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Full Length Article

Green extraction of vanadium resources: A process for the preparation of vanadium oxide in an ammonia-free system

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ABSTRACT

The current vanadium extraction process from sodium roasted vanadium slag poses risks such as ammonia pollution. This study proposes a novel calcium-based vanadium extraction and hydrolysis precipitation process, achieving clean and efficient vanadium recovery. The introduction of CaO facilitates the targeted reconstruction and conversion of vanadium and calcium in the solution, forming acid-soluble calcium vanadate intermediates. Under optimal conditions, n(Ca)/n(V) ratio of 1.75, extraction temperature of 90 °C, and extraction time of 90 min, the vanadium extraction ratio reached 99.83%. This process also separates vanadium from sodium and silicon, enabling one-step purification of the vanadium solution. Subsequent sulfuric acid leaching, conducted at pH of 4.0, 90 °C, and 60 min, achieved a vanadium leaching ratio of 99.72%, further separating vanadium from calcium and other impurities. Finally, the purified vanadium solution underwent hydrolysis precipitation at pH of 2.1 and 95 °C for 60 min, achieving a precipitation ratio of 98.69%. The calcined product yielded V_2O_5 with a purity of 98.60%. Compared to the conventional sodium roasting–water leaching along with ammonium salt precipitation process, this innovative method eliminates ammonia-nitrogen wastewater emissions. This study provides a foundation for the development of new vanadium extraction technologies from vanadium slag.

1. Introduction

Vanadium is a critical strategic metal resource, widely utilised in industries such as steel [1–5], aerospace [6–8], chemical engineering [9–11], and nuclear energy [12–14]. Ensuring a stable supply of vanadium is therefore a significant challenge for national economic development. Vanadium is primarily sourced from vanadium-titanium magnetite. After smelting in blast furnaces and converters, vanadium slag is produced as a by-product.

Roasting vanadium slag mixed with sodium or calcium salt to obtain water-soluble or acid-soluble vanadates in the roasted clinker, and leaching of the clinker is currently the mainstream vanadium extraction process in vanadium metallurgy worldwide. Among them, the sodium roasting–water leaching process is well known for its high vanadium extraction ratio (more than 90%). Sodium roasting typically involves additives such as sodium carbonate (Na_2CO_3) [15–17], sodium sulfate (Na_2SO_4) [18], sodium hydroxide (NaOH) [19,20] or sodium chloride (NaCl) [21], which are roasted at 750–900 °C for 1–3 h to convert vanadium into water-soluble sodium vanadate ($NaVO_3$), this is then extracted *via* water leaching.

The preparation of vanadium pentoxide (V_2O_5) from vanadium-bearing solution primarily involves ammonium salt and hydrolysis precipitation [22]. Due to its mature technology and high recovery ratio, ammonium salt precipitation has become the mainstream process in the global vanadium recovery industry. The process relies on the strong binding affinity between vanadate and ammonium ions to form an insoluble ammonium metavanadate precipitate, thereby achieving the selective separation and recovery of vanadium. Xiong *et al.* [23] investigated the process

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characteristics of ammonium salt precipitation under varying pH conditions. The results showed that under alkaline conditions, sodium vanadate crystals form in the precipitate, reducing the purity of the V_2O_5 product. Under acidic conditions, magnesium sulfate needs to be introduced to remove the phosphorus element in order to improve the vanadium precipitation rate. However, this process produces acidic wastewater that is highly polluting due to its high salinity and ammonia-nitrogen content. This wastewater can cause irreversible damage to water bodies, soil, and ecosystems. Given the increasingly stringent environmental regulations, the development of an environmentally friendly, ammonia-free vanadium precipitation process has become a pressing issue in vanadium metallurgy.

Hydrolysis precipitation, is one of the earliest industrialised vanadium precipitation methods and has garnered widespread attention due to its environmental friendliness. The core mechanism of this technology involves a polymerisation reaction between vanadate and hydrogen ions under acidic conditions to form insoluble vanadium oxide precipitates ($V_2O_5 \cdot nH_2O$) [24]. However, studies have also found that vanadates exhibit a strong binding affinity for cations such as Na^+, K^+, Ca^{2+}, and Mn^{2+} [25], which can easily become embedded in the vanadate crystal lattice. This forms co-precipitates with V_2O_5, which significantly reduces the purity of the final product. This impurity co-precipitation phenomenon limits the industrial application of hydrolysis precipitation technology.

Therefore, the selective purification of vanadium from solution and its separation from other components is crucial for improving the precipitation ratio and V_2O_5 purity in hydrolysis precipitation processes. Preliminary studies have revealed that calcium exhibits a strong affinity for vanadium [26]. Under specific roasting conditions, vanadium and calcium form calcium vanadate, which is soluble in sulfuric acid. This enables the conversion of solid vanadium into a vanadium solution [27,28]. This finding paves the way for clean and efficient V_2O_5 production from vanadium slag *via* hydrolysis precipitation.

The present study investigates the composition, properties, and performance of vanadium-containing solution from sodium roasting vanadium slag. A systematic examination of the effects of vanadium extraction conditions on CaO-based vanadium recovery, acid leaching conditions on vanadium extraction efficiency, and hydrolysis precipitation conditions on vanadium recovery ratio is undertaken. In conclusion, the precipitated product is subjected to a washing and calcination process in order to obtain V_2O_5, with its purity subsequently analysed.

2. Experimental

2.1. Materials

The vanadium slag utilised in this study was produced from Sichuan Xichang Vanadium Product Co., Ltd, China, with its chemical composition delineates in Table 1. The content of V_2O_3 and Cr_2O_3 in the vanadium slag utilised in this study is 12.63% and 1.65%, respectively. All chemical reagents employed in the experiments, including Na_2CO_3, CaO, H_2SO_4 and $(NH_4)_2Fe(SO_4)_2$, were of analytical grade, obtained from China National Pharmaceutical Group Reagent Co., Ltd, with a purity exceeding 98%. All aqueous solutions were prepared with deionized water.

Table 1
Chemical composition of vanadium slag.

Composition	FeO	V_2O_3	SiO_2	TiO_2	MnO	CaO	Al_2O_3	Cr_2O_3	P_2O_5	Total
Content/%	44.74	12.63	14.41	11.11	7.53	2.71	1.92	1.65	0.18	96.88

After Na_2CO_3 roasting and H_2O leaching, vanadium and sodium were enriched in the leaching solution with major ion concentrations as shown in Table 2. In addition to vanadium and sodium ions in the solution, a small portion of silicon, calcium, chromium and manganese also entered into the liquid phase during the leaching process. Furthermore, the presence of sodium ions is founded to be elevated, a consequence of the incorporation of substantial quantities of sodium salts.

2.2. Experimental process

2.2.1. Vanadium extraction by CaO

CaO was added to the leaching solution to achieve the separation of vanadium with the impurities, such as sodium and silicon. 30 ml of leaching solution was put into the conical flask, then, it was put into a constant-temperature water bath pot for vanadium extraction by CaO. CaO is first added to some water to form a slurry (m(CaO)/m(H_2O) was 1:10 during the slurry process), and then added to the leaching solution to extract vanadium. The amount of CaO added, expressed as the molar ratio of calcium in CaO to vanadium in the leaching solution n(Ca)/n(V), along with the extraction temperature and extraction time were set as the variables to study the effect of extraction conditions on the vanadium extraction behavior. After the reaction was completed, calcium vanadate precipitation as the intermediate product and the waste liquid were obtained and separated by vacuum filtration. The calcium vanadate intermediate was subjected to drying in an oven at 110 °C for 24 h to allow for the subsequent characterization of phase composition and microstructure. The waste liquid was subsequently diluted to 100 ml for detecting the extraction ratio of vanadium with Eq. (1).

$$\text{Extraction ratio of vanadium} = \left(m_0 - \frac{m_1}{m_0}\right) \times 100\% \quad (1)$$

where m represents vanadium, calcium, sodium and silicon; m_1 represents the mass of m in the CaO extraction waste liquid, g; m_0 represents the mass of m in the vanadium-containing leaching solution, g.

2.2.2. Vanadium leaching by H_2SO_4 solution

Calcium vanadate intermediate was leached with H_2SO_4 solution to further separate vanadium with impurities, such as calcium. During this process, 2 g of calcium vanadate intermediate and 20 ml deionized water was added into a 100 ml three-necked flask, then H_2SO_4 solution was gradually introduced to adjust the leaching pH to a certain value. The leaching reaction was maintained at 60 °C for 30 min. After reaction, the acid leaching solution and leaching residue were separated *via* vacuum filtration. The leaching residue was dried at 110 °C for 24 h in a drying oven, and the acid leaching solution was diluted to 100 ml for subsequent calculation of leaching ratios of vanadium, calcium, sodium, and silicon with Eq. (2).

$$\text{Leaching ratio} = \left(m_2 - \frac{m_3}{m_2}\right) \times 100\% \quad (2)$$

where m represents vanadium, calcium, sodium and silicon; m_3 represents the mass of m in the waste liquid after leaching by

Table 2
Concentrations of ions in the leaching solution after H_2O leaching.

Element species	V	Na	Si	Ca	Cr	Mn
Concentration/g·L^{-1}	21.40	18.90	1.05	0.011	7.60×10^{-4}	7.20×10^{-5}

H_2SO_4 solution, g; m_2 represents the mass of m in the CaO extraction solution, g.

2.2.3. Vanadium precipitation by hydrolysis and V_2O_5 preparation

Vanadium-containing leaching solution was poured into a three-necked flask. H_2SO_4 solution was gradually introduced to adjust the hydrolysis pH to a certain value, moreover, the temperature and time of hydrolysis reaction were also varied within a certain range. After the hydrolysis reaction was completed, vacuum filtration was carried out to separate the hydrolysis product and hydrolysis waste liquid. The hydrolysis product was put into an oven at 110 °C and dried for 24 h. Subsequently, the V_2O_5 product was obtained through roasting at 550 °C for 2 h. The hydrolysis waste liquid was diluted to 100 ml for the calculation of hydrolytic precipitation ratios of vanadium with Eq. (3). The experimental parameters and variables for the three processes are shown in Table 3, and the process flow diagram of this work was shown in Fig. 1.

$$\text{Hydrolysis ratio} = \left(m_4 - \frac{m_5}{m_4}\right) \times 100\% \quad (3)$$

where m represents vanadium, calcium, sodium and silicon; m_5 represents the mass of m in the hydrolysis waste liquid, g; m_4 represents the mass of m in the leaching by H_2SO_4 solution, g.

2.3. Characterization

Inductively coupled plasma atomic emission spectrometry (ICP-OES, Optima-4300DV, PerkinElmer, USA) was used to determine vanadium slag composition and elements such as calcium, sodium, and silicon. The concentration of vanadium in the liquid was determined by ammonium ferrous sulfate titration with Eq. (4). The phases of vanadium extraction intermediate product by CaO, vanadium precipitation products by hydrolysis and V_2O_5 were identified by a powder X-ray diffraction system (XRD, X' Pertpro, PANalytical B.V., Netherlands). The surface morphology of the product was observed utilizing a scanning electron microscope (SEM, Ultra plus, Zeiss, Germany). The valence states of the elements in the hydrolysis products were determined using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA).

$$\text{Titration ratio} = n \times C_v \times V_v \times 50.94/1000\% \quad (4)$$

where n is the volume of solution, C_v is the concentration of $(NH_4)_2Fe(SO_4)_2$ standard titration solution, mol·L^{-1}; V_v is the volume of $(NH_4)_2Fe(SO_4)_2$ standard titration solution consumed by 1 ml solution; 50.94 is the molar mass of vanadium.

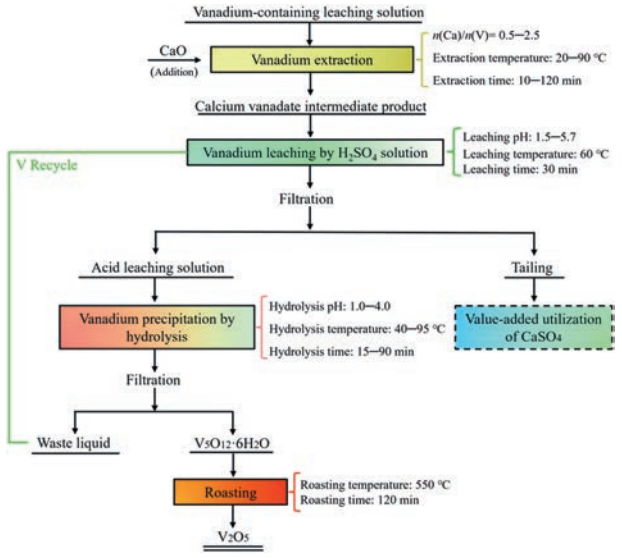

Fig. 1. Process flow diagram of this work.

Table 3
Experimental parameters designed in this work.

Parameters setting	n(Ca)/n(V)	pH	T/°C	t/min
Vanadium extraction by CaO	0.5–2.5	–	20–90	10–120
Acid leaching	–	1.5–5.7	60	30
Hydrolysis	–	1.0–4.0	40–95	15–90

3. Results and Discussion

3.1. Vanadium extraction by CaO

3.1.1. Effect of n(Ca)/n(V), temperature and time

Fig. 2 shows the effect of vanadium extraction conditions by CaO on the vanadium extraction ratios. The vanadium extraction ratios under different n(Ca)/n(V) are shown in Fig. 2(a). Results show that the vanadium extraction ratio increases significantly with the increase of n(Ca)/n(V) and then stabilized. The vanadium extraction ratio increases from 13.88% to 99.83% as n(Ca)/n(V) increasing from 0.5 to 1.75, which stabilizes at 99.83% after n(Ca)/n(V) is above 1.75. This indicates that when n(Ca)/n(V) is less than 1.75, the added CaO is not sufficient to extract all the vanadium in the vanadium-containing leaching solution. When n(Ca)/n(V) is greater than 1.75, there is an excess of calcium relative to vanadium. The addition of excessive CaO not only increases costs, but also leads to the residual calcium ions in the waste liquid after vanadium extraction, thereby increasing the difficulty of wastewater treatment. Therefore, n(Ca)/n(V) of 1.75 is the optimal value of CaO addition during vanadium extraction.

With the increase of vanadium extraction temperature, the ratio of vanadium extraction by CaO increases gradually as shown in Fig. 2(b). When the extraction temperature increases from 20 to 90 °C, the vanadium extraction ratio increases from 53.67% to 99.83%. This is due to the fact that as the reaction temperature increases, the kinetic energy of the molecules increases, the activated molecules involved in the reaction increase, the collision probability between molecules increases, and the effective intermolecular reaction increases.

Furthermore, with the extension of extraction time, the vanadium extraction ratio firstly increases gradually and then decreases as shown in Fig. 2(c). The vanadium extraction ratio increases from 68.74% to 99.83% as the reaction time increasing from 10 to 90 min. When the reaction time is further extended to 120 min, the vanadium extraction ratio decreases to 83.81%. The above results indicate that the reaction between vanadium and calcium requires a certain amount of time. Excessive extraction time may lead to the side reaction of vanadium with the rest of the elements in the solution, thus reducing its extraction efficiency.

Hence, when CaO is added as n(Ca)/n(V) of 1.75, the extraction temperature and time are 90 °C and 90 min, respectively, the vanadium extraction ratio reaches a maximum value of 99.83%.

3.1.2. Characterization of calcium vanadate intermediate

After CaO extraction, the chemical compositions of the intermediate products obtained with n(Ca)/n(V) of 1.75 at 90 °C for 90 min are shown in Table 4. The content of CaO is 49.06%, and the content of V_2O_5 is 21.03%.

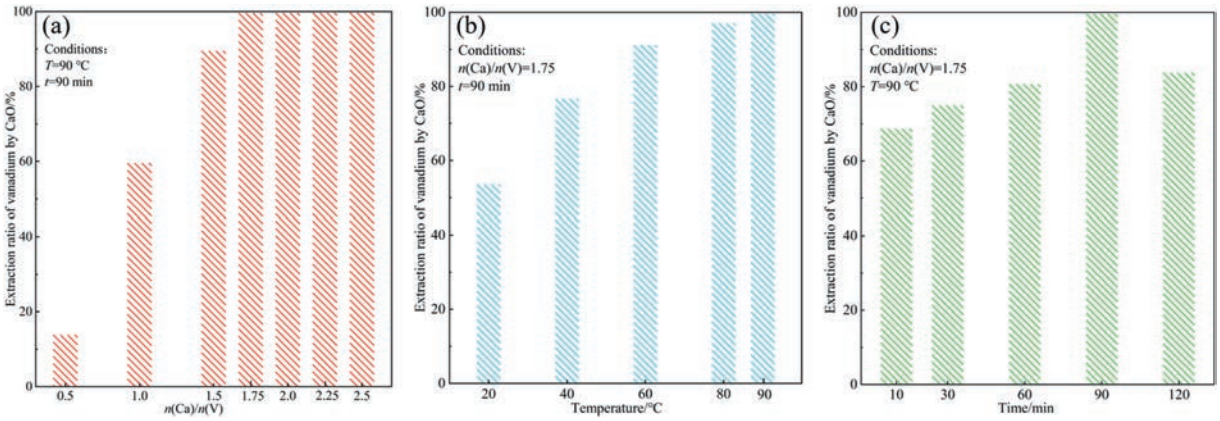

Fig. 2. Effects of (a) n(Ca)/n(V), (b) temperature and (c) time on the vanadium extraction ratios.

Table 4
Chemical compositions of the intermediate products.

Composition	V_2O_5	CaO	SiO_2	Na_2O
Content/%	21.03	49.06	2.66	0.75

The phase composition of the intermediate product obtained from vanadium extraction by CaO from vanadium-containing leaching solution is shown in Fig. 3(a). In the process of increasing n(Ca)/n(V) from 0.5 to 1.75, the diffraction peaks of the intermediate products are consistent with the standard card of calcium vanadate $Ca_7V_4O_{17}$ (JCPDS card number: 00-028-0251). This indicates that the intermediate product after CaO extraction is $Ca_7V_4O_{17}$, whose reaction equation is as shown in Eq. (5). It can be seen that n(Ca)/n(V) of 1.75 is just the theoretical amount of $Ca_7V_4O_{17}$ generation, which is consistent with the optimum n(Ca)/n(V) for the CaO extraction process. In addition, the diffraction peaks intensity of $Ca_7V_4O_{17}$ increases significantly with the increase of the value of n(Ca)/n(V), indicating that the amount of $Ca_7V_4O_{17}$ generated increases with the increase of n(Ca)/n(V) from 0.5 to 1.75. Continuing to increase n(Ca)/n(V) to 2 and 2.5, the diffraction peaks of calcium silicate Ca_3SiO_5 are observed in the intermediate products, in addition to $Ca_7V_4O_{17}$, which indicates that when CaO is in excess, it would react with the silicon ions in the leaching solution to generate Ca_3SiO_5 as shown in Eq. (6).

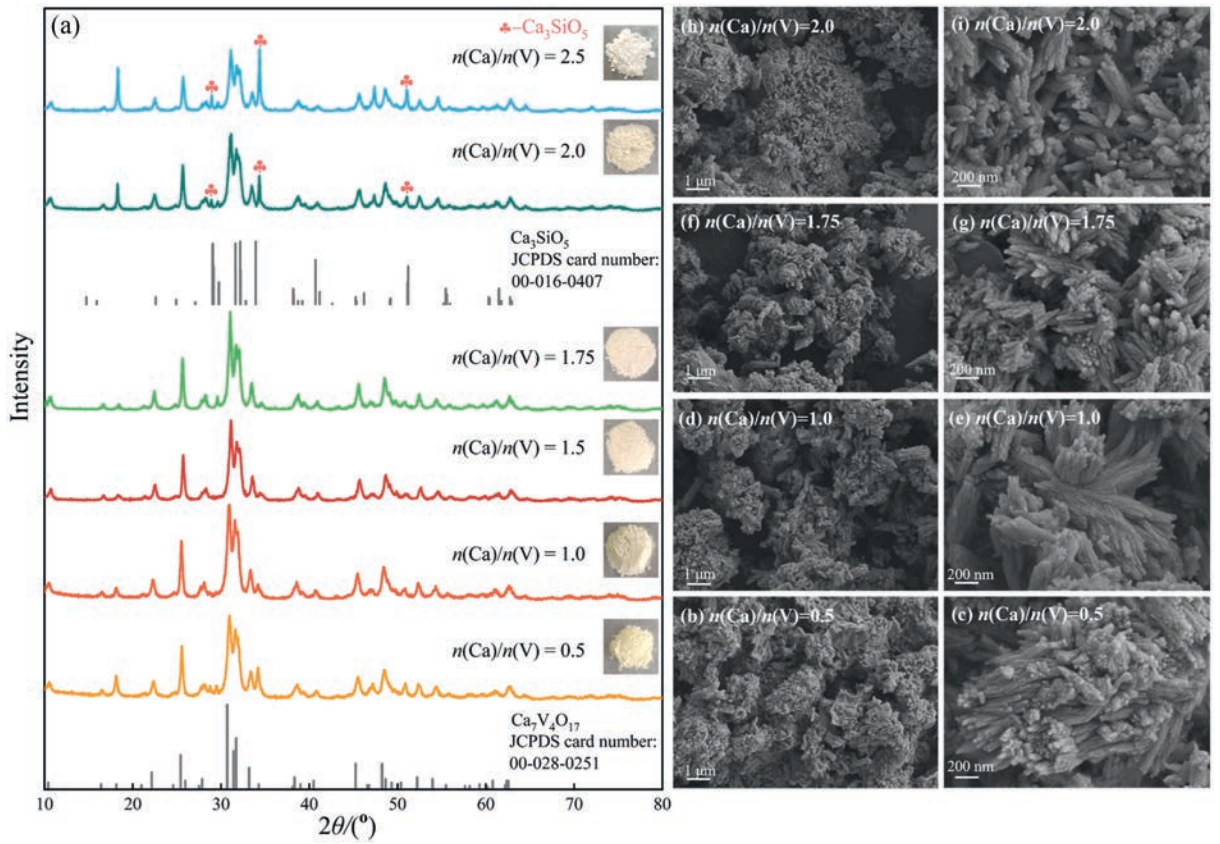

Fig. 3. (a) XRD patterns and (b)–(i) SEM images of calcium vanadate intermediate products.

However, the existence of Ca_3SiO_5 affects the purity of calcium vanadate intermediate product. Therefore, in this experiment, n(Ca)/n(V) is selected to be 1.75 as the basis for the amount of CaO added.

$$7CaO + 4NaVO_3 + 2H_2O = Ca_7V_4O_{17}\downarrow + 4NaOH \quad (5)$$

$$3CaO + SiO_2 = Ca_3SiO_5\downarrow \quad (6)$$

The microscopic morphology of the intermediates obtained with different n(Ca)/n(V) is shown in Fig. 3(b)–(i), from which it can be seen that the calcium vanadate $Ca_7V_4O_{17}$ generated with different n(Ca)/n(V) are nanorods with severe agglomeration. The length of the nanorod particles is about 200–500 nm and the diameter is tens of nanometers.

3.2. Vanadium leaching by H_2SO_4 solution

3.2.1. Effect of leaching pH

During the acid leaching reaction, the chemical reactions involved are mainly solid–liquid reactions. In order to explore the optimal experimental conditions for the preparation of acid leaching solution by acid leaching of calcium vanadate, the pH value is set at 1.5 to 5.7, and the effect of acid leaching pH on the vanadium leaching ratio is investigated under the conditions of acid leaching temperature of 60 °C and holding time of 30 min. The acid leaching reaction equation of calcium vanadate intermediate is shown in Eq. (7). The effect of reaction pH on the vanadium leaching ratio is shown in Fig. 4, the results show that with the increase of pH, the vanadium leaching ratio first increases and then decreases. As pH increasing from 1.5 to 4.0, the vanadium leaching ratio increases from 3.65% to 99.72%. The vanadium leaching ratio decreases a little after the pH of 4.0. When pH value ranges from 3.1 to 5.0, all of leaching ratio can reach more than 98%, indicating that $Ca_7V_4O_{17}$ intermediate product has good acid solubility within this pH range.

$$2Ca_7V_4O_{17} + 36H^+ + 14SO_4^{2-} = 4(VO_2)_2^{2+} + 11H_2O + 14CaSO_4\cdot 0.5H_2O\downarrow \quad (7)$$

During the leaching reaction, as the pH of the system increases, all elements except vanadium are leached, as shown in Fig. 5. In Fig. 5, when the leaching pH is 2.2 to 4.0, the leaching ratio of calcium, sodium and silicon are relatively stable, around 10.14%, 42.33% and 46.62%, respectively. When the pH is increased to 5.7, the calcium leaching ratio increases to 20.25%, because the higher the pH, the smaller the sulfate concentration in the leaching system, resulting in the greater the calcium leaching ratio of the acid leaching solution. Therefore, in order to inhibit the leaching of calcium, the leaching pH should be appropriately reduced. The leaching ratio of sodium increases significantly and stabilized at about 99%, which indicated that pH value has a great influence on sodium leaching ratio, and the increase of acid concentration could effectively inhibit sodium leaching. The leaching ratio of silicon remaines stable at about 47% with almost no fluctuation, indicating that the pH value of the system has no significant effect on the leaching ratio of silicon.

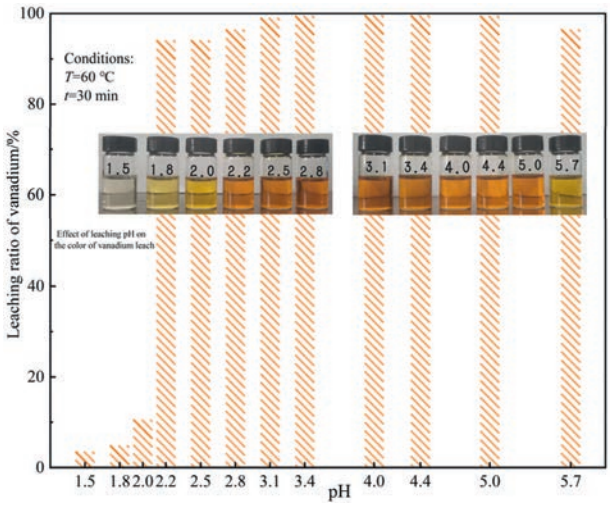

Fig. 4. Effects of pH value on the leaching ratio of vanadium.

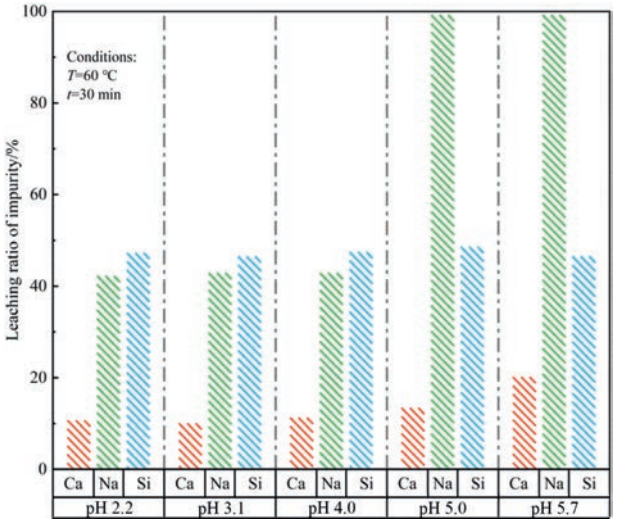

Fig. 5. Effects of pH value on the leaching ratio of other elements.

Table 5
Concentrations of ions in the acid leaching solution of calcium vanadate intermediate.

Element species	V	Na	Si	Ca
Concentration/g·L^{-1}	4.98	0.082	0.26	1.11

Moreover, the ionic type and concentration among the acid leaching solution of the $Ca_7V_4O_{17}$ intermediate products after leaching at pH value of 4.0 at 60 °C for 30 min are shown in Table 5. The concentration of vanadium ions is significantly higher than that of other impurity ions, especially the concentration of sodium ions, which is effectively controlled during the CaO extraction and acid leaching processes. The obtained vanadium containing leaching solution can be used as the raw material for the next step of hydrolysis precipitation of vanadium.

3.2.2. Characterization of acid leaching residues

The phase composition and micromorphology of the acid leaching residues at different pH values are depicted in Fig. 6. As the pH value increases from 1.8 to 5.7, the diffraction peaks of the acid leaching residues in Fig. 6(a) align with the standard peaks corresponding to JCPDS card number 01-083-0439, indicating that the product is $CaSO_4\cdot 0.5H_2O$. The acid leaching residues obtained at various pH values exhibit a rod-like structure as shown in Fig. 6 (b) and (c), with rod-shaped particles measuring approximately 10–20 μm in length and a few micrometers in diameter, which is consistent with the study of Luo *et al.* [29]. Fig. 6(d)–(f) illustrate that the distribution areas of calcium, sulfur, and oxygen elements

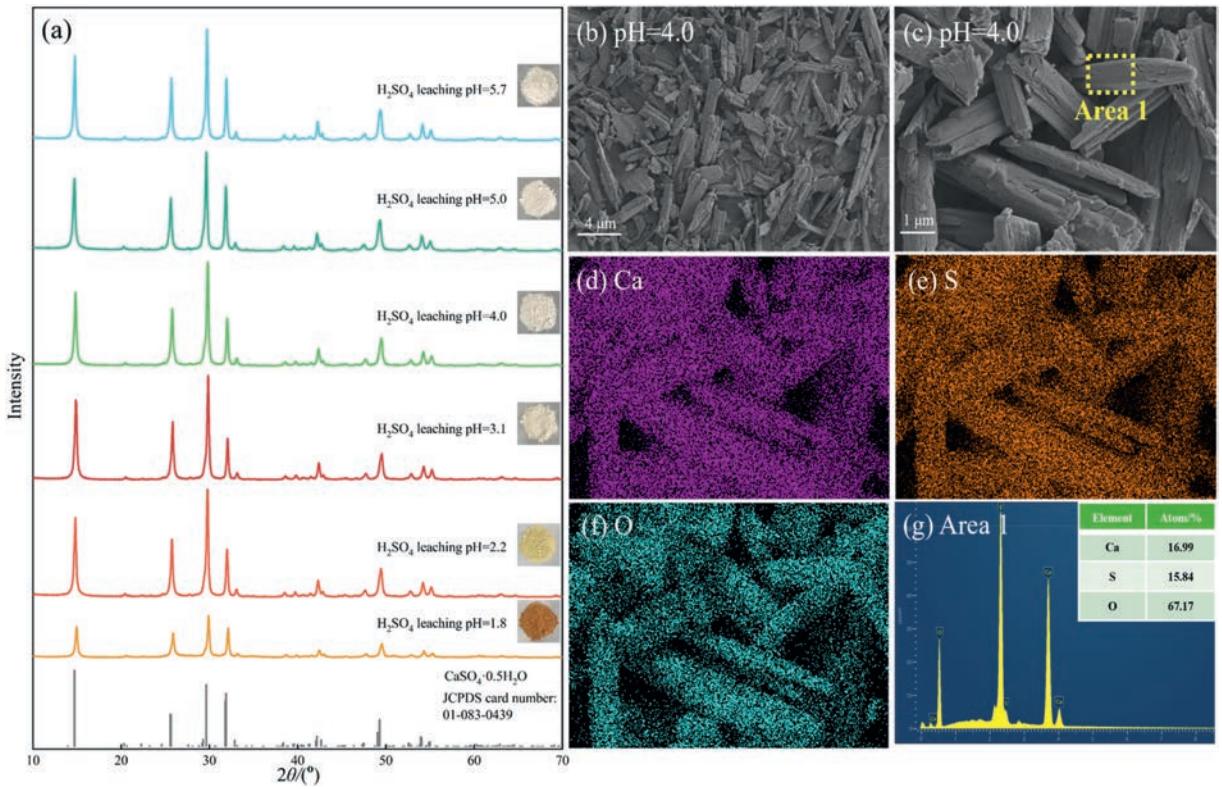

Fig. 6. (a) XRD patterns, (b)–(f) SEM image with elements mapping and (g) EDS analysis of area A in (c).

substantially overlap, confirming that the primary component of the acid leaching residues is calcium sulfate. Fig. 6(g) presents the EDS results for region 1 in Fig. 6(c), revealing that the residues primarily contain calcium, sulfur, and oxygen elements, with the atomic ratio of calcium to sulfur close to 1, further corroborating that the main component of the acid leaching residues is $CaSO_4$. No other elements were detected in the acid leaching residues, suggesting a high purity of calcium sulfate, which could be considered for subsequent applications in the preparation of building materials.

3.3. Vanadium precipitation by hydrolysis

3.3.1. Effect of hydrolysis pH, temperature and time

Fig. 7 shows the effect of vanadium precipitation conditions on the vanadium precipitation ratios. With the increase of hydrolysis pH, the precipitation ratio of vanadium after hydrolysis firstly increases and then decreases in Fig. 7(a). As pH increases from 1.0 to 2.1, the vanadium leaching ratio increases from 22.59% to 98.69%, the vanadium leaching ratio gradually decreasing to 3.67% after pH value of 2.1. Considering the consumption of sulfuric acid and the ratio of vanadium precipitation by hydrolysis, pH of 2.1 is the optimum pH value.

With the increase of hydrolysis temperature, the precipitation of hydrolysis vanadium firstly increased and then stabilizes in Fig. 7(b). When the hydrolysis temperature was increased from 40 °C to 95 °C, the precipitation ratio of hydrolysis vanadium increased rapidly from 2.94% to 98.69%, indicating that the increase in reaction temperature favoured intermolecular collisions and accelerated the precipitation of vanadate solid. Continued increase in temperature stabilizes the precipitation ratio at 98.69%.

With the increase of hydrolysis time, the precipitation ratio of vanadium increases first, and then stabilizes in Fig. 7(c). The hydrolysis time increases from 15 to 60 min, the hydrolysis vanadium precipitation ratio increases from 97.68% to 98.69%, and the vanadium leaching ratio is stabilized at about 98.69% after the hydrolysis time of 60 min.

Hence, when the hydrolysis pH, temperature and time are 2.1, 90 °C and 60 min, respectively, the vanadium precipitation ratio reaches a maximum value of 98.69%.

3.3.2. Characterization of hydrolysis product and V_2O_5

Fig. 8 shows XRD patterns, V 2p XPS spectra and SEM images of the hydrolysis product and V_2O_5 product. In Fig. 8(a), the diffraction peaks of the hydrolyzed vanadium product are consistent with the standard peaks of JCPDS card number 01-085-0601, indicating that the product of hydrolyzed vanadium is $V_5O_{12}\cdot 6H_2O$. The V 2p XPS region was observed, located at 524.89/523.38 eV and 517.32/515.74 eV that are respectively assigned to the V $2p_{1/2}$ and V $2p_{3/2}$ of V^{5+}/V^{4+} [30,31]. The vast majority of the vanadium is present as pentavalent in the hydrolysis products, which is consistent with the XRD pattern results.

The microscopic morphology of vanadate solids prepared by hydrolysis of acid leaching solution for vanadium precipitation is shown in Fig. 8(b), from which it can be seen that the hydrolysis products obtained are rod-like in structure, and the surface is loose and porous. The rod-like particles are 8–20 μm with a diameter of about a few micrometers.

After roasting the hydrolysis product at 550 °C for 2 h, the main element content of V_2O_5 product is shown in Table 6, the V_2O_5 content is 98.60% and the CaO content of 1.19%. The diffraction peaks of the solid are consistent with the standard peaks of JCPDS card number 00-041-1426, indicating that the product is mainly V_2O_5. The diffraction peaks of calcium vanadate CaV_2O_6 appeared in the product in addition to V_2O_5, which is due to the fact that the calcium ions in the leaching solution during the roasting process

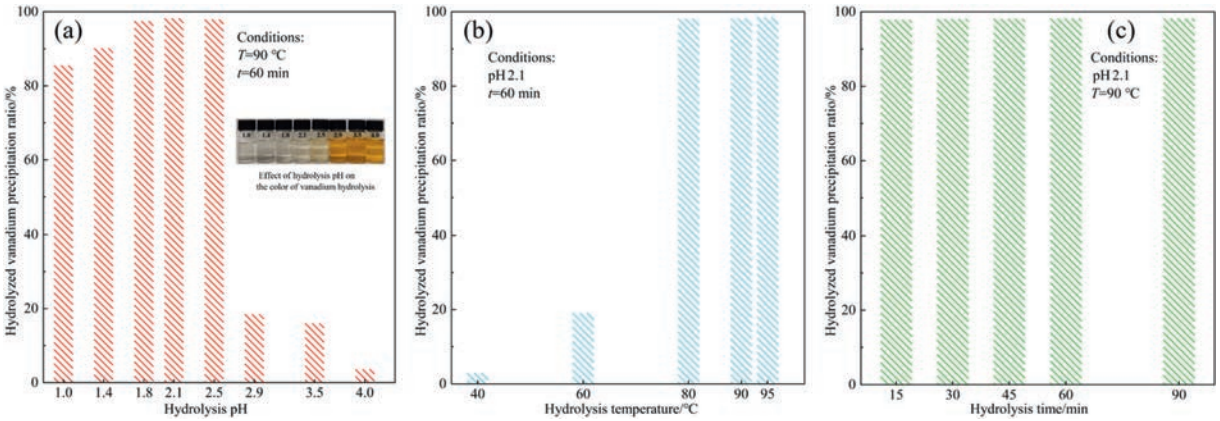

Fig. 7. Effects of (a) hydrolysis pH, (b) temperature and (c) time on the vanadium precipitation ratios.

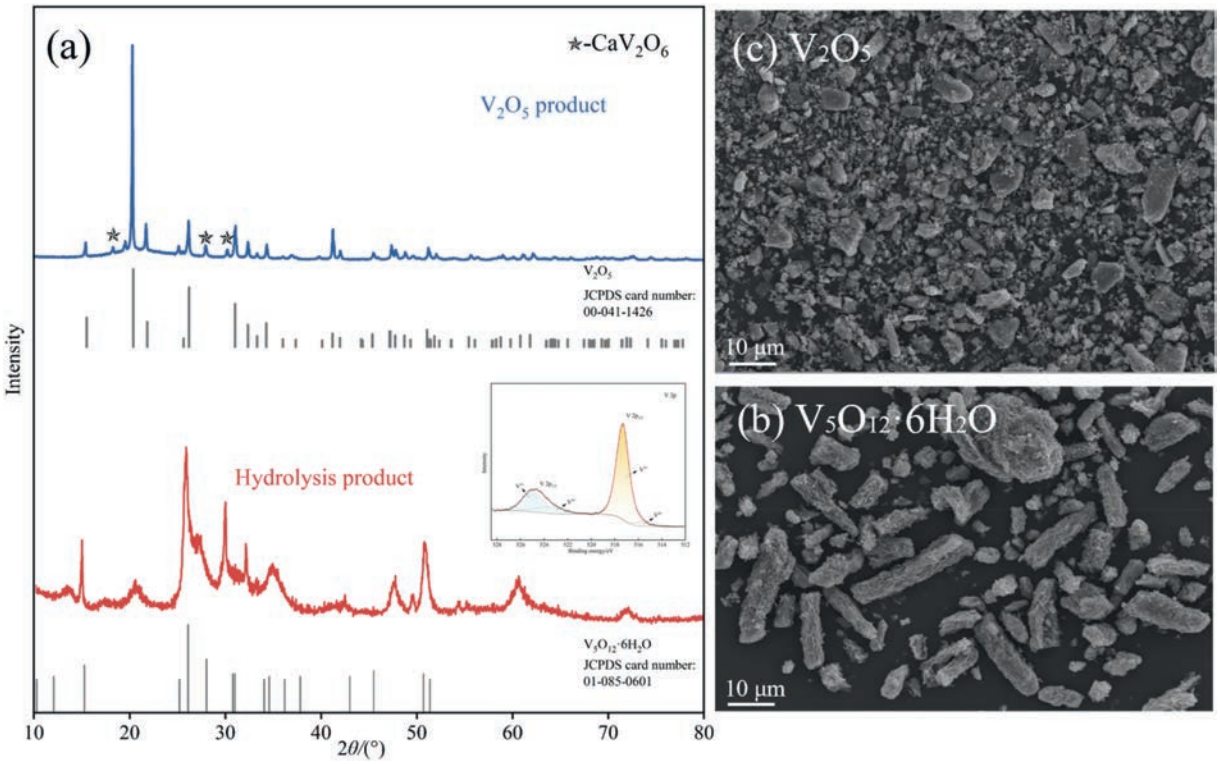

Fig. 8. (a) XRD patterns and V 2p XPS spectra, (b) SEM images of hydrolysis product, (c) SEM images of V_2O_5 product.

Table 6
Chemical compositions of V_2O_5 product.

Composition	V_2O_5	CaO
Content/%	98.60	1.19

would be synthesized with vanadium to produce calcium vanadate, and turn affects the purity of V_2O_5 product. Hydrolysis product can be washed with water repeatedly, and the content of CaO in V_2O_5 products should be continued to be reduced in future experiments to improve the quality of V_2O_5 products.

The microscopic morphology of V_2O_5 product obtained after roasting $V_5O_{12}·6H_2O$ is shown in Fig. 8(c), from which it can be seen that V_2O_5 product obtained have a rod-like structure. The rod-like particles are about 1–2 μm long with a diameter of about

Table 7
Comparison with vanadium precipitation process.

Vanadium precipitation process	Precipitation efficiency/%	Ammonia nitrogen wastewater	Product purity/%	Impurity content/%	Ref.
Ammonium salt precipitation of vanadium	99.52	Yes	92.37	$Na_2O + K_2O$: 5.88	[23]
	99.75	Yes	95.71	MnO: 2 Fe_2O_3: 2.08	[32]
	94.8	Yes	99.1	$Na_2O + K_2O$: 0.05	[33]
Conventional hydrolysis precipitation of vanadium	99	No	–	Na_2O: 6.36	[24]
	91.61	No	–	Na_2O: 7.71	[34]
	95	No	–	Na_2O: 4–5	[35]
Hydrolysis based on vanadium extraction by CaO	98.69	No	98.60	CaO: 1.19	This work

several hundred nanometers, which is consistent with the study of Wen *et al.* [32].

4. Evaluation

Comparison with vanadium precipitation process is shown in Table 7. The widely used ammonium salt vanadium precipitation process currently produces a large amount of ammonia-nitrogen wastewater during the precipitation process, which is a serious pollution to the environment, difficult to treat and costly. In this work, the directional reconstruction and conversion of vanadium is promoted by introducing low-cost CaO, and the vanadium yields in all stages are high, avoiding the generation of ammonia-nitrogen wastewater from the source and providing a new direction for the clean preparation of vanadium compounds.

The traditional hydrolytic precipitation has the phenomenon of impurity co-precipitation, which prevents the high purity vanadium oxide product from being obtained. In this work, by introducing CaO and sulfuric acid leaching, the sodic roasting leachate was purified twice, and the V_2O_5 product with a purity of 98.60% was obtained, which made up for the disadvantage of the existing hydrolysis precipitation of vanadium. And we have systematically studied and optimised the parameters of calcium salt dosage, sulfuric acid leaching and hydrolysis precipitation to obtain a complete industrial system with high potential for industrial application. In the future, we will further improve the process and promote the development of vanadium metallurgy.

5. Conclusions

In order to solve the problem of ammonia and nitrogen wastewater discharge in the existing vanadium precipitation process by ammonium salt, a new process including vanadium extraction by CaO, acid leaching and hydrolysis was proposes. The following conclusions were drawn in this study.

(1) The results showed that 99.83% of vanadium was extracted in the form of $Ca_7V_4O_{17}$ by adding CaO to a vanadium-containing solution with $n(Ca)/n(V)$ of 1.75 for 90 min at 90 °C. The contents of impurity silicon and sodium components were only 2.66% and 0.75%.
(2) During acid leaching, the leaching ratio of vanadium reached a maximum value of 99.72% after leaching for 30 min at 60 °C in the sulfuric acid solution at pH of 4.0. The leaching ratios of calcium, sodium and silicon were 11.36%, 43.00% and 47.56% respectively.
(3) In the process of hydrolysis, the precipitation ratio of vanadium reached a maximum value of 98.69% after hydrolyzing the vanadium-containing solution at 90 °C for 60 min under the condition of pH at 2.1. The hydrolyzed product was vanadic acid, which could be decomposed into V_2O_5 with a purity of 98.60% after roasting. This study provides a foundation for the development of new vanadium extraction technologies from vanadium slag.

CRediT Authorship Contribution Statement

Xinyu Liu: Writing – review & editing, Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. Yue Sun: Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. Jing Wen: Writing – review & editing, Visualization, Funding acquisition, Conceptualization. Tao Jiang: Writing – review & editing, Visualization, Funding acquisition, Conceptualization. Lan Zhang: Visualization, Investigation, Conceptualization. Jinchao Yang: Visualization, Conceptualization. Jiayu Dai: Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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