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Integrated Hydrometallurgical Recovery of Vanadium from Spent Petrochemical Catalysts for the Production of High-Purity Ammonium Metavanadate

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Abstract

An integrated hydrometallurgical process for the recovery of vanadium from spent petrochemical catalysts and the production of high-purity ammonium metavanadate (AMV) was developed and experimentally validated. Alkaline leaching of roasted vanadium-bearing catalysts resulted in vanadium extraction of 90%–95%, producing a solution containing 37.0 g/L V_2O_5 together with phosphorus, sulfur, silicon, and molybdenum impurities. Two purification approaches, ion-exchange sorption and magnesium oxide treatment, were evaluated for impurity removal. Sorption using the macro porous anion-exchange resin Biolite 200U provided effective silicon removal but resulted in significant vanadium losses (up to 19.6%) due to co-sorption of vanadium and phosphorus. In contrast, magnesium oxide treatment at 70–80 °C reduced the phosphorus concentration from 0.39 to 0.04 g/L (approximately 90% removal) and completely removed silicon while limiting vanadium losses to less than 2.5%. Following purification, ammonium metavanadate was precipitated using ammonium chloride at a V_2O_5:NH_4Cl molar ratio of 1:2 and pH 8.8–9.0, achieving approximately 99% vanadium recovery. X-ray diffraction analysis confirmed the formation of single-phase NH_4VO_3 after solution purification, whereas precipitation from untreated solutions resulted in contamination by alumina-bearing phases. The proposed process provides an effective route for producing purified ammonium metavanadate suitable for subsequent conversion into metallurgical-grade V_2O_5. The ultimate goal of the proposed technology is the production of metallurgical-grade ferrovanadium (FeV80). Because AMV is thermally converted to V_2O_5 with a weight loss of approximately 24%–25%, phosphorus and sulfur concentrations in AMV must be maintained below approximately 0.04 wt.% to ensure compliance with the impurity requirements of FeV80 according to GOST 27130-94.

Keywords: vanadium; ammonium metavanadate; alkaline leaching; magnesium oxide; solution purification; spent catalysts

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1. Introduction

Vanadium is considered a critical and strategic metal due to its extensive application in the production of high-strength steels, ferroalloys, and advanced energy storage systems, including vanadium redox flow batteries. The steadily increasing global demand for vanadium has driven the development of technologies for the recovery of vanadium from

secondary resources as a complementary alternative to conventional primary ore processing routes [1–4].

Among the various types of secondary vanadium-bearing materials, spent heterogeneous catalysts from the petrochemical and petroleum refining industries, particularly hydrodesulfurization (HDS) and sulfuric acid production catalysts, have attracted considerable attention [5,6]. The vanadium content in such materials can reach 10–25 wt.% as V_2O_5, making them a valuable feedstock for hydrometallurgical processing. However, during catalyst operation and regeneration, significant amounts of associated impurities, including sulfur, phosphorus, silicon, nickel, molybdenum, and organic residues, accumulate in the catalyst matrix [7–10]. The presence of these components considerably complicates subsequent processing and adversely affects the quality of the resulting vanadium products.

Among the reagent-based methods used for the removal of phosphorus and silicon from alkaline vanadate solutions, treatment with magnesium oxide or magnesium hydroxide and ion-exchange sorption are among the most extensively studied approaches [11–13]. Both methods are based on the formation and precipitation of sparingly soluble phosphate and silicate compounds; however, they differ significantly in terms of purification efficiency and vanadium selectivity [14–16]. In the present study, a systematic comparison of these purification methods was conducted for vanadium-bearing solutions prior to ammonium metavanadate precipitation.

The scientific significance of this work lies in the development of an integrated approach for the processing of vanadium-bearing secondary resources, taking into account the influence of associated impurities such as phosphorus and sulfur. An improved solution purification scheme was proposed to enhance vanadium recovery and enable the production of high-purity vanadium compounds. The obtained results contribute to a better understanding of hydrometallurgical processing routes for secondary vanadium resources and may serve as a basis for improving the efficiency of industrial vanadium recovery technologies.

2. Materials and Methods

2.1. Materials

The feed material used in this study consisted of roasted spent vanadium-bearing catalysts from the petrochemical industry. Ammonium chloride (analytical grade) and ammonium sulfate (chemically pure grade) were used as precipitants for ammonium metavanadate (AMV). Magnesium oxide, used for the precipitation of phosphorus and silicon impurities, was supplied by Labkhimprom LLP (Almaty, Kazakhstan). Alkaline leaching of the roasted spent catalyst was carried out using a sodium carbonate solution to achieve complete extraction of vanadium by converting it into soluble sodium vanadate.

2.2. Solution Purification Methods

Vanadium-bearing solutions were purified from phosphorus and silicon impurities using three alternative approaches:

Method 1 (cation-exchange sorption):

Following alkaline leaching of the roasted spent catalyst, the solution was filtered using a laboratory vacuum filtration unit. A volume of 20 mL of KU-2 cation-exchange resin was added to 300 mL of the filtrate. After 2 h of contact, an aliquot was withdrawn for chemical analysis. Vanadium was determined by titrimetric analysis. Phosphorus concentrations in both solid and liquid samples were measured by photocolorimetry in accordance with GOST 22536.3 [17]. Sodium concentrations were determined using a flame photometer (FPA-2-01, ZOMZ JSC, Sergiev Posad, Russia). The concentrations of the remaining elements were determined by conventional wet chemical methods.

Method 2 (anion-exchange sorption):

After filtration, 20 mL of the macroporous anion-exchange resin Biolite 200U (Sunresin New Materials Co., Ltd., China) was added to 300 mL of the productive solution. Following 2 h of contact, an aliquot was collected and analyzed for vanadium and phosphorus contents. The V_2O_5 concentration decreased from 37 to 27 g/L, while the phosphorus concentration decreased from 0.39 to 0.11 g/L.

Method 3 (magnesium oxide treatment):

Magnesium oxide was added portionwise to the productive solution preheated to 70–80 °C at a 30% excess relative to the stoichiometric amount required for phosphorus removal. The suspension was stirred for 30–60 min at pH 8.8–9.2. The purification mechanism is based on the precipitation of sparingly soluble magnesium phosphate compounds according to the following Reactions (1) and (2):

$$MgO + Na_2HPO_4 \rightarrow MgHPO_4\downarrow + Na_2O \quad (1)$$

$$2Na_3PO_4 + 3MgO \rightarrow Mg_3(PO_4)_2\downarrow + 3Na_2O \quad (2)$$

After precipitation, the suspension was filtered, and the resulting precipitate was subjected to elemental and phase composition analyses.

2.3. AMV Precipitation

AMV was precipitated from the purified solutions using ammonium chloride at a molar ratio of V_2O_5:NH_4Cl = 1:2 while maintaining the pH in the range of 8.8–9.0. The precipitation process was carried out under gentle stirring conditions to promote the formation of larger crystals. Unlike the commonly used ammonium sulfate, the use of ammonium chloride prevents the introduction of additional sulfur into the final product.

Following precipitation, the slurry was filtered, and the resulting solid product was subjected to elemental and phase composition analyses. The residual V_2O_5 concentration in the mother liquor ranged from 0.2 to 0.5 g/L. The vanadium recovery achieved during the precipitation stage was approximately 99%.

The overall process flowsheet developed in this study is presented in Figure 1.

2.4. Analytical Methods

The phase composition of the solid samples was determined by X-ray powder diffraction (XRD). The morphology and elemental distribution of the solid products were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS). The SEM–EDS analysis was used for qualitative elemental characterization and microstructural examination. The vanadium content in the roasted spent catalyst and ammonium metavanadate (AMV) products was determined by volumetric titration according to GOST 19863.2-91 using Mohr's salt as the titrant. Prior to analysis, solid samples were fused with a mixture of sodium peroxide and sodium carbonate, dissolved in sulfuric acid, and analyzed according to the standard procedure. The concentrations of Fe, Al, Mo, and Ni were determined by atomic absorption spectrometry using an Agilent Duo AA240 FS/Zeeman atomic absorption spectrometer (Agilent Technologies, Mulgrave, Australia). The sodium content was determined using an FP6450 flame photometer (BOYN (Hangzhou Boyn Instrument Co., Ltd.), Hangzhou, Zhejiang Province, China) after dissolution of weighed solid samples and dilution to a defined volume.

The silicon content was determined by conventional wet chemical analysis. Phosphorus was determined photometrically according to GOST 22536.3 using a KFK-3-01 photoelectric colorimeter (OJSC Zagorsk Optical-Mechanical Plant, Sergiev Posad, Russia) at a wavelength of 440 nm. Sulfur was determined gravimetrically as $BaSO_4$.

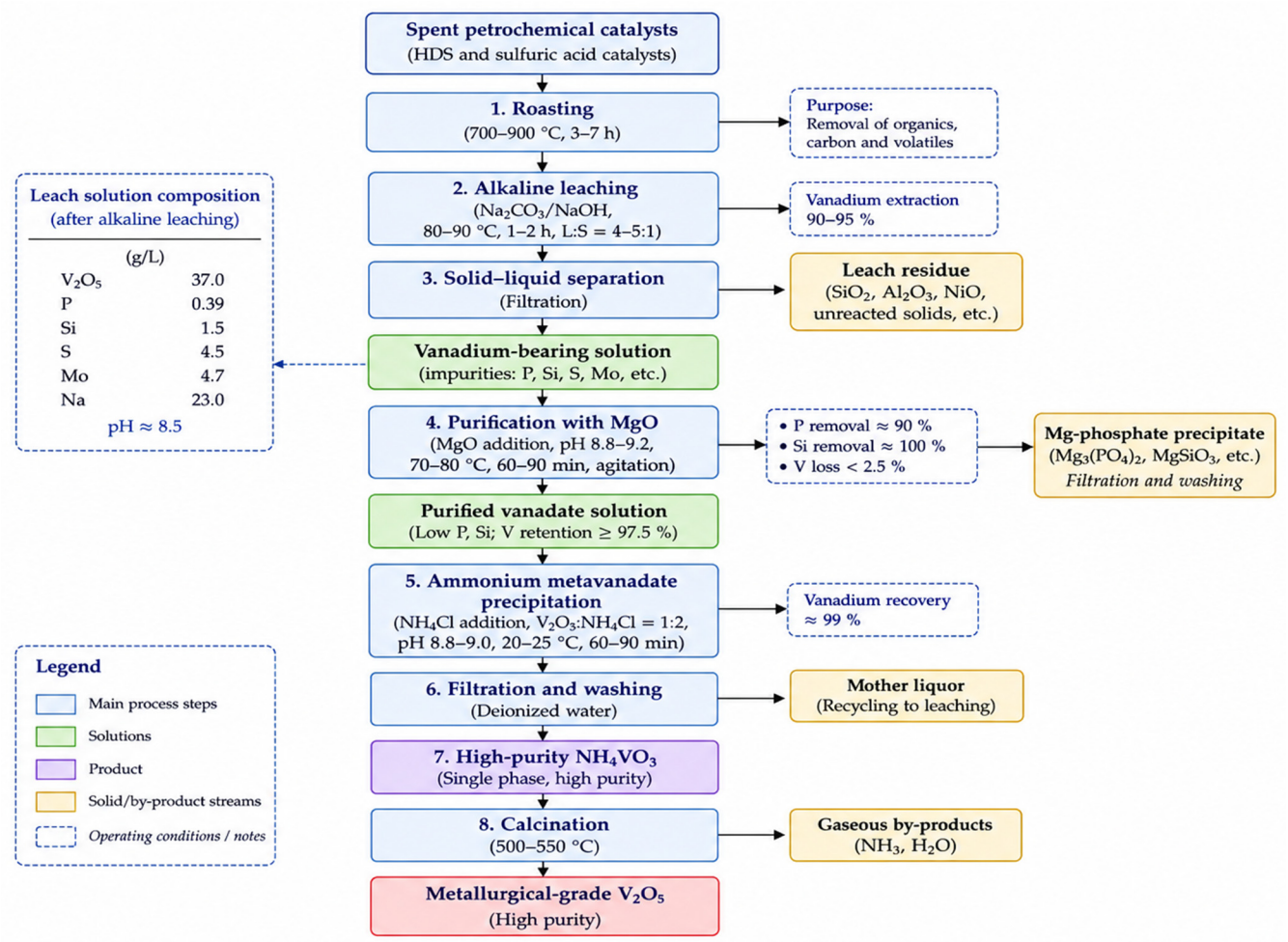


Figure 1. Proposed integrated hydrometallurgical flowsheet for the production of high-purity AMV from spent petrochemical catalysts.

3. Results and Discussion

3.1. Characterization of Feed Material

Prior to hydrometallurgical processing, the spent catalysts were subjected to roasting to remove organic residues and carbonaceous deposits. The spent catalysts were roasted at 700–900 °C for 3–7 h, depending on the oil and sulfur contents. Excessive roasting was avoided because it caused partial melting of the material and pellet formation in the rotary kiln. The completion of roasting was assessed by periodically withdrawing a small sample, performing alkaline leaching, and determining the vanadium content in the leach solution.

Representative SEM–EDS spectra of the roasted catalyst are presented in Table 1 and Figure 2 for qualitative characterization only. The quantitative chemical composition determined by laboratory analytical methods is presented in Table 2.

Table 1. Representative SEM–EDS spectra of the roasted catalyst.

Spectrum	O	Na	Al	Si	P	S	Ca	Ti	V	Fe	Ni
Spectrum 1	35.14	8.46	32.08	1.54	0.30	3.52	0.37	0.26	10.14	0.59	7.61
Spectrum 2	34.47	8.87	31.72	0.76	0.49	3.81	0.32	0.52	10.47	0.55	8.04
Spectrum 3	34.27	8.93	32.97	0.71	0.43	3.54	0.29	0.25	10.40	0.32	7.88
±SD, wt.%	34.63	8.75 ±	32.26	1.00 ±	0.41 ±	3.62 ±	0.33 ±	0.34 ±	10.34	0.49 ±	7.84 ±
(n = 3)	± 0.46	0.26	± 0.64	0.47	0.10	0.16	0.04	0.15	± 0.17	0.15	0.22

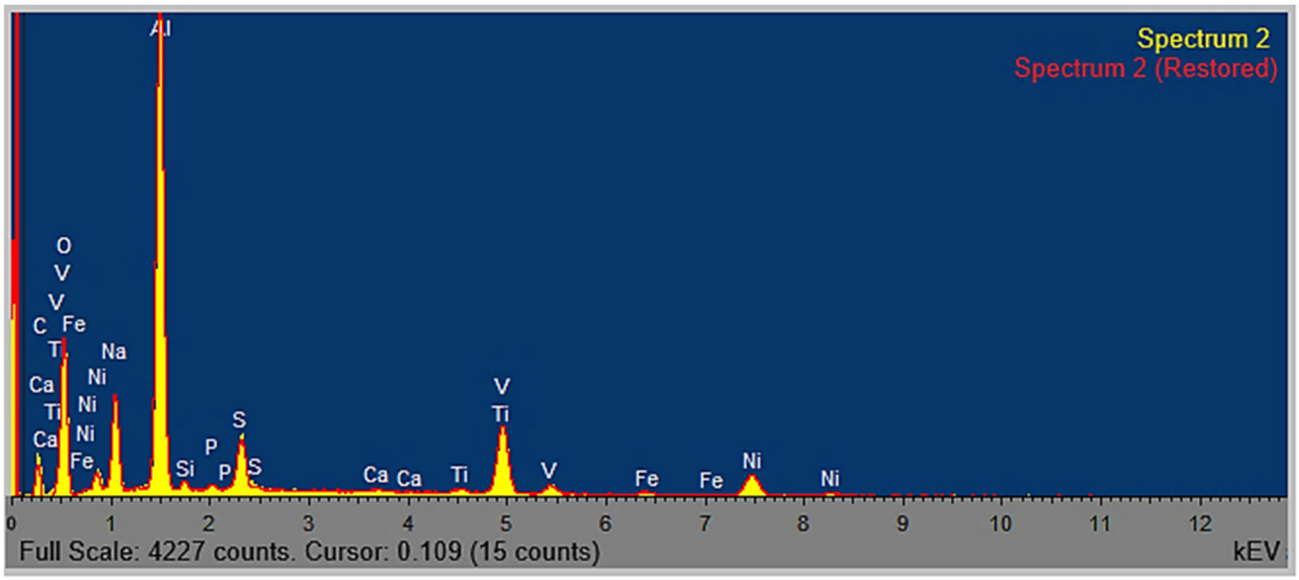


Figure 2. EDS analysis of spent vanadium-bearing catalyst.

Table 2. Chemical composition of the roasted spent vanadium-bearing catalyst.

Component	V_2O_5	Al	Na	Mo	Ni	Si	S	P	Fe
Content, wt.%	12.9	37.20	8.90	7.35	6.15	4.67	2.07	0.42	0.37

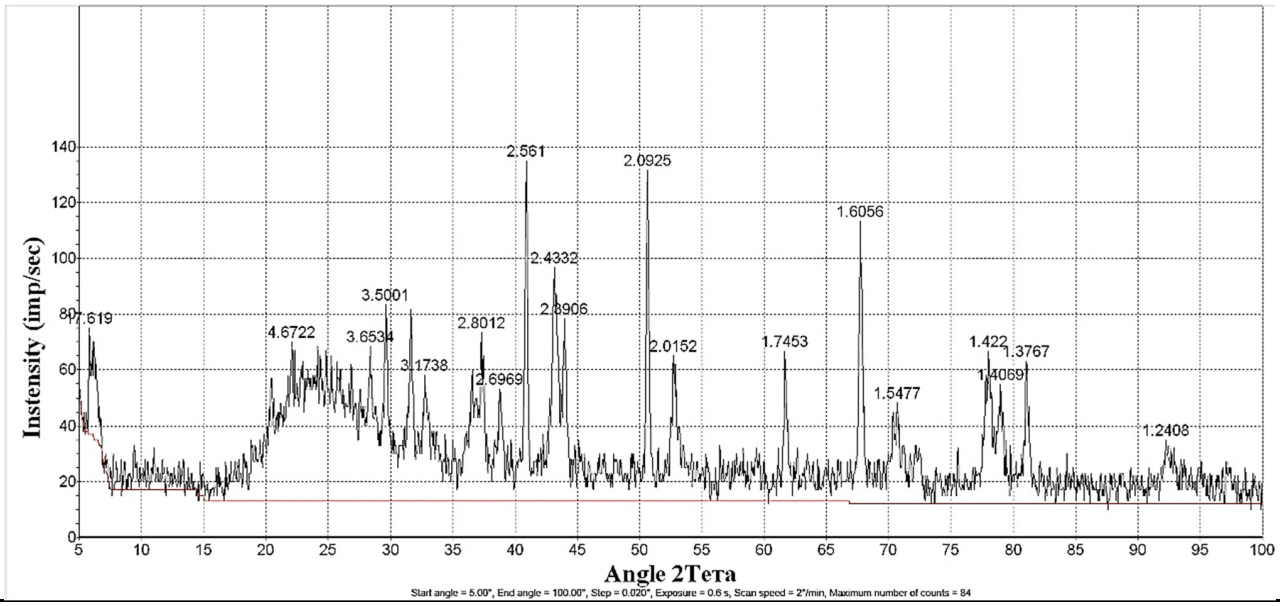
The chemical composition of the roasted spent catalyst was determined using quantitative laboratory analytical methods and is presented in Table 2. Vanadium was determined by volumetric titration according to GOST 19863.2-91, sodium by flame photometry, Fe, Al, Mo, and Ni by atomic absorption spectrometry, and Si, S, and P by wet chemical methods.

The phase composition of the ore and processing products was investigated by X-ray diffraction (XRD) using an automated DRON-3 diffractometer (Bourevestnik Inc., Saint Petersburg, Russia) with CuKα radiation and a β-filter. Diffraction patterns were recorded under the following conditions: voltage U = 35 kV, current I = 20 mA, θ–2θ scanning mode, and detector scanning rate of 2°/min. Diffractogram interpretation was conducted using the ICDD PDF-2 database (Powder Diffraction File, Release 2022) and HighScore Plus software (version: HighScore suite 4.0).

X-ray diffraction (XRD) analysis of the roasted material revealed the presence of two major crystalline phases: aluminum oxide (Al_2O_3), represented by γ-alumina and corundum (combined content of approximately 83 wt.%), and sodium vanadate ($NaVO_3$, approximately 17 wt.%). This phase composition is typical of vanadium-alumina catalysts subjected to high-temperature roasting. The corresponding XRD pattern of the roasted material is presented in Figure 3.

The chemical composition of the vanadium-bearing solution obtained after alkaline leaching of the roasted material at pH ≈ 8.8 was as follows (g/L): V_2O_5–37.0; P–0.39; S–4.5; Mo–4.7; Si–1.5; and Na–23.0.

After vanadium recovery, the molybdenum-containing mother liquor is collected separately for subsequent processing. In industrial practice, molybdenum is commonly recovered from such solutions by anion-exchange sorption followed by the production of calcium molybdate.



Phase Name	Formula	
Corundum (Cr-doped), syn	Al_2O_3	3.48; 2.55; 2.38; 2.17; 2.09; 1.96; 1.74; 1.60; 1.54; 1.51; 1.51; 1.40; 1.37; 1.33; 1.27; 1.24; 1.23; 1.19; 1.19;
Nickel Aluminum Oxide	$NiAl_2O_4$	4.64; 2.84; 2.42; 2.01; 1.64; 1.54; 1.42; 1.22;
Disodium bis(catena-vanadate)	$Na_2V_2O_6$	6.92; 5.03; 4.76; 3.95; 3.63; 3.46; 3.28; 3.19; 3.16; 2.86; 2.80; 2.77; 2.69; 2.46; 2.26; 2.19; 2.10; 1.97; 1.97; 1.96; 1.82; 1.81; 1.76; 1.51; 1.51; 1.47; 1.38;

Phase name	Content (%)
Corundum (Cr-doped), syn	12.1
Nickel Aluminum Oxide	60
Disodium bis(catena-vanadate)	28

Figure 3. X-ray diffraction pattern of the roasted spent vanadium-bearing catalyst from the petrochemical industry.

AMV was precipitated from the solution using ammonium sulfate at a V_2O_5:$(NH_4)_2SO_4$ ratio of 1:3. The precipitation process was carried out at room temperature for 60–90 min and continued until the residual vanadium concentration in the solution decreased below 0.5 g/L. The elemental composition of the resulting AMV product is presented in Table 3.

Table 3. Elemental composition of AMV precipitated using ammonium sulfate.

Spectrum	N	O	Na	Mg	Si	P	S	Ca	V
Spectrum 1	10.72	37.34	3.27	0.82	0.00	0.65	1.13	0.00	46.07
Spectrum 2	13.26	39.01	3.31	0.50	0.62	0.50	1.15	0.58	41.07
Spectrum 3	10.73	39.10	3.56	0.58	0.00	0.53	1.18	0.42	43.89
±SD, wt.% (n = 3)	11.57 ± 1.46	38.48 ± 0.99	3.38 ± 0.16	0.63 ± 0.17	0.21 ± 0.36	0.56 ± 0.08	1.15 ± 0.03	0.33 ± 0.30	43.68 ± 2.51

The analytical results indicate that the precipitated AMV contains significant amounts of impurity elements, highlighting the necessity of either solution purification prior to AMV precipitation or subsequent recrystallization of the product. Therefore, the present study focuses on the purification of vanadium-bearing solutions before AMV precipitation.

3.2. Direct Precipitation of AMV Without Solution Purification

To evaluate the effect of solution purification on the quality of the final product, control experiments were carried out by precipitating AMV directly from the productive leach solution without prior removal of phosphorus, silicon, and sulfur impurities. Ammonium sulfate, a conventional and economically favorable precipitating reagent for vanadium recovery, was used for AMV precipitation. The results showed that, in the absence of solution purification, a considerable amount of impurities was incorporated into the precipitated product. The average impurity contents in the obtained AMV samples were as follows: P–0.56 wt.%, S–1.16 wt.%, Si–0.21 wt.%, and Na–3.38 wt.%. Such impurity levels significantly limit the subsequent production of high-grade ferrovanadium (FeV80), since phosphorus, sulfur, and other impurities adversely affect the quality of the final alloy. This sensitivity of vanadium precipitation to residual impurities is consistent with earlier findings showing that phosphorus is the most detrimental impurity for vanadate precipitation, capable of reducing vanadium recovery from 98.9% to as low as 34.5% in acidic sulfate-based precipitation systems [18]. The presence of phosphorus and sodium in the untreated solution used in this study similarly compromised both the purity and the crystallinity of the precipitated product.

Representative SEM–EDS analyses of the untreated AMV are presented in Table 3 and Figure 4. Quantitative chemical composition determined by laboratory analytical methods is presented in Table 4.

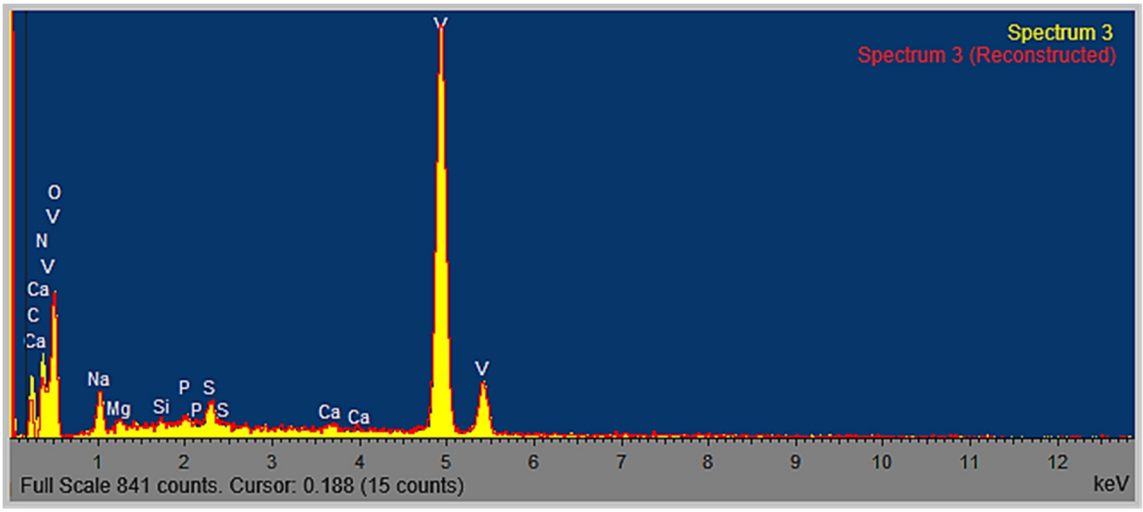


Figure 4. EDS spectrum of AMV precipitated using ammonium sulfate (precipitation carried out at room temperature for 60–90 min).

Table 4. Chemical composition of crude ammonium metavanadate precipitated from the untreated solution.

Component	V_2O_5	Al	Na	Mo	Ni	Si	S	P	Fe
Content ± SD, wt.% (n = 3)	75.30 ± 1.9	0.020 ± 0.004	0.78 ± 0.07	0.001 ND	0.022 ± 0.005	0.23 ± 0.11	0.33 ± 0.03	0.04 ± 0.006	0.0097 ND

The results of the elemental analysis demonstrated that AMV precipitated from the untreated leach solution obtained after alkaline leaching of the roasted spent catalyst contained significant amounts of impurity elements, including phosphorus, sulfur, silicon, and sodium. Such impurity levels prevent the production of a commercial-grade vanadium product and highlight the necessity of solution purification prior to AMV precipitation.

To evaluate the incorporation of impurities during direct precipitation, the chemical composition of crude AMV obtained from the untreated vanadium-bearing solution was determined using quantitative laboratory methods. The results are presented in Table 4.

The chemical composition of AMV precipitated from the MgO-purified solution is presented in Table 5. Compared with crude AMV, the purified product was characterized by substantially lower contents of sodium, silicon, sulfur, phosphorus, aluminum, molybdenum, nickel, and iron.

Table 5. Chemical composition of AMV obtained after solution purification and of the magnesium precipitate formed during purification (wt.%).

Component	V_2O_5	Al	Na	Mo	Ni	Si	S	P	Fe
Content ±SD, wt.% (n = 3)	76.80 ± 0.8	<0.001 ND	ND	<0.001 ND	0.0005 ND	0.040 ± 0.005	0.030 ± 0.0045	<0.001 ND	0.005 ND

3.3. Comparative Evaluation of Solution Purification Methods

The results obtained using ion-exchange sorption and magnesium oxide treatment for the purification of vanadium-bearing solutions from phosphorus and silicon impurities are summarized in Table 6.

Table 6. Efficiency of impurity removal from vanadium-bearing solution using two purification methods.

Parameter	Initial Solution	After Biolite 200U Anion-Exchange Treatment	After MgO Treatment	Removal Efficiency by Sorption (%)	Removal Efficiency by MgO (%)
V_2O_5, g/L	37.0 ± 1.3	27.0 ± 1.5	36.3 ± 1.01	-	-
P, g/L	0.39 ± 0.025	0.11 ± 0.03	0.04 ± 0.006	71.8	~90
Si, g/L	1.2 ± 0.05	0.065 ± 0.004	0.0 ± ND	~95	~100
V, loss, %	-	19.6 ± 0.93	<2 ± ND	-	-

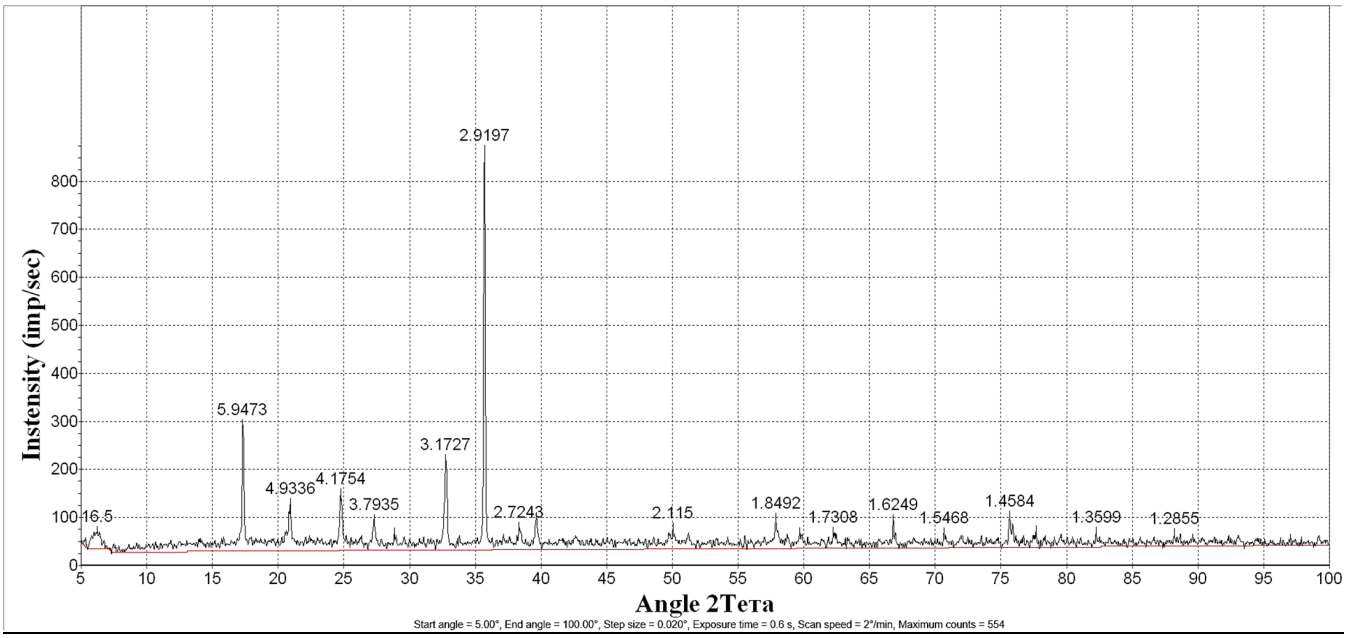
Preliminary experiments with cation-exchange resin (KU-2) showed no significant change in solution composition, indicating that cation exchange is not suitable for phosphorus/silicon removal from this alkaline vanadate solution. Anion-exchange treatment with Biolite 200U reduced phosphorus from 0.39 to 0.11 g/L (71.8% removal), but was accompanied by a pronounced decrease in V_2O_5 concentration, indicating simultaneous co-sorption of phosphorus and vanadium. This finding rules out anion exchange as a selective purification route and motivated the evaluation of the magnesium oxide method described below.

The vanadium loss observed during sorption purification (19.6%) is considerably higher than that reported for alternative silicon-removal approaches, such as sodium alumino-silicate precipitation, which achieved 97.3% silicon removal with a vanadium loss of only 1.6% [13]. This indicates that co-sorption of vanadium and phosphorus on the anion-exchange resin represents an intrinsic limitation of the sorption route when applied to productive vanadium-bearing solutions containing phosphorus.

These results compare favorably with other magnesium-based purification routes reported in the literature. A magnesium oxide treatment achieving complete phosphorus removal and 86.80% silicon removal has been reported to cause a substantially higher vanadium loss of 5.98% [15], nearly twice that observed in the present study, suggesting that the moderate treatment temperature (70–80 °C) and pH range (8.8–9.2) applied here favor selective phosphate/silicate precipitation while limiting vanadate co-precipitation. This is also in line with earlier observations that magnesium-based purification of vanadate

solutions is generally associated with non-negligible vanadium losses due to the formation of sparingly soluble magnesium vanadates [6].

X-ray diffraction analysis of the precipitates formed during magnesium oxide treatment (Figure 5) revealed the presence of brucite, $Mg(OH)_2$, and magnesium vanadate phases (MgV_2O_5).



Phase Name	Formula	
Ammonium Metavanadate	NH_4VO_3	5.93; 4.91; 4.15; 3.78; 3.17; 2.91; 2.72; 2.64; 2.50; 2.45; 2.13; 2.11; 2.07; 1.87; 1.84; 1.79; 1.73; 1.63; 1.55;
Corundum, syn	Al_2O_3	3.45; 2.35; 2.06; 1.94; 1.59; 1.50; 1.50; 1.35; 1.26; 1.22;

Phase name	Content (%)
Ammonium metavanadate	95.0
Corundum, syn	5.0

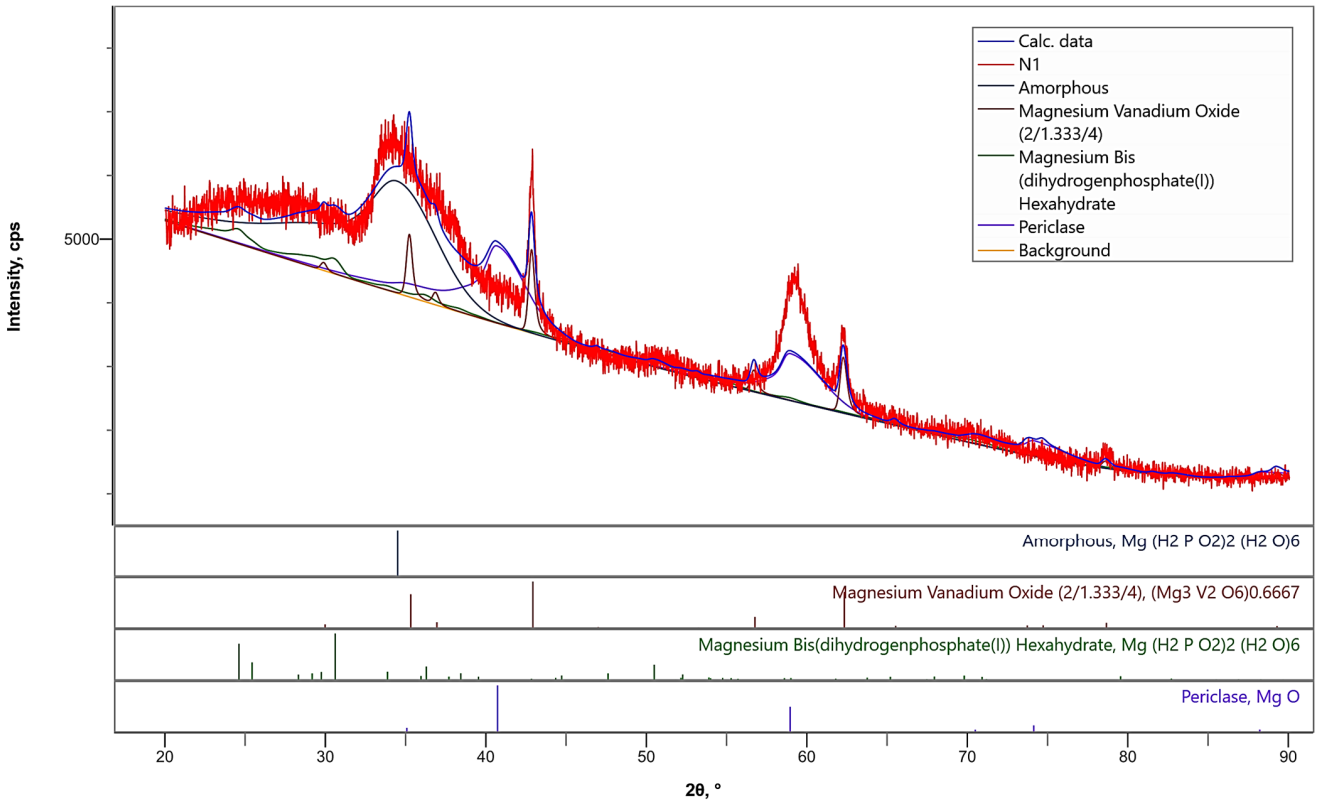
Figure 5. XRD pattern of AMV obtained from the untreated leach solution.

The formation of MgV_2O_5 confirms the co-precipitation of vanadium with the magnesium-bearing precipitate, resulting in vanadium losses of approximately 2%–2.5% and reducing the overall process efficiency of the magnesium-based purification method.

According to the chemical analysis results, the phosphorus removal efficiency reached 90%.

X-ray diffraction analysis of the AMV sample precipitated directly from the untreated leach solution identified two crystalline phases: AMV and corundum (Al_2O_3). The presence of corundum in the product indicates significant mechanical entrainment of catalyst support particles (γ-Al_2O_3) during AMV precipitation in the absence of a preliminary solution purification step. This finding is consistent with the high aluminum content determined in the precipitate by elemental analysis (Tables 1 and 2) and confirms that the production of a single-phase product is not feasible without prior purification of the solution.

According to the X-ray diffraction analysis (Figure 6), the precipitate formed during the treatment of the vanadium-bearing solution with magnesium oxide consists of four phases: periclase MgO (49 wt.%, a = 4.430 Å), an amorphous phosphate phase $Mg(H_2PO_4)_2{\cdot}6H_2O$ (27.2 wt.%), magnesium dihydrogen phosphate hexahydrate $Mg(H_2PO_4)_2{\cdot}6H_2O$ (13 wt.%), and magnesium–vanadium oxide $(Mg_3V_2O_6)_{0.67}$ (10.9 wt.%).



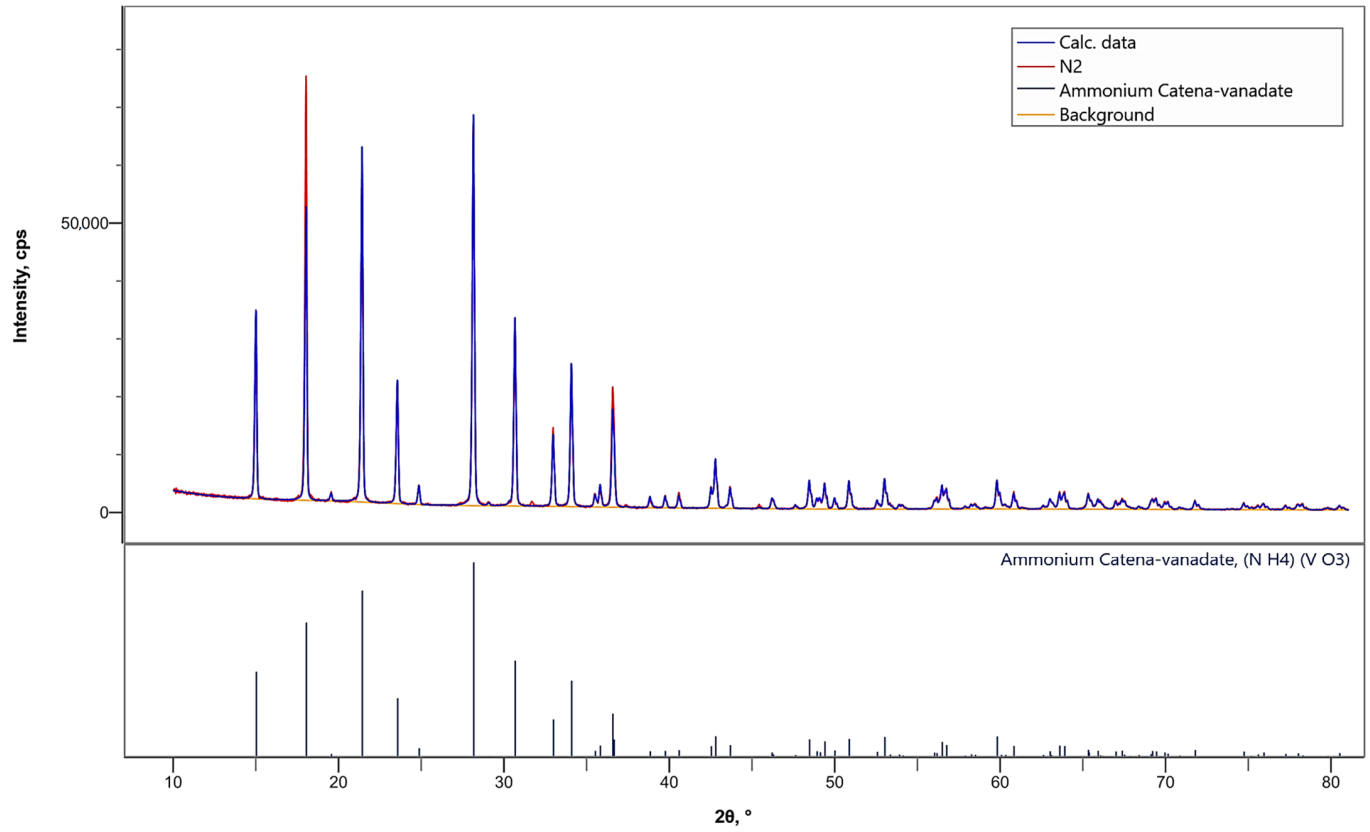
Phase	Formula	Mass Fraction, wt.%
Periclase	MgO	49(2)
Amorphous phase	$Mg(H_2PO_4)_2{\cdot}6H_2O$	27.2(14)
Magnesium–vanadium oxide	$(Mg_3V_2O_6)_{0.67}$	10.9(11)
Magnesium dihydrogen phosphate hexahydrate	$Mg(H_2PO_4)_2{\cdot}6H_2O$	13(3)

Figure 6. Phase composition of the MgO precipitate.

The predominance of periclase indicates an excess of unreacted reagent, which is attributed to the limited dissolution kinetics of MgO under alkaline conditions at pH 8.8–9.2. The combined proportion of phosphate phases (~40 wt.%) confirms the effective binding of phosphorus into sparingly soluble magnesium compounds. The presence of the vanadate phase $(Mg_3V_2O_6)_{0.67}$ provides direct evidence of vanadium co-precipitation, resulting in vanadium losses of approximately 2%–2.5%. At the same time, the relatively low content of this phase is consistent with thermodynamic data indicating that magnesium vanadate compounds are less stable than magnesium phosphate compounds in alkaline media.

X-ray diffraction analysis (XRD) of the AMV sample obtained from the purified solution revealed the presence of a single crystalline phase, AMV, with a content of 100.0% (Figure 7).

The absence of secondary crystalline phases (corundum, sulfates, or phosphates) confirms the high degree of product purification and the effectiveness of the magnesium oxide treatment stage. This result differs fundamentally from the phase composition of the AMV sample obtained without prior purification (Figure 6), in which the presence of corundum (Al_2O_3) was detected.



Compound Name	Formula	Content
Ammonium metavanadate	NH_4VO_3	100.0%

Figure 7. XRD analysis of the AMV sample obtained from the purified solution.

3.4. Comparative Evaluation

A comparison of the X-ray diffraction data for the three samples clearly demonstrates that preliminary purification of the solution with magnesium oxide is a prerequisite for obtaining single-phase, high-purity NH_4VO_3. This finding aligns with previous reports indicating that the formation of a single-phase, high-purity AMV product requires effective prior removal of co-leached impurities such as aluminum, phosphorus, and silicon [5,6], since their incorporation into the precipitate is otherwise unavoidable regardless of the precipitating reagent used.

The introduction of the purification stage prevents the co-precipitation of aluminum-containing phases and reduces contamination of the final product to a level that meets the requirements for metallurgical-grade V_2O_5. The partial vanadium losses (2%–2.5%) associated with the formation of $Mg_3V_2O_6$ are considered an acceptable technological trade-off for achieving the observed purification efficiency (~90% P removal and ~100% Si·removal).

3.5. Quality of AMV After Solution Purification

The precipitation of ammonium metavanadate using ammonium chloride from the magnesium oxide-purified solution yielded a product containing less than 0.001 wt.% phosphorus and 0.03 wt.% sulfur, while sodium was not detected. The significant reduction in impurity concentrations confirms the effectiveness of the developed purification process and demonstrates its suitability for the production of high-purity ammonium metavanadate.

The substitution of ammonium sulfate with ammonium chloride eliminated the introduction of additional sulfur into the final product and extends the purification strategy previously proposed for vanadium-bearing secondary raw materials contaminated with phosphorus and sulfur [5]. Furthermore, the developed process provides a greater reduction in phosphorus content than that achieved by sorption-based purification alone [11,12].

The residual sulfur content (0.03 wt.%) can be attributed to the partial incorporation of sulfate ions remaining in the process solution into the adsorption layer of the growing AMV crystals, a phenomenon commonly observed in sulfate-containing systems.

X-ray diffraction analysis confirmed that the purified product consisted of a single orthorhombic NH_4VO_3 phase (PDF Card No. 00-076-0191), indicating that the developed purification process effectively prevented the formation of secondary crystalline phases.

3.6. Limitations of the Study

The present study has several analytical and methodological limitations that should be considered when interpreting the results. First, some impurity concentrations in the purified ammonium metavanadate were close to or below the detection limits of the analytical methods used. Therefore, values reported as "ND" or below a specified concentration should be interpreted as being below the detection limit of the corresponding analytical method rather than as confirming the complete absence of the element. More sensitive instrumental techniques, such as inductively coupled plasma optical emission spectrometry (ICP–OES) or inductively coupled plasma mass spectrometry (ICP–MS), could provide more accurate quantification of trace impurities in future studies.

Second, X-ray diffraction was used to identify the principal crystalline phases in the roasted catalyst, the AMV products, and the precipitate formed during MgO purification. Although XRD provided important information on the phase transformations occurring during processing, conventional laboratory XRD has limited sensitivity for minor, poorly crystalline, and amorphous phases. Consequently, trace secondary phases may remain undetected. Complementary characterization by Fourier-transform infrared spectroscopy (FTIR) could provide additional information on vanadate, phosphate, sulfate, and hydroxyl-containing species, particularly in the precipitates formed during solution purification.

Particle-size distribution was not determined in the present study. Such measurements could provide additional information on AMV crystal growth, agglomeration, settling, and filtration behavior and could help clarify the influence of precipitation conditions on the physical properties of the final product. Future studies should therefore include an appropriate particle-size characterization technique, including dynamic light scattering (DLS) where applicable to the particle-size range and dispersion state of the investigated material.

Finally, the experiments were conducted at laboratory scale. Although the proposed process is based on conventional hydrometallurgical operations and commercially available reagents, scale-up may affect mixing and mass-transfer conditions, reagent consumption, solid–liquid separation, recycle streams, and impurity accumulation. Therefore, pilot-scale validation, together with more sensitive trace-element analysis, complementary structural characterization, particle-size measurements, and a detailed techno-economic assessment, is required before full-scale industrial implementation.

4. Conclusions

In this study, an integrated process flowsheet for the treatment of spent vanadium-bearing catalysts from the petrochemical industry was developed and validated, enabling

the production of high-purity AMV as an intermediate product for V_2O_5 synthesis. Alkaline leaching of roasted catalysts ensured the transfer of vanadium into solution with an extraction efficiency of 90%–95%, while simultaneously dissolving significant amounts of impurities, including phosphorus (0.39 g/L), sulfur (4.5 g/L), silicon (1.5 g/L), and molybdenum (4.7 g/L), thereby precluding the production of a commercial-grade product without prior solution purification.

A comparative evaluation of two purification methods for vanadium-bearing solutions revealed substantial differences in their efficiency and selectivity. Sorption on the macroporous anion-exchange resin Biolite 200U provided effective silicon removal (~95%); however, it was accompanied by considerable vanadium losses (up to 19.6%) due to co-precipitation with phosphorus, rendering this approach unsuitable for the purification of productive vanadium-bearing solutions. In contrast, treatment with magnesium oxide at 70–80 °C and pH 8.8–9.2 reduced the phosphorus concentration from 0.39 to 0.04 g/L (approximately 90% removal efficiency) and completely removed silicon, while limiting vanadium losses to no more than 2%–2.5%, demonstrating the high selectivity of this reagent.

The precipitation of AMV using ammonium chloride from the magnesium oxide-purified solution at a molar ratio of V_2O_5:NH_4Cl = 1:2 and pH 8.8–9.0 resulted in a vanadium recovery of 99%, with a residual V_2O_5 concentration of 0.2–0.5 g/L in the mother liquor. The obtained product contained less than 0.001 wt.% phosphorus and 0.03 wt.% sulfur, while sodium was not detected. X-ray diffraction analysis confirmed the formation of a single orthorhombic NH_4VO_3 phase. The use of ammonium chloride instead of the conventionally employed ammonium sulfate eliminated the introduction of additional sulfur into the final product.

The results demonstrate that the optimal processing route comprises alkaline leaching, solution purification with magnesium oxide, and AMV precipitation using ammonium chloride. The developed flowsheet enables the production of high-purity NH_4VO_3 suitable for subsequent thermal decomposition to metallurgical-grade V_2O_5 and provides an effective route for the hydrometallurgical processing of vanadium-bearing secondary raw materials.

From a practical standpoint, the purity of the obtained product supports the feasibility of the proposed technology: the AMV/V_2O_5 product meets the requirements of GOST 27130-94 for ferrovanadium FeV80 (impurity metals $\leq$ 0.3 wt.%, S $\leq$ 0.05 wt.%, P $\leq$ 0.06 wt.%, Si $\leq$ 2.0 wt.%, V_2O_5 $\geq$ 80 wt.%) and approaches the technical-grade ammonium metavanadate specification of GOST 2548-44 used for vanadium electrolyte production, with a single additional recrystallization step sufficient to reach electrolyte-grade purity for vanadium redox-flow battery applications. All process stages (alkaline leaching, MgO-based purification, and ammonium chloride precipitation) employ low-cost, commercially available reagents and conventional hydrometallurgical equipment operated at atmospheric pressure and moderate temperature, which is favorable for scale-up to pilot and industrial levels. Compared with ion-exchange-based purification, the proposed reagent-based route is expected to reduce processing costs by eliminating an additional desulfurization step, although a detailed techno-economic evaluation remains the subject of future work.

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Abbreviations

The following abbreviations are used in this manuscript:

HDS	Hydrodesulfurization
AMV	Ammonium Metavanadate
EDS	Energy-Dispersive X-Ray Spectroscopy
XRD	X-ray diffraction analysis

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