

Article

Short-Process Preparation of High-Purity V_2O_5 from Shale Acid Leaching Solution via Chlorination

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Abstract: The conventional V_2O_5 preparation processes include ion exchange, chemical precipitation, solvent extraction, and other processes. Given the long process and complex operation nature of traditional V_2O_5 production methods, we herein developed a short-process, low-temperature, and convenient operation method of isolating vanadium (in the form of V_2O_5) from shale acid leaching solution. The acid leaching solution was oxidized with $NaClO_3$ and pH-adjusted with $NaOH$ to form a vanadium-containing precipitate, which was mixed with $AlCl_3$ ($V:AlCl_3 = 1:5$, mol/mol) and roasted for 120 min at 170 °C to afford vanadium oxytrichloride ($VOCl_3$) with a purity of 99.59%. In addition, the vanadium-containing precipitate was mixed with $AlCl_3$ and $NaCl$ ($V:AlCl_3:NaCl = 3:12:8$, mol/mol/mol) and roasted for 120 min at 170 °C to afford $VOCl_3$ with a purity of 99.94%. $VOCl_3$ (purity of 99.94%) was dissolved in ultrapure water, and the solution (32 g_{vanadium}/L) was treated with $NH_3 \cdot H_2O$ ($NH_3:V = 1.34$, mol/mol) at 50 °C for 120 min. The obtained precipitate (vanadium precipitation rate = 99.28%) was roasted at 550 °C for 3 h to afford high-purity vanadium pentoxide (V_2O_5) with a purity of 99.86%. Compared with the traditional hydrometallurgical method of V_2O_5 preparation, our method avoided solvent extraction and other undesired processes and the overall process flow is greatly shortened, thus having high practical value.

Keywords: chlorination; high-purity vanadium pentoxide; short-process; aluminum chloride; vanadium oxytrichloride



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1. Introduction

The application scope of vanadium has expanded beyond iron-/steelmaking, military, and medical industries [1–4] to include functional materials (e.g., nanocomposites), high-performance alloys, and all-vanadium liquid-flow batteries [5–13]. In particular, the abovementioned batteries represent a new high-efficiency energy storage technology and energy-development direction, which highlights the strategic importance of vanadium resources [14–16]. The steel industry is a major area of interest for vanadium products. Vanadium has greatly helped to improve the hardness, toughness, wear resistance, and high temperature-resistance of steel alloys products. With the continuous development and expansion of new fields, such as vanadium-based materials, vanadium nitrogen alloys, vanadium electrode products, high-purity vanadium-containing materials, and all vanadium liquid flow batteries, the market demand for high-quality vanadium-containing products will continue to increase. This rapid expansion places high requirements on the quality and quantity of vanadium compounds, of which V_2O_5 is the most stable and

widely used [17,18]. Therefore, much attention has been drawn to the facile and efficient production of high-purity V_2O_5 .

V_2O_5 is mainly produced through hydrometallurgical and chlorination methods, among which the most common method of separating and purifying metallurgical-grade vanadium products is through hydrometallurgical methods to achieve the purification and enrichment of vanadium [19,20]. However, all hydrometallurgical processes widely used for vanadium recovery, e.g., ion exchange, solvent extraction, adsorption, and precipitation [21], exhibit certain drawbacks. For example, emulsification and flocculation during solvent extraction, rapid extractant loss, organic phase loss through entrainment, re-extraction difficulty, and impurity transfer compromise product quality and complicate organic-phase purification. The ion exchange method has a long cycle time and high salt consumption and generates excessive regeneration waste streams, and the presence of organic substances can contaminate ion exchange resins and discharge a large amount of salty wastewater [22–24], which can easily cause the corrosion of pipelines. In addition, when there are multiple ions in the solution, different resins need to be selected for different ions, resulting in poor universality. The use of chemical precipitation requires the introduction of large amounts of chemical agents, resulting in the secondary pollution of precipitated waste residues.

Unlike their hydrometallurgical counterparts, chlorination-based processes offered the benefits of simplicity, low pollution, low cost, and high selectivity [25–32], and the preparation of V_2O_5 from vanadium-containing raw materials with chlorinating agents is therefore drawing much attention [33]. Chlorination is typically performed using Cl_2 , and the resulting $VOCl_3$ (purity $\geq 99.9\%$) reacts with $NH_3 \cdot H_2O$ in an aqueous medium to afford precipitates that are subsequently converted into V_2O_5 [34–36]. Although this method is time-efficient, it requires the handling of the highly corrosive and toxic Cl_2 and $VOCl_3$, thus necessitating the use of highly corrosion-resistant industrial equipment and strict safety protocols. In addition, the use of high roasting temperatures increases energy consumption and, hence, production costs. Zheng et al. [37] used $FeCl_x$ as a chlorination agent to extract vanadium from vanadium-bearing titanium magnetite. Under a roasting temperature of 900–1300 K and oxygen atmosphere, the extraction rate of vanadium increases with the increase in temperature and then decreases with the increase in temperature. Using $FeCl_3$ as a chlorinating agent and holding at 1100 K for 2 h, the extraction rate of vanadium can reach 32%. Du et al. [38] extracted 96.36% V and 4.23% Ti from tailings containing 10% petroleum coke via chlorination roasting for 1 h at 800 °C with a chlorine pressure fraction of $[P(Cl_2)/P(Cl_2 + N_2)] = 0.5$. Further purification of the collected chlorinated products resulted in the production of $VOCl_3$ with a purity higher than 99.99%. Wu et al. [27] proposed a method of recovering vanadium from carbonaceous gold ores based on the use of NaCl as a chlorinating agent to separate vanadium, gold, zinc, and iron. However, the temperature of the suggested chlorination reaction is as high as 800 °C. Further, we found that $VOCl_3$ can be prepared below 200 °C when $AlCl_3$ is used as a chlorinating agent. Jiang et al. [1] used anhydrous aluminum chloride and sodium chloride to purify industrial-grade V_2O_5 with a purity of 96% at low temperatures of 170 °C, and the high-purity V_2O_5 with a purity of at least 99.97% was obtained. The novel method of V_2O_5 preparation is highly selective for vanadium. Therefore, using a chlorination method to prepare high-purity V_2O_5 has received great attention.

Herein, based on the abovementioned previous works, we developed a short-process method of preparing V_2O_5 from shale acid leaching solution. Based on the difference in boiling points of $VOCl_3$ and $FeCl_3$, $MgCl_2$, $NaCl$, KCl , $CrCl_3$, $MoCl_6$ and $NiCl_2$, through the use of chlorinated metallurgical methods, a vanadium precipitate was obtained by precipitating vanadium from acid leaching solution; the vanadium precipitate was roasted with $AlCl_3$ at a low temperature, and then, a high-purity $VOCl_3$ product was obtained, which was then hydrolyzed through treatment with $NH_3 \cdot H_2O$, and the precipitate was roasted to obtain high-purity V_2O_5 . Unlike conventional chlorination techniques, our method avoided the ion exchange, chemical precipitation, solvent extraction, and other undesired processes, and the overall preparation process of V_2O_5 has been shortened. The

short preparation process of V_2O_5 in this study also avoids the use of the toxic and corrosive Cl_2 and does not require excessively high temperatures, thus holding great promise for cost-effective and facile vanadium recovery.

2. Materials and Methods

2.1. Materials

The acid leaching solution used in this study originated from Xi'an, Shanxi, China. Table 1 lists the concentrations of major elements in the shale acid leaching solution used as the raw material. Other reagents were chemically pure and did not require further purification. Nitrogen (99.999%, Wuhan NRD, China) was used as a protective gas, and ultrapure water was used throughout the experiments.

Table 1. Concentrations of major elements in the shale acid leaching solution (g/L).

Element	V	Na	K	Mg	Fe	Al	P	Ni	Mo	Cr	S
Concentration	2.32	0.69	0.81	14.02	3.76	2.11	0.58	1.74	0.02	0.23	51.24

2.2. Procedure for Short-Process Preparation of V_2O_5

The short-process preparation of V_2O_5 includes three steps; the first step is vanadium precipitation from the shale acid leaching solution, and the precipitate is obtained. The second step is precipitate chlorination (using nitrogen for protection); vanadium and impurities of the precipitate are separated in one step via chlorination, and the high-purity $VOCl_3$ is obtained. The third step is ammonolysis of the $VOCl_3$ to obtain NH_4VO_3 , which is calcined to obtain V_2O_5 . The diluted sulfuric acid solution is used to absorb the ammonia gas generated during the calcination process. Figure 1 represents the flow chart of this process.

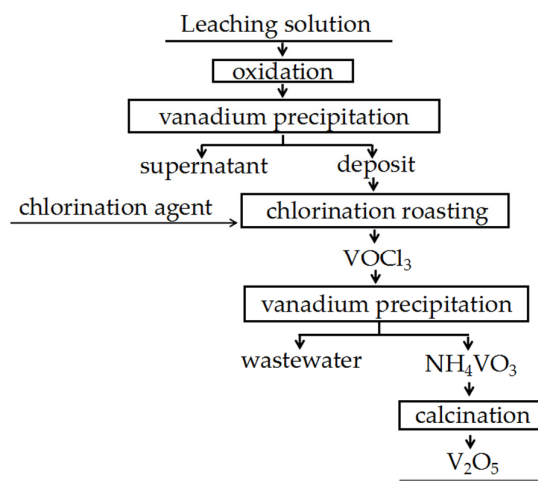


Figure 1. Flow chart of short-process preparation of V_2O_5 .

2.2.1. Precipitation of Vanadium from Acid Leaching Solution

The acid leaching solution was oxidized by adding $NaClO_3$ (2.8 g $NaClO_3$ was added to 500 mL of acid leaching solution), pH-adjusted to 5.5 using $NaOH$, and stirred at 30 °C for 150 min. The precipitate was isolated via filtration and dried at 60 °C for 3 h.

2.2.2. Chlorination of Precipitate Isolated from Leaching Solution

Before conducting chlorination experiments, nitrogen gas needs to be continuously introduced into the reaction device to eliminate excess water vapor. The precipitate isolated from the leaching solution was mixed with the chlorinating agent and roasted in the three-necked flask at a set roasting temperatures and times. The generated gaseous $VOCl_3$ was condensed into a liquid and collected in a flask. The tail gas treatment device equipped

with NaOH solution was used to absorb the uncondensed gaseous VOCl_3 and other tail gases in the chlorination reaction. The diagram of the chlorination reaction experimental device is shown in Figure 2.



Figure 2. The experimental device of the chlorination reaction.

The vanadium extraction rate (ω_v) was calculated as follows:

$$\omega_v = \frac{m_1 \times 50.942}{m_0 \omega_0 \times 173.299} \times 100\%, \quad (1)$$

where m_0 is the mass of the vanadium-containing precipitate (g), ω_0 is the mass fraction of vanadium in the precipitate, m_1 is the mass of VOCl_3 (g), 50.942 is the molar mass of V (g/mol), and 173.299 is the molar mass of VOCl_3 (g/mol).

2.2.3. Ammonolysis of VOCl_3

VOCl_3 is very unstable, generating red smoke upon contact with water or water vapor. Herein, VOCl_3 was dissolved in ultrapure water, and the solution was treated with $\text{NH}_3 \cdot \text{H}_2\text{O}$ at different $\text{NH}_3\text{:V}$ molar ratios. The resulting precipitate was roasted at 550 °C for 3 h to afford V_2O_5 .

2.3. Characterization of VOCl_3 and V_2O_5

The concentrations of major elements in the shale acid leaching solution, the composition content of the precipitate isolated from the acid leaching solution, the impurity content in the VOCl_3 , and the high-purity V_2O_5 product were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES; model 730, Agilent Co., Ltd., Shanghai, China). The compositions of V_2O_5 and the chlorination residue were determined via X-ray diffraction (XRD) (Smart-Lab SE, Rigaku Co., Ltd., Tokyo, Japan). The operation conditions for XRD were as follows: light tube voltage, 40 Kv; light tube current, 40 Ma; scanning angle range, 5°–90°; scanning speed, 15.6°/min. Moreover, micro-morphologies and elemental distributions were determined via scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) (JSM-IT300, JEOL Co., Ltd., Tokyo, Japan). The operation conditions for SEM–EDS were as follows: acceleration voltage, 20–30 Kv; the mode was switched to high current one when analyzing samples. The pH of the solution was measured using a pH meter (PHS-3C Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China).

3. Results and Discussion

3.1. Analysis of Precipitate Isolated from Acid Leaching Solution

Table 2 represents the composition of the resulting precipitate, while Figures 3 and 4 represent the corresponding XRD pattern and SEM–EDS data, respectively.

Table 2. Composition (wt%) of the precipitate isolated from the acid leaching solution.

Component	V ₂ O ₅	Fe ₂ O ₃	MgO	Al ₂ O ₃	Na ₂ O	Cr ₂ O ₃	P ₂ O ₅	NiO	MoO ₃	K ₂ O	SO ₃
Content	7.52	3.81	14.10	12.88	17.45	0.21	0.68	0.43	0.15	1.76	36.15

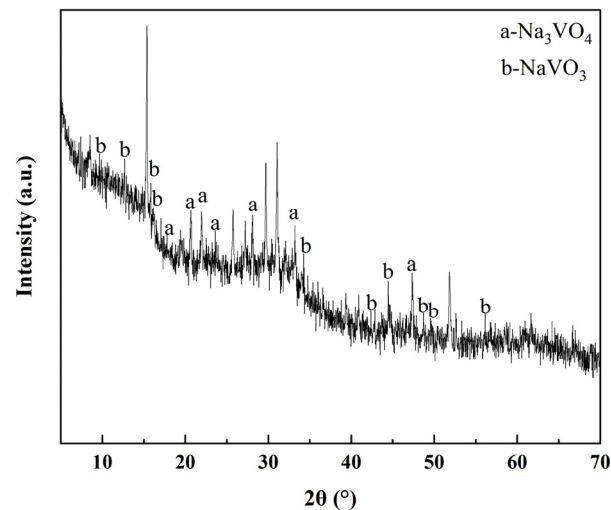
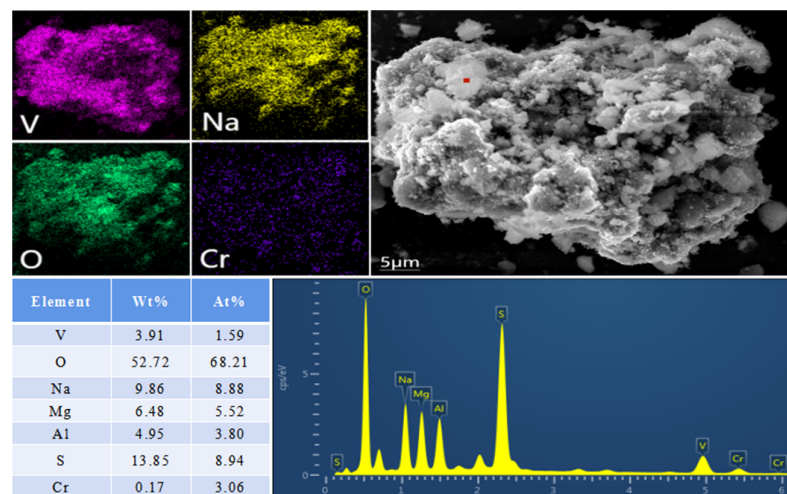
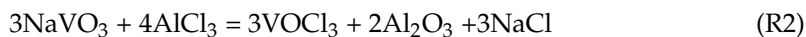
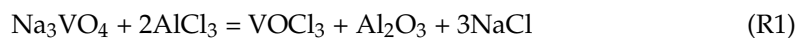
**Figure 3.** XRD pattern of the precipitate isolated from the acid leaching solution.**Figure 4.** SEM-EDS characterization of the precipitate isolated from the acid leaching solution.

Figure 3 shows that the diffraction peaks of Na_3VO_4 and NaVO_3 were present in the XRD patterns of the precipitate isolated from the acid leaching solution. Figure 4 shows that in addition to vanadium, the precipitate contained sodium and oxygen, which is consistent with the results of the XRD analysis. The precipitate contained a significant amount of sodium; the reason is that the acid leaching solution introduces a large amount of sodium when the pH is adjusted with NaOH. Due to the high concentrations of magnesium, aluminum, and sulfur in the acid leaching solution, magnesium, aluminum, and sulfur are introduced into the precipitate during the vanadium precipitation process.

3.2. Thermodynamic Analysis of Chlorination Reaction

The precipitate isolated from the acid leaching solution was used as raw material, and AlCl_3 was used as the chlorination agent. Based on the composition of the precipitate

isolated from the acid leaching solution, the following reactions (R1)~(R10) may occur in the chlorinated system:



The Gibbs free energy changes of the above reactions, (R1)~(R10), at different temperatures were calculated based on corresponding thermodynamic data from the HSC 6.0 software package, as shown in Figure 5.

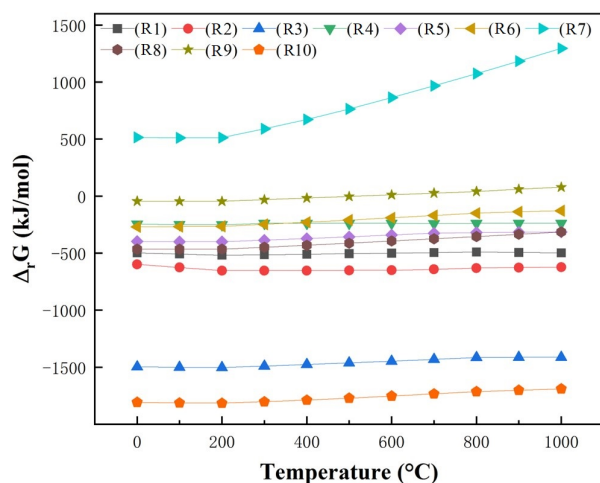


Figure 5. Gibbs free energy changes of related reactions at different temperatures.

Figure 5 shows that AlCl_3 was used as a chlorination agent, and Gibbs free energy changes were negative below 1000 °C for the chlorination reaction of Na_3VO_4 and NaVO_3 , which indicates that VOCl_3 can be formed in chlorinated systems. Gibbs free energy changes were positive below 1000 °C for the chlorination reaction of P_2O_5 , which indicates that the chlorination reaction of P_2O_5 is not favorable. Even though Gibbs free energy changes were negative below 500 °C for the chlorination reaction of Na_2O , Fe_2O_3 , MgO , Cr_2O_3 , NiO , MoO_3 , and K_2O , according to Table 3, we know that FeCl_3 , MgCl_2 , NaCl ,

MoCl_6 , NiCl_2 , CrCl_3 , and KCl were non-volatile below 200 °C. Therefore, we speculated that when AlCl_3 functioned with the vanadium-containing precipitate isolated from the acid leaching solution, the high-purity VOCl_3 could be prepared.

Table 3. Physical and chemical properties of chloride.

Chloride	Melting Point/°C	Boiling Point/°C
VOCl_3	−77	126
FeCl_3	306	316
MgCl_2	714	1412
AlCl_3	194	178
NaCl	801	1465
MoCl_6	249	352
NiCl_2	1001	973
CrCl_3	1152	1300
PCl_5	180	375
KCl	773	1500

3.3. Effects of Chlorination Parameters

3.3.1. Temperature

The effects of the chlorination temperature (100–220 °C) were explored under a protective atmosphere of nitrogen at a reaction time of 120 min and a $\text{V}:\text{AlCl}_3$ molar ratio of 1:4 (Figure 6).

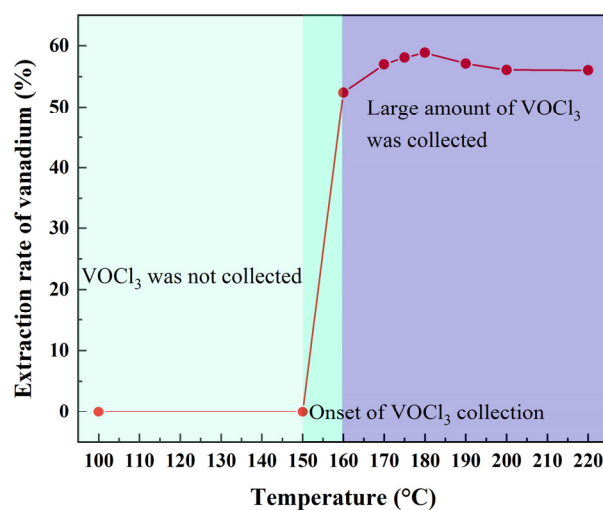


Figure 6. Effects of chlorination temperature on the extraction rate of vanadium.

Figure 6 shows that VOCl_3 collection started at 150 °C and that the extraction rate increased with increasing temperature and reached a maximum at 180 °C. After 180 °C, the extraction rate decreased with increasing temperature and plateaued after 200 °C. The decrease in the vanadium extraction rate is due to the boiling point of AlCl_3 being 178.8 °C, and when the chlorination reaction temperature is above 180 °C, AlCl_3 is heavily sublimated, resulting in a less efficient chlorination reaction.

3.3.2. Dosage of AlCl_3

The effects of the AlCl_3 dosage ($\text{V}:\text{AlCl}_3 = 1:1, 1:2, 1:3, 1:4$, and $1:5$ mol/mol) on the vanadium extraction rate and VOCl_3 purity were examined at 170 °C using a reaction time of 120 min and nitrogen as the carrier and protective gas (Figure 7 and Table 4).

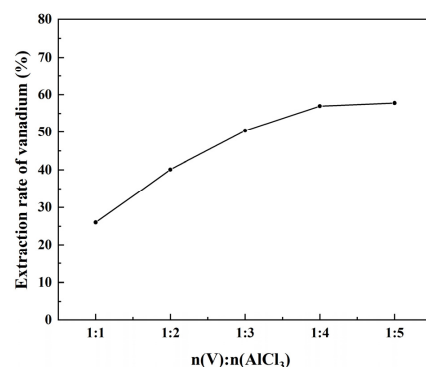


Figure 7. Effects of AlCl₃ dosage on the vanadium extraction rate.

Table 4. Effects of AlCl₃ dosage on the purity of VOCl₃.

N(V):n(AlCl ₃)	Impurity Content (%)									VOCl ₃ Purity (%)
	Na	Fe	Mg	Al	Ni	Mo	Cr	P	K	
1:1	0.1157	0.1134	0.1016	0.1970	0.1061	0.0517	0.1110	0.0515	0.1012	99.05%
1:2	0.1166	0.1032	0.1028	0.1365	0.1075	0.0250	0.1032	0.0222	0.0230	99.26%
1:3	0.1078	0.1009	0.1021	0.1083	0.1063	0.0508	0.1004	0.0024	0.0515	99.27%
1:4	0.1053	0.1055	0.1044	0.1040	0.0507	0.0503	0.0505	0.0193	0.0505	99.38%
1:5	0.0531	0.0531	0.0557	0.1065	0.0502	0.0201	0.0502	0.0101	0.0101	99.59%

With an increasing AlCl₃ dosage, the vanadium extraction rate increased, while the purity of VOCl₃ remained above 99%. Thus, considering the vanadium extraction rate, VOCl₃ purity, and cost, we identified the optimum V:AlCl₃ molar ratio as 1:5, which corresponded to a VOCl₃ purity of 99.59%.

3.3.3. Effect of Temperature on Chlorination in the Presence of NaCl

Based on FactSage-7.2 software package, with an AlCl₃:NaCl molar ratio of 3:2, the chlorination temperature is above 156.70 °C and AlCl₃ and NaCl can form a molten salt liquid (NaAlCl₄). Further, the effects of temperature on chlorination in the presence of NaCl were explored under a protective atmosphere of nitrogen at a reaction time of 120 min, a V:AlCl₃ molar ratio of 1:4, and an AlCl₃:NaCl molar ratio of 3:2.

Figure 8 shows that VOCl₃ collection started at 150 °C and that the extraction rate increased with an increasing temperature and plateaued after 160 °C. AlCl₃ and NaCl were used as the chlorinating agent, and there was no AlCl₃ sublimation; the reason is that the boiling point of NaAlCl₄ is much higher than the chlorination reaction temperature. Therefore, 170 °C was chosen as the optimal temperature.

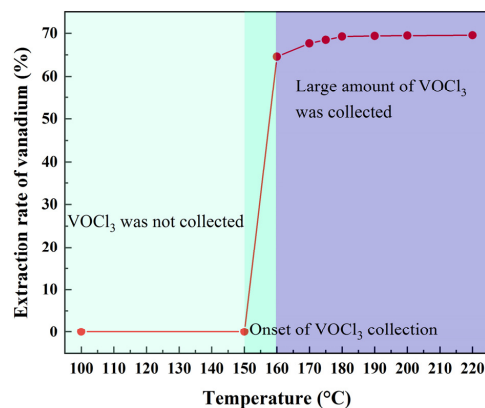


Figure 8. Effects of temperature on the vanadium extraction rate in the presence of NaCl.

3.3.4. Effect of AlCl_3 and NaCl Dosage on Chlorination

The effects of the AlCl_3 and NaCl dosage ($\text{V}:\text{AlCl}_3:\text{NaCl} = 3:3:2, 3:6:4, 3:9:6, 3:12:8$, and $3:15:10$ mol/mol) on the vanadium extraction rate and VOCl_3 purity were examined at 170°C using a reaction time of 120 min and nitrogen as the carrier and protective gas (Figure 9 and Table 5).

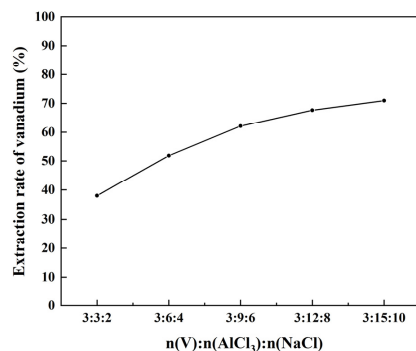


Figure 9. Effects of AlCl_3 and NaCl dosage on the vanadium extraction rate.

Table 5. Effects of AlCl_3 and NaCl dosage on the purity of VOCl_3 .

N(V):n(AlCl ₃):n(NaCl)	Impurity Content (%)									VOCl ₃ Purity (%)
	Na	Fe	Mg	Al	Ni	Mo	Cr	P	K	
3:3:2	0.0157	0.0134	0.0016	0.0470	0.0061	0.0017	0.0110	0.0015	0.0012	99.91%
3:6:4	0.0166	0.0032	0.0028	0.0465	0.0075	0.0030	0.0032	0.0002	0.0030	99.91%
3:9:6	0.0078	0.0009	0.0021	0.0483	0.0063	0.0008	0.0004	0.0004	0.0005	99.93%
3:12:8	0.0053	0.0055	0.0044	0.0440	0.0007	0.0003	0.0005	0.0003	0.0005	99.94%
3:15:10	0.0031	0.0031	0.0057	0.0465	0.0002	0.0001	0.0002	0.0001	0.0001	99.95%

Molten salt liquid (NaAlCl_4) can improve the vanadium extraction rate and purity of VOCl_3 . With the addition of NaCl , the vanadium extraction rate increased, while the purity of VOCl_3 remained above 99.9%. Thus, considering the vanadium extraction rate, VOCl_3 purity, and cost, we identified the optimum $\text{V}:\text{AlCl}_3:\text{NaCl}$ molar ratio as 3:12:8, which corresponded to a VOCl_3 purity of 99.94%.

3.4. Analysis of Chlorination Residue

After the chlorination reaction was completed, fibrous substances were found in the chlorination residue. Afterwards, we extracted the fibrous substances from the chlorination residue for analysis. Figure 10 shows that aluminum, oxygen, and chlorine had obvious interactions in the fibrous substances, which had an $\text{Al}:\text{O}:\text{Cl}$ molar ratio close to 1:1:1 according to SEM-EDS analysis.

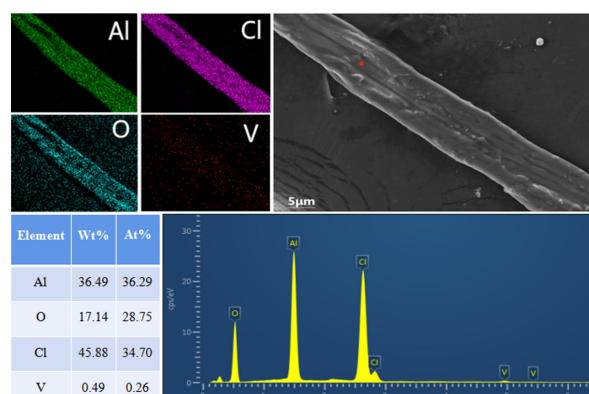


Figure 10. SEM-EDS characterization of fibrous substances formed during chlorination.

Figure 11 represents the XRD pattern of the chlorination residue and shows that the diffraction peaks of NaAlCl_4 and AlOCl appeared in the chlorination residue, which is consistent with the SEM–EDS analysis of fibrous substances and the fact that AlCl_3 and NaCl can form a molten salt liquid (NaAlCl_4). Thus, we concluded that these fibrous substances corresponded to AlOCl .

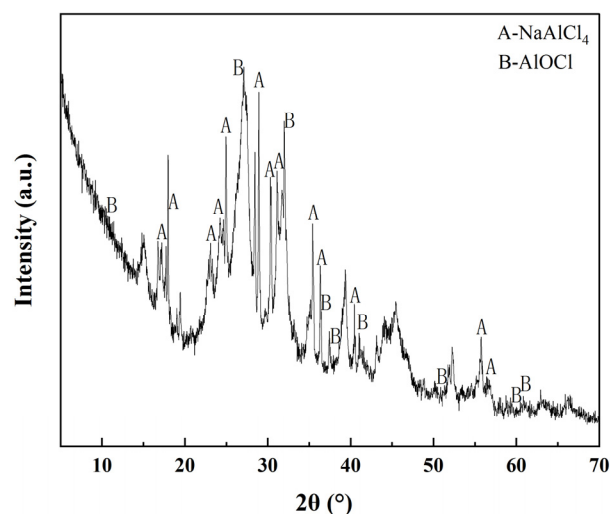


Figure 11. XRD pattern of chlorination residue during chlorination.

Based on the above conclusion, regardless of the presence of NaCl in the chlorination system, we speculate that the chlorination reaction mechanism is that the oxygen atoms in Na_3VO_4 and NaVO_3 first replace the two chlorine atoms in AlCl_3 . The replaced chlorine atoms chlorinate Na_3VO_4 and NaVO_3 to generate VOCl_3 . The chlorine atom in AlCl_3 is gradually replaced, resulting in a transition from AlCl_3 to AlOCl to Al_2O_3 . The corresponding chemical equations are as follows:



3.5. V_2O_5 Preparation from VOCl_3 Solution

3.5.1. Effects of VOCl_3 Hydrolysis Parameters

Given the extreme instability of VOCl_3 and considering the loss of vanadium and operation feasibility, we dissolved VOCl_3 in ultrapure water to prepare a solution with a vanadium concentration of 32 g/L and then treated it with $\text{NH}_3 \cdot \text{H}_2\text{O}$ to afford a precipitate that was subsequently converted to V_2O_5 .

Figure 12a–c shows the influence of the NH_3 :V molar ratio, precipitation temperature, and precipitation time on the vanadium precipitation rate. For this investigation, the vanadium precipitation temperature was 20 °C and the vanadium precipitation time was 30 min. With an increasing NH_3 :V molar ratio, the vanadium precipitation rate increased to a maximum of 96.54% at a ratio of 1.34 and then decreased, which was ascribed to the dissolution of vanadium species in the presence of excess ammonia. Thus, the NH_3 :V molar ratio of 1.34 was selected as optimal.

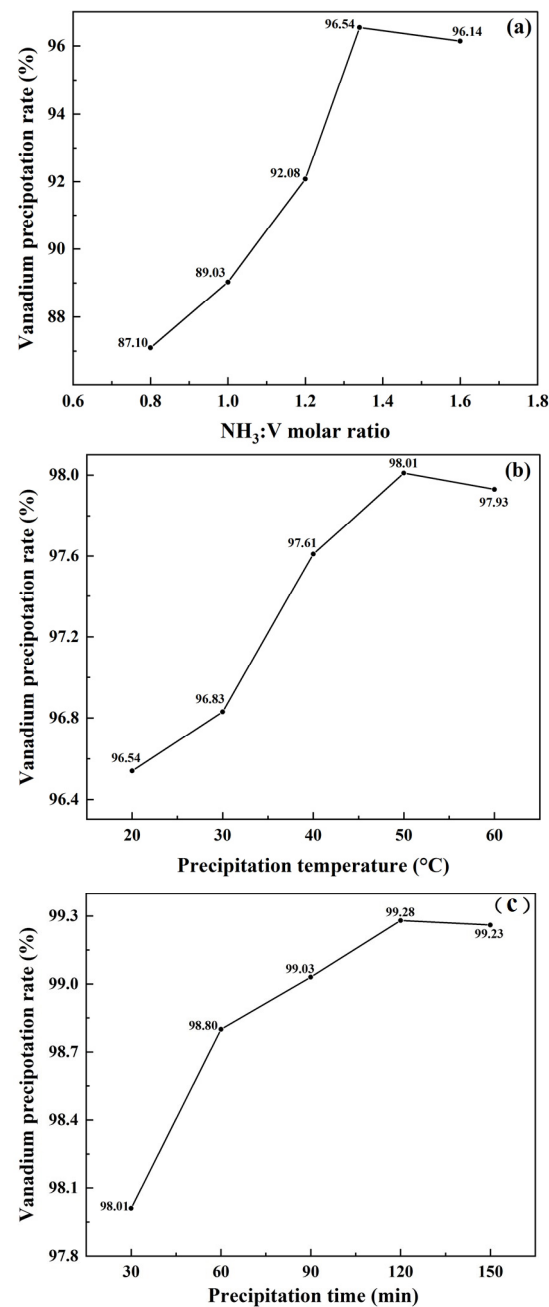


Figure 12. Effects of (a) the $\text{NH}_3\text{:V}$ molar ratio, (b) precipitation temperature, and (c) precipitation time on the vanadium precipitation rate.

Furthermore, at the $\text{NH}_3\text{:V}$ molar ratio of 1.34 and the vanadium precipitation time of 30 min, with an increase in temperature, the vanadium precipitation rate increased to a maximum of 98.01% at 50 $^{\circ}\text{C}$ and then decreased because of the solubilization of vanadium species at high temperatures. Therefore, the optimal vanadium precipitation temperature was selected as 50 $^{\circ}\text{C}$.

At the $\text{NH}_3\text{:V}$ molar ratio of 1.34 and the vanadium precipitation temperature of 50 $^{\circ}\text{C}$, with an increasing precipitation time, the vanadium precipitation rate increased to a maximum of 99.28% at 120 min and then slightly decreased because of the dissolution of some vanadium species during prolonged exposure to the aqueous solution. Thus, the optimal vanadium precipitation time was selected as 120 min.

3.5.2. Characterization of V_2O_5

Based on the above optimal conditions, V_2O_5 was prepared by roasting the precipitate isolated from the $VOCl_3$ solution at 550 °C for 3 h. The obtained product had a purity of 99.86% and thus met the standard of grade 99 V_2O_5 stipulated by YB/T 5304-2011 [39]. Table 6 lists the compositions of standard V_2O_5 and that obtained herein, while Figure 13 shows the XRD pattern of the V_2O_5 obtained herein and the reference V_2O_5 pattern.

Table 6. Compositions of the V_2O_5 standard and the V_2O_5 obtained herein (wt%).

Constituent	V_2O_5	Si	Fe	P	S	As	$Na_2O + K_2O$
V_2O_5 (99% standard *)	>99	<0.15	<0.20	<0.03	<0.01	<0.01	<1.0
V_2O_5 obtained herein	99.86	0.0005	0.0384	0.0004	0.0087	0.0005	0.0315

* Standard reference YB/T 5304-2011.

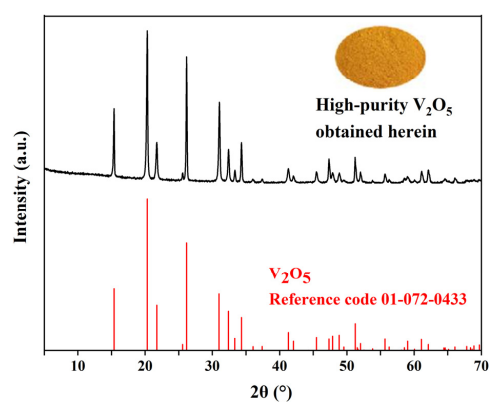


Figure 13. XRD pattern and image (inset) of V_2O_5 obtained herein.

The XRD pattern of our V_2O_5 matched well with that of the V_2O_5 standard (standard card code 01-072-0433) and did not contain any impurity peaks.

Figure 14 shows the results of the surface SEM–EDS analysis of the V_2O_5 product, revealing that the V_2O_5 particles were associated with sodium and magnesium, which indicated a part of sodium and magnesium present in the precipitate isolated from the $VOCl_3$ solution, which was consistent with the high concentrations of sodium and magnesium in the precipitate isolated from the acid leaching solution. Further, sodium and magnesium were confirmed to be the main impurity via point-scan elemental composition analysis. Moreover, carbon was derived from the substrate adhesive.

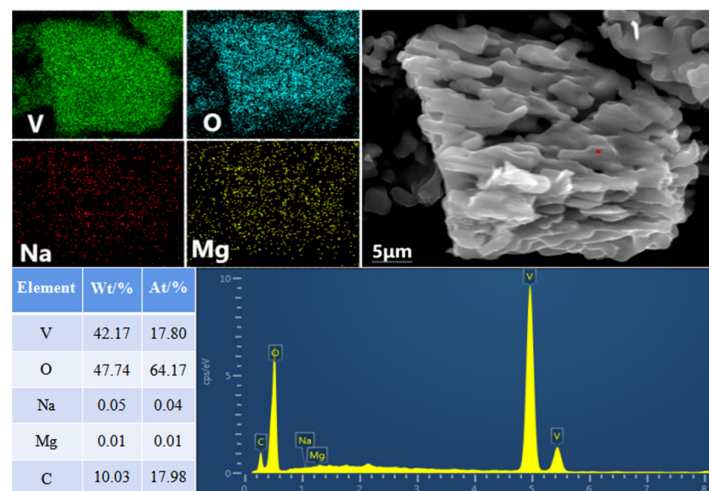


Figure 14. SEM–EDS characterization of V_2O_5 obtained herein.

3.6. Comparison with Traditional Hydrometallurgical Method of V_2O_5 Preparation

As shown in Figure 15, compared with the traditional V_2O_5 preparation process [40], the short-process preparation of V_2O_5 in this study avoided the steps of the reduction of the neutralization solution, solvent extraction of the extraction solution, and backwash extractor of the loaded organic phase. By using the chlorination metallurgy method, the chlorination agent was mixed with the vanadium-containing precipitate from the acid leaching solution and roasted for 120 min at 170 °C to afford $VOCl_3$ with a purity of at least 99.9%, vanadium and impurities were separated in one step, and the overall process flow was shortened. A short process to produce V_2O_5 from vanadium shale at a low temperature via chlorination had been achieved. In addition, compared to the traditional V_2O_5 preparation process with a vanadium recovery rate of 83.81%, the vanadium recovery rate in this study was only 60.03%, and we will optimize the recovery rate data in the next experimental work. Currently, the focus of this article is to prepare a high-purity $VOCl_3$ intermediate product with a purity of 99.94% from the vanadium precipitate; vanadium and impurities were separated in one step, and then, V_2O_5 with a purity of 99.86% was prepared in a short process.

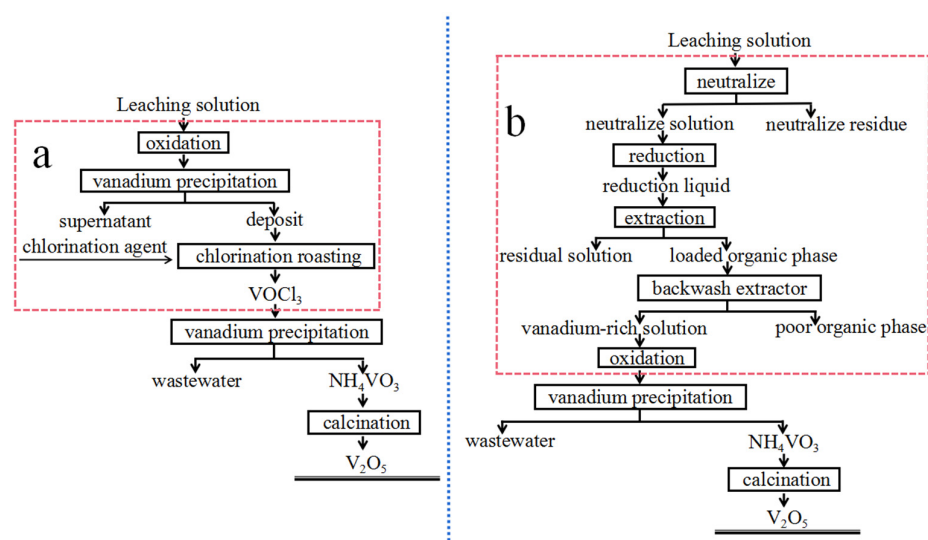


Figure 15. V_2O_5 preparation process flow charts of (a) newly developed and (b) traditional methods.

4. Conclusions

This study describes a short process of preparing V_2O_5 from shale acid leaching solution at a low temperature via precipitation followed by chlorination with $AlCl_3$ at a low temperature (170 °C). The addition of NaCl can improve the vanadium extraction rate and purity of $VOCl_3$. The obtained $VOCl_3$ (purity $\geq 99.9\%$) is dissolved in ultrapure water, the solution is treated with aqueous ammonia, and the precipitate is roasted to afford V_2O_5 . The optimal process parameters are as follows: chlorination temperature = 170 °C, chlorination time = 120 min, $V:AlCl_3:NaCl = 3:12:8$ (mol/mol/mol) [chlorination], precipitation temperature = 50 °C, precipitation time = 120 min, $NH_3:V = 1.34$ (mol/mol), and vanadium concentration = 32 g/L [precipitation]. The V_2O_5 obtained under the optimal conditions had a purity of 99.86%. Compared with the traditional hydrometallurgical process of V_2O_5 preparation, our method is characterized by simple operation and a short preparation process.

In addition, we found fibrous substances in the residue of the chlorination reaction. By means of XRD and SEM-EDS analysis of fibrous substances, this was determined to be $AlOCl$. Based on the formation of $AlOCl$ during the chlorination reaction, the chlorination reaction mechanism was defined as the oxygen atoms in Na_3VO_4 and $NaVO_3$ first replacing the two chlorine atoms in $AlCl_3$ and the replaced chlorine atoms chlorinating Na_3VO_4 and $NaVO_3$ to generate $VOCl_3$. The chlorine atom in $AlCl_3$ is gradually replaced.

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