellow. The solution was condensed on a hot plate at 95 °C to halve its volume. Then, the solution's pH was adjusted to 6 using $\text{NaOH}(\text{aq})$ (15 mol/L) to form the precipitate (Precipitate A in Scheme 1). After being separated from the solution by filtration, Precipitate A was treated with 30 mL $\text{NaOH}(\text{aq})$ (1.5 mol/L). After stirring for 1 h, the insoluble residue (Precipitate B in Scheme 1) was filtered off from the solution. As discussed later in detail, the vanadium component was precipitated as Precipitate A at Step 2, and was transferred back to the liquid phase by treatment with $\text{NaOH}(\text{aq})$ at Step 3. Then, the pH of the filtrate was adjusted to 2 by adding $\text{HNO}_3(\text{aq})$ (13 mol/L) to condense the vanadate ions into the solid phase (Precipitate C) in the solution during aging at 95 °C for 120 h.

The chemical reagents used in this work are shown in Table 2.

The control experiments were carried out using the chemical reagents V_2O_5 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and CaCO_3 (Table 2) to examine the individual effects of iron, aluminum, and calcium ions coexisting. Fe^{3+} , Al^{3+} , or Ca^{2+} were added to a 50 mL $\text{HNO}_3(\text{aq})$ (mol/L) solution, dissolving 0.3 g of V_2O_5 at the molar ratio that was determined by XRF. The precipitating behaviors were investigated at several pHs, and the precipitates were heat-treated at 700 °C to improve the crystallinity to allow for the identification of the crystallographic phases by X-ray diffraction (XRD) (Rigaku, Tokyo, Japan).



Scheme 1. Procedure for extracting vanadium from ammonia slag by pH control.

Table 2. Chemical reagents used in this work.

Reagent	Reagent Information
KClO ₃	99.5% (Kanto Chem. *1)
NaOH	95% (Kanto Chem.)
HNO ₃ (aq)	60–61% (Kanto Chem.)
H ₂ SO ₄	96% (Kanto Chem.)
(COOH) ₂ ·2H ₂ O	99.5–100.2% (Kanto Chem.)
H ₂ O	Deionized water
(for control experiments)	
V ₂ O ₅	99.0% (Kanto Chem.)
Fe(NO ₃) ₃ ·9H ₂ O	99.9% (Wako *2)
Al(NO ₃) ₃ ·9H ₂ O	98.0% (Kanto Chem.)
CaCO ₃	99.99% (Kanto Chem.)

*1 Kanto Chemical, Tokyo, Japan; *2 Wako Pure Chemical Industries, Osaka, Japan.

2.3. Instruments

The concentrations of vanadate ions in the solution were determined using ultraviolet-visible-ray (UV-Vis) spectroscopy (PD-303, APEL, Saitama, Japan) with an absorbance curve calibrated with reference solutions prepared at several concentrations. (COOH)₂·2H₂O was used as a reduction agent from V⁵⁺ to V⁴⁺ to use the absorption of VO²⁺(aq) at 760 nm to determine the concentration [23].

XRD (MiniFlex600, Rigaku, Tokyo, Japan) with Cu K α radiation was used to identify the compounds with the samples being heat-treated at elevated temperatures to improve the crystallinity beforehand because they did not necessarily exhibit appreciable diffraction peaks in their as-prepared conditions. The compositions were analyzed with energy-dispersive X-ray spectroscopy (EDS) (Link ISIS, Oxford Instruments, Oxon, UK) attached to scanning electronic microscopy (SEM) (JSM-T330, JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV with a working distance of 20 mm, for which the powder samples were dried at 300 °C in air and were pressed into compacts with a small amount of polyvinyl alcohol (PVA) (Kuraray Poval PVA-217) as a binder. The carbon coating was vacuum-evaporated onto the pellet samples before SEM-EDS and a Co foil was used as a calibration standard.

3. Results and Discussion

3.1. Extraction Process from the Slag (Step 1 in Scheme 1)

Figure 2 compares the EDS spectra of the starting slag and the precipitates that are formed at the subsequent extraction steps. EDS detected 12 elements in the slag (Figure 2a) other than vanadium, which was consistent with the elemental analysis using XRF (Table 1). The slag was mainly composed

of Si, Ca, Al, V, and Fe. The carbon peak was attributed to the residual coke in the slag and to carbon coating for the SEM-EDS experiment.

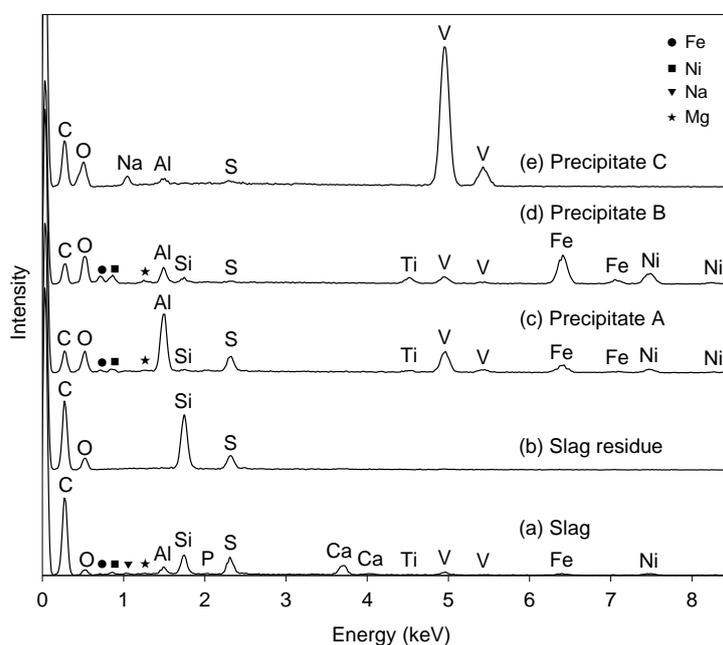


Figure 2. Energy-dispersive X-ray spectroscopy (EDS) spectra of the slag (a) and the precipitates obtained in the subsequent extraction steps in Scheme 1; (b) Residue after extraction at Step 1; (c) Precipitate A; (d) Precipitate B; and (e) Precipitate C (see Scheme 1).

Figure 2b shows the EDS spectrum of the residue after the extraction by nitric acid at Step 1. The residue was composed of C, O, Si, and S. The peaks of Ca, V, and Fe were clearly weakened, indicating that they were effectively transferred into the filtrate from the slag.

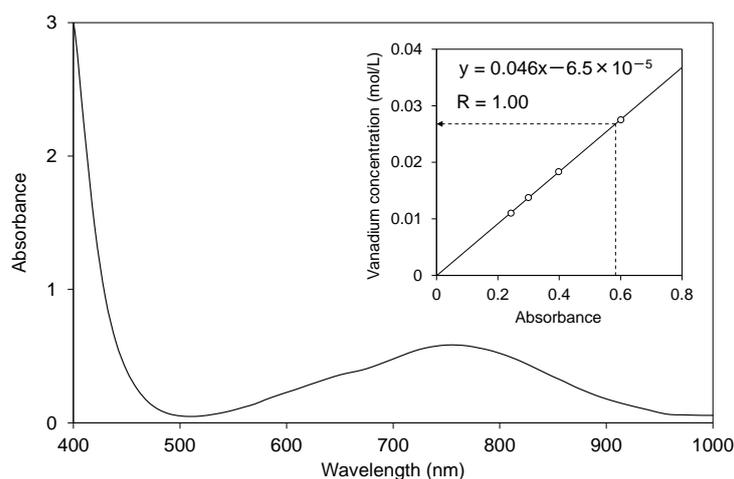


Figure 3. Ultraviolet-visible-ray (UV-Vis) spectrum of the extracted solution. The vanadate species in the solution were reduced to VO^{2+} by $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ so that the concentration of $\text{VO}^{2+}(\text{aq})$ could be determined by the absorption at 760 nm. The inset shows the calibration curve drawn with the prepared solutions at several concentrations.

Figure 3 shows the absorption spectrum of the extracted solution at Step 1 after the addition of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ to reduce V^{5+} vanadate ions to $\text{VO}^{2+}(\text{aq})$, which exhibits a broad absorption peak at

around 760 nm. The inset shows the calibration curve, indicating an absorbance proportional to the $\text{VO}^{2+}(\text{aq})$ concentration with a correlation coefficient of $R = 1.00$. The extraction yield from the slag to the solution at this step was estimated to be above 97%, based on the vanadium content in the slag and the $\text{VO}^{2+}(\text{aq})$ concentration in the solution.

3.2. Precipitation of Aluminum Vanadate and Iron Vanadate (Step 2)

The EDS spectrum of Precipitate A is shown in Figure 2c, where Precipitate A was collected at Step 2 from the solution at pH 6. Figure 2c indicates that Precipitate A was mainly composed of aluminum, vanadium, and iron. The crystallographic phases of Precipitate A were identified as Fe_3O_4 (ICDD #26-1136) and FeVO_4 (ICDD #38-1372) (Figure 4). Although vanadate ions are stably soluble in this pH region (Figure 1), the vanadium component precipitated as vanadate salts with Fe and Al (FeVO_4 and AlVO_4) at this step. Since an Al-related crystallographic phase was not observed in Figure 4, the Al component was considered to exist as amorphous or to be incorporated into FeVO_4 . Fe_3O_4 originated from the conversion of iron hydroxide into Fe_3O_4 during heat treatment for XRD. The absence of a Ca peak at 3.69 keV in EDS is characteristic of Precipitate A, indicating that $\text{Ca}^{2+}(\text{aq})$ was left in the solution. The solution after the filtration was colorless.

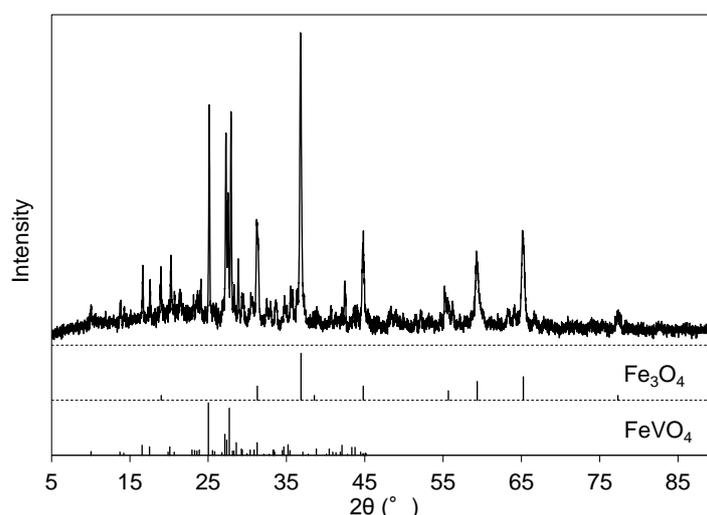


Figure 4. X-ray diffraction (XRD) pattern of Precipitate A after the heat treatment at 700 °C. The line diagram below the pattern indicates the peak positions of Fe_3O_4 (ICDD #26-1136) and FeVO_4 (ICDD #38-1372).

3.3. Separation of Vanadium from Fe and Al (Step 3)

Figure 2d presents the EDS spectrum of Precipitate B, which was the residue at pH 13 after Precipitate A was dissolved in $\text{NaOH}(\text{aq})$. The peak intensities of Fe, Ni, and Ti increased after this step relative to Precipitate A (Figure 2d). The vanadate compound was preferentially dissolved into the solution from Precipitate A, leaving the Fe, Ni, and Ti components in Precipitate B. The XRD peaks of Precipitate B after heat treatment at 700 °C (Figure 5) were attributed to Fe_2O_3 (ICDD #33-664) and Fe_3O_4 (ICDD #26-1136), and the main component of the residue (Precipitate B) was assumed to be iron hydroxide with impurities of Ni and Ti. The Al component was not effectively separated from V at this step as the peak intensity of Al decreased from Figure 2c to Figure 2d. The peaks of V were still recognized in EDS (Figure 2d), and vanadium partly remained in Precipitate B.

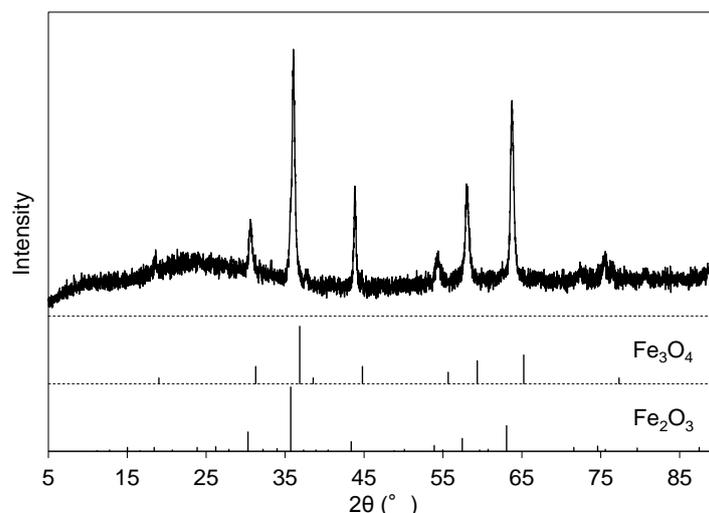


Figure 5. XRD pattern of Precipitate B after heat treatment at 700 °C for 1 h.

3.4. Precipitation of Vanadate Compounds (Step 4)

The pH of the filtrated solution at Step 3 was adjusted to 2 with HNO₃(aq). A reddish-brown precipitate (Precipitate C) was obtained during aging at 95 °C. The EDS (Figure 2e) revealed that the main component of Precipitate C was vanadium with minor impurities of Na, Al, and S. Quantitative analysis by EDS gave a molar ratio of V:Na = 7.7:1, which is consistent with the observation of NaV₆O₁₅ (ICDD #24-1155) and V₂O₅ (ICDD #41-1426) in XRD for Precipitate C (Figure 6).

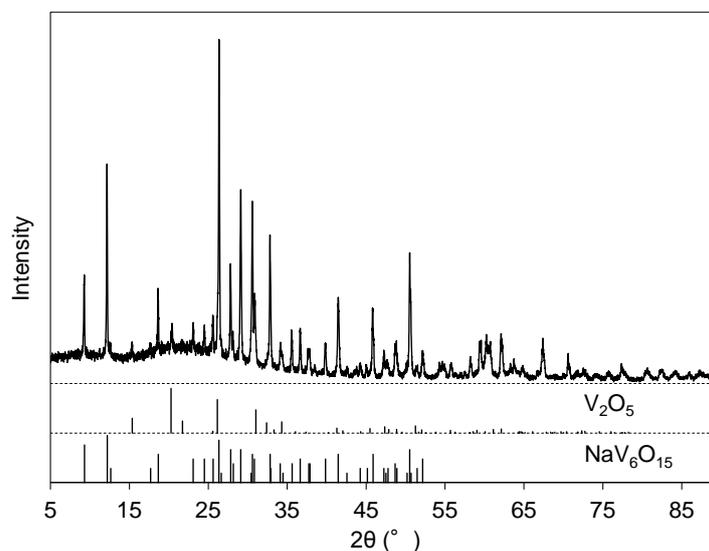


Figure 6. XRD pattern of Precipitate C after heat treatment at 500 °C for 1 h.

Sodium vanadates are used together with vanadium oxides as raw materials in vanadium metallurgy [2], and therefore, Precipitate C can be regarded as a goal of our extraction process. The yield of vanadium from the slag was evaluated at 80.7% based on the vanadium content in the slag and the mass of obtained Precipitate C as a mixture of NaV₆O₁₅ and V₂O₅ at molar ratio V:Na = 7.7:1. The estimated content of the vanadate compounds (NaV₆O₁₅ and V₂O₅) was 97 mass % in Precipitate C.

The Al component that was dissolved in the NaOH(aq) solution together with V at Step 3 was separated at Step 4 by leaving it as Al³⁺(aq) in the solution at pH 2. Contamination by Al was

recognized in Precipitate C in Figure 2e and lowering the pH below 2 could suppress it to some degree, but reduce the V yield instead.

3.5. Control Experiments with Chemical Reagents and Mechanisms for Vanadium Extraction

Several cationic species are contained in the slag, as shown in Table 1, and this makes it difficult to specify reactions that occur at Steps 2, 3, and 4. Then, the control experiments were carried out using chemical reagents for each pair of V and Fe, Al, or Ca (Table 3), where a chemical reagent of V_2O_5 was dissolved in $HNO_3(aq)$ and $Fe(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, or $CaCO_3$ was added to the solution. The solution's pH was initially lower than 1. This was then adjusted to 2, 6, or 13 with $NaOH(aq)$ to collect the precipitate at each pH. The precipitates were heat-treated at $700\text{ }^\circ\text{C}$ for 1 h in order to improve the crystallinity prior to XRD.

Table 3. Crystallographic phases identified in the precipitates at pH 2, 6, and 13 with combinations of vanadate ions and (a) Fe^{3+} , (b) Al^{3+} , or (c) Ca^{2+} .

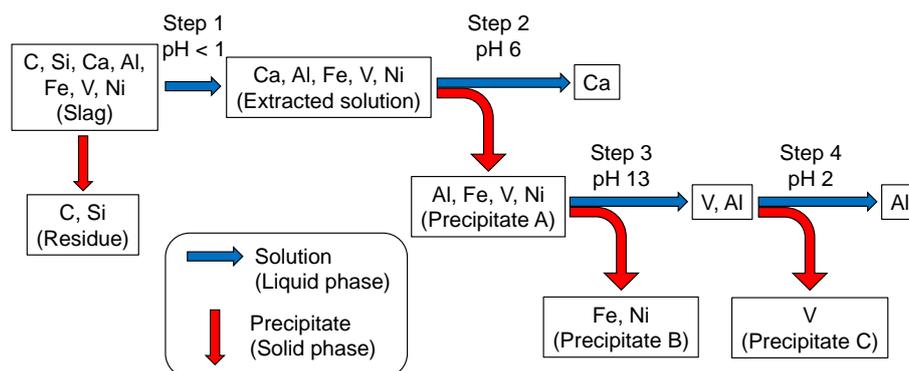
Coexisting Cation	Product Phase		
	pH 2	pH 6	pH 13
(a) Fe^{3+}	$FeVO_4$	$FeVO_4$ & Fe_2O_3	Fe_2O_3
(b) Al^{3+}	V_2O_5 & NaV_6O_{15}	$AlVO_4$	No precipitation
(c) Ca^{2+}	V_2O_5 & NaV_6O_{15}	No precipitation	$Ca_{10}V_6O_{25}$ & CaO

As shown in Figure 1, vanadate ions themselves are stably soluble over a wide-pH region, except around pH 2. On the other hand, the coexistence of $Fe^{3+}(aq)$ led to the insolubility of iron vanadate, with $FeVO_4$ being collected at pH 2. The precipitate at pH 6 was composed of $FeVO_4$ and Fe_2O_3 , indicating that Fe^{3+} precipitated as vanadate and hydroxide until pH 6. On the other hand, the main phase at pH 13 became Fe_2O_3 , and therefore, the vanadium component was dissolved back into the liquid phase from $FeVO_4$ in the higher-pH region.

$Al^{3+}(aq)$ did not form a vanadate salt at lower pH as the precipitate at pH 2 was V_2O_5 and NaV_6O_{15} , with sodium coming from $NaOH$ to adjust the pH. The $AlVO_4$ that was recognized in the product at pH 6 was dissolved again at higher pH with no precipitate at pH 13. $Ca^{2+}(aq)$ did not interact with the vanadate ions at a pH of 6 or lower. $Ca_{10}V_6O_{25}$ and CaO were recognized in the precipitate at pH 13, where CaO resulted from $Ca(OH)_2$ during the heat treatment for XRD.

The above results reveal rather complicated correlations between the vanadate ions and Fe^{3+} , Na^+ , Al^{3+} , and Ca^{2+} , depending on the solution's pH. $FeVO_4$ is more favorably formed in the lower-pH region around 2, although Na^+ also tends to form the vanadate salt NaV_6O_{15} . $AlVO_4$ precipitates near the neutral-pH region when the solution's pH is raised. These vanadates ($FeVO_4$, NaV_6O_{15} , and $AlVO_4$) are dissolved in the $NaOH(aq)$ solution, whereas calcium vanadate stably exists in the higher-pH region even up to pH 13.

Scheme 2 summarizes the vanadium-condensation procedure from the slag through Scheme 1. Si is left in the residue during the extraction at Step 1. Precipitate A at Step 2 is composed of iron and aluminum vanadates with minor metals (Ni, Ti, etc.) and Ca^{2+} are separated at this step, being left in the solution. The vanadate compounds are dissolved in the solution by raising its pH, leaving Fe and other metals, such as Ni and Ti in the solid phase, as Precipitate B. The vanadate component is condensed from the solution into the solid phase (NaV_6O_{15} , V_2O_5 , etc.) during aging at pH 2, leaving $Al^{3+}(aq)$ in the solution.



Scheme 2. Major streams of elemental transfers of cations in the slag during the extraction process of this work. The contamination by impurities is ignored.

4. Conclusions

The extraction of vanadium from the ammonia slag was demonstrated by pH control based on the aqueous solution near ambient conditions (≤ 95 °C). The effects of the concomitant cations of Fe^{3+} , Al^{3+} , and Ca^{2+} were investigated on the precipitation behaviors of the vanadate salts were investigated. Fe^{3+} and Al^{3+} brought the vanadate salts up to a pH of 6. The vanadate components in these salts were dissolved in the $\text{NaOH}(\text{aq})$ solution until a pH of 13, which left Fe^{3+} in the insoluble residue. The vanadate component was separated from the Al component at pH 2 by forming solid-state $\text{NaV}_6\text{O}_{15}$ and V_2O_5 during aging. The maximum yield of vanadium was estimated to be 80.7%, obtaining for $\text{NaV}_6\text{O}_{15}$ and V_2O_5 with a purity of 97 mass %.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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