

Article

Efficient Separation of Silicon and Vanadium by Sodium Roasting-Water Leaching from Vanadium Slag and CaV_2O_6 Preparation

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Abstract: Calcium vanadate (CaV_2O_6), a new product of vanadium precipitation, was obtained from vanadium slag by sodium roasting-water leaching and calcium precipitation. The separation behavior of vanadium and silicon in vanadium slag during sodium roasting and water leaching was systematically studied, and micro-morphology and valence migration behavior of vanadium and Fe in vanadium slag, roasting slag, and residue were revealed. The Na_2CO_3 was added to the vanadium slag at 20% mass fraction, roasted at 790 °C, and kept for 120 min, the roasted sample was added to the deionized aqueous solution with a liquid-solid ratio of (L/S) 5mL/g, and then heated at 90 °C for 60 min, 89.54% vanadium and 1.96% chromium were extracted. Sodium carbonate tends to combine with vanadium to form sodium vanadate, while silicon is easy to combine with Fe and Na to form acmite ($\text{NaFeSi}_2\text{O}_6$). When the molar ratio of N (Ca/V) is 0.6 and CaO, is added to adjust the pH of vanadium leaching solution to 6.7 ± 0.1 and precipitate 90 min at 90 °C, vanadium is precipitated in the form of CaV_2O_6 with a purity of 95.69%, under these conditions, the precipitation ratio is 95.03%.

Keywords: separate; vanadium slag; calcium vanadate; sodium roasting; kinetics



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1. Introduction

Vanadium is a strategic rare metal element. Because of its high melting point, tensile strength, hardness, and fatigue strength, vanadium is almost all used in the field of black or non-ferrous alloys [1–7]. It is difficult for vanadium to exist alone in nature. Vanadium is mainly symbiotic with other minerals or occurs in vanadium-titanium magnetite. Vanadium-titanium magnetites are smelted in a blast furnace to obtain vanadium-bearing hot metal, and then vanadium is oxidized into the slag phase to obtain vanadium slag and semi-steel [8]. As a result, vanadium in vanadium titanomagnetite is enriched into vanadium slag.

At present, the main method of extracting vanadium from vanadium slag to prepare vanadium oxide is sodium roasting of vanadium slag-water leaching treatment-ammonia precipitation of vanadium-ammonia. The process mainly uses NaCl , Na_2CO_3 and NaOH as sodium salt additives, roasting in an oxygen atmosphere at high temperature, so that the trivalent vanadium and tetravalent vanadium in vanadium slag are converted into pentavalent soluble sodium vanadate [9]. After water leaching, the supernatant of sodium vanadate is obtained by removing impurities, and then ammonium vanadate is precipitated by ammoniation. Vanadium pentoxide was obtained after calcination. This method of extracting vanadium, which is widely used at present, has the problem of high energy consumption and polluting gases such as Cl_2 , NH_3 , and so on [10]. It is worth noting that there is a high content of silicon in vanadium slag. After sodium roasting-water leaching of vanadium slag, only a little silicon is leached, which can effectively achieve

the purpose of separating vanadium from silicon. However, there are few studies on the mechanism of phase transformation, valence migration, and difficult leaching of silicon in the whole process, and the leaching behavior of silicon has not been studied, which only stays at the empirical level, therefore, it is of great significance to study and understand the leaching behavior of silicon for industrial production. By studying the leaching behavior of silicon, we can guide the practice and determine the best experimental conditions under the condition of the highest yield of vanadium. To achieve the purpose of minimizing the leaching of impurity silicon.

The roasted clinker obtained by sodiumization of vanadium slag is leached with water to obtain a sodium vanadate solution. Ammonium salt precipitation method is mainly used to separate sodium vanadate and vanadium, that is, $(\text{NH}_4)_2\text{SO}_4$ or NH_4Cl solution reacts with sodium vanadate solution to form ammonium metavanadate or ammonium polyvanadate precipitation with low solubility [11,12]. According to the pH value of the solution during precipitation, the ammonium salt precipitation method can be divided into weak basic ammonium salt precipitation method, weak acid ammonium salt precipitation method, and acid ammonium salt precipitation method. The weak basic ammonium salt precipitation method needs to adjust the pH value of the solution to 7.5–8.5, and the vanadium in the solution is precipitated in the form of NH_4VO_3 , but because of the high solubility of ammonium metavanadate, the vanadium content in the residual vanadium solution is up to 1–2.5 g/L [13]. The weakly acidic ammonium salt precipitation method requires that the pH value of the solution be 6 and vanadium precipitates in the form of decavanadate, but the chemical combination of alkali metal ions and decavanadate leads to the loss of vanadium in the subsequent roasting process [14]. The pH value of vanadium solution precipitated by acidic ammonium salt should be adjusted to 2–2.2, and vanadium forms ammonium hexavanadate precipitate. the quality of the vanadium product is good and the precipitation rate of vanadium is high. However, there are still the following problems in this process: first, a large amount of high ammonia nitrogen vanadium precipitation wastewater is produced, and the treatment cost is high; second, the potassium and sodium content in the prepared ammonium polyvanadate is high, in the subsequent vanadium-nitrogen alloy smelting process, sodium and potassium oxides are reduced and converted into sodium and potassium vapors, which easily react with refractory materials to bond and corrode the refractory materials, block the dust removal flue, and shorten the life of the furnace lining and furnace age; third, ammonium polyvanadate as a primary raw material for the production of other vanadium-containing chemical products, its sulfur, potassium, and sodium impurity content has an impact on the rear purification process. Precipitating calcium vanadate can avoid the problem of wastewater in the process of producing vanadium oxide. after further treatment of calcium vanadate, ammonium polyvanadate with lower content of potassium and sodium can be produced. at the same time, calcium vanadate, as an important intermediate product of vanadium, can provide raw materials for the preparation of ferrovandium [15] and biomedical medicine [16].

In previous studies, calcium precipitation of vanadium is mainly used to remove low concentration vanadium impurities in high concentration sodium chromate solution. There are few reports on the preparation of CaV_2O_6 by high concentration calcium precipitation of vanadium, mainly because calcium oxide is mostly carried out under alkaline conditions during vanadium precipitation. Under these conditions, calcium salt is easily hydrolyzed to form calcium hydroxide, resulting in the decrease of effective calcium concentration in the solution, resulting in poor utilization of calcium salt. Therefore, the double dose consumption of calcium oxide will be caused during the precipitation of vanadium, which is usually about 10 times of the theoretical calculation consumption, which is also the reason why calcium salt is rarely used to precipitate vanadium with high concentration, so to inhibit the hydrolysis of calcium salt and increase the concentration of available calcium in the solution, we propose to prepare calcium metavanadate by precipitation of vanadium under weak acid conditions.

In this paper, the leaching separation of silicon and vanadium from vanadium slag was systematically studied based on the technology of sodization calcination and aqueous leaching. The roasting leaching conditions were optimized by a single factor experiment. CaV_2O_6 was further prepared by precipitation of vanadium with CaO .

2. Experiments

2.1. Materials

Vanadium slag came from Chengde (Hebei, China). Its composition is shown in Table 1. Other chemicals used in the whole process such as Na_2CO_3 and CaO were all of analytical grade. All of the solutions during the leaching process and analysis of vanadium content were produced with deionized water. It can be seen from Table 1 that the content of silicon dioxide is high, and soluble sodium salt is easy to form during sodium roasting. Therefore, attention must be paid to the content of silicon in the leaching solution.

Table 1. Chemical composition (wt%) of vanadium slag in Chengde Iron and Steel Co.

Composition	TFe	V_2O_5	SiO_2	TiO_2	CaO	MgO	Cr_2O_3	MnO	P_2O_5
Vanadium slag	45.61	9.88	16.51	12.53	2.89	3.24	1.17	7.24	0.93

2.2. Sodium Roasting

Mix a certain proportion of Na_2CO_3 (16–24%) with vanadium slag ($< 74 \mu\text{m}$) evenly, feed the mixture into the muffle furnace, heat up from room temperature to the experimental set temperature (710°C – 870°C) at a heating rate of $10^\circ\text{C}/\text{min}$, and then kept for 30–150 min. When heating, the muffle furnace door is kept in a semi-closed state and sufficient oxygen is kept in the muffle furnace. At the end of the experiment, the roasted samples are cooled to room temperature, and then ground and sifted into powders for analysis and leaching experiments.

2.3. Water Leaching

First of all, a predetermined amount of deionized water is added to a flask with three necks, and the water in the flask with three necks is heated to a preset temperature under the action of a constant temperature water bath pot (50 to 99°C). To prevent the evaporation of water, the flask with three necks are connected with a reflux condenser. After the temperature reaches the preset temperature, the roasted clinker is added to the three-port flask (solid—liquid ratio 2 to 7 mL/g), and then start the stirring device (300 rpm) to make the roasted clinker fully leach for a certain time (20–70 min), then sample, wash and detect, and analyze the content of vanadium and silicon in the leaching liquid. The formula for calculating the leaching rate of vanadium and Si is as follows:

$$\eta = \frac{m_1}{m_2} \times 100\% \quad (1)$$

where η represents the leaching rate of vanadium and Si, m_1 is the content of vanadium and Si in the leaching solution, and m_2 is the quality of vanadium and Si in roasted clinker.

2.4. Calcification and Precipitation of Vanadium

Take a certain amount of vanadium leaching solution in a flask with three necks, add a certain amount of CaO (the molar ratio of $N_{\text{Ca}}/N_{\text{V}}$ is 0.45 to 0.7), and 2 times the molar amount of hydrochloric acid at a certain temperature (60 – 99°C) in a water bath for a certain time (45 min~95 min). In the process of reaction, the pH of the solution is kept at 6.7 ± 0.1 with the appropriate amount of hydrochloric acid. After the reaction, the filtrate and solid phase were obtained by vacuum pumping, and the content of vanadium in the filtrate was analyzed. Figure 1 is a schematic diagram of the whole process of vanadium slag roasting-leaching-calcification and vanadium precipitation.

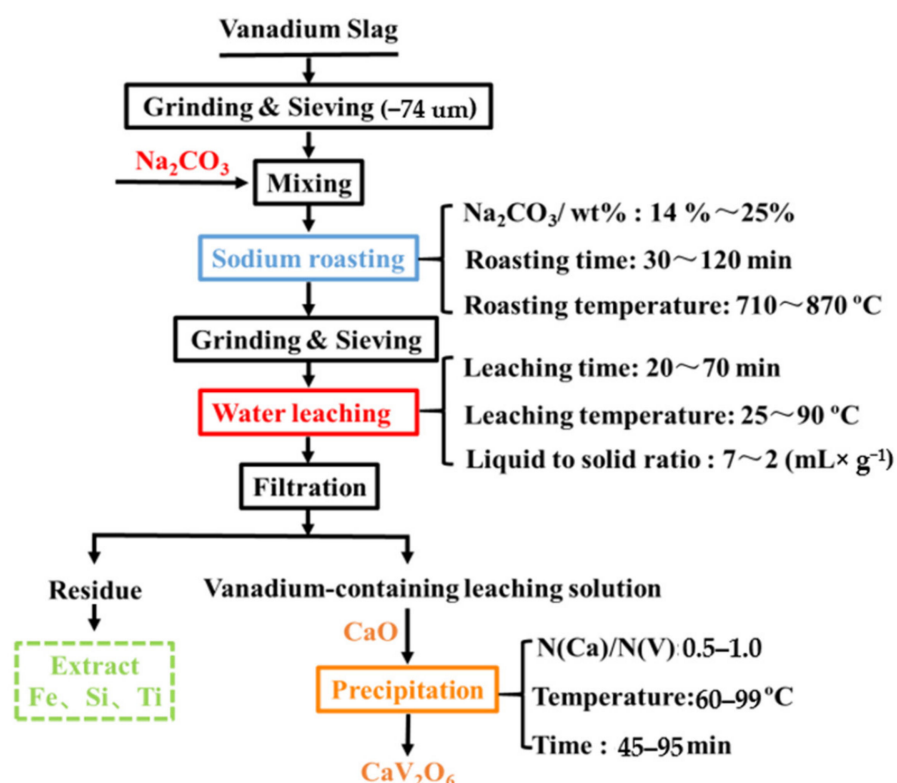


Figure 1. Flow chart of the whole process.

The formula for calculating the precipitation rate of vanadium is:

$$\zeta = 1 - \frac{m_1}{m_2} \times 100\% \quad (2)$$

where ζ represents the vanadium precipitation rate, m_2 is the quantity of vanadium in the vanadium purification solution, and m_1 is the quantity characterization of vanadium in the supernatant of vanadium precipitation.

2.5. Characterization

The content of various elements in the leaching solution and the content of vanadium in the vanadium precipitation wastewater was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 5300D, Perkin-Elmer Instruments Co., Ltd., New York, NY, USA). The chemical components of vanadium slag and vanadium precipitated products were analyzed by X-ray fluorescence spectroscopy. An X-ray diffractometer (XRD, Panak Amsterdam, The Netherlands) using Cu-K α rays ($\lambda = 1.5406 \text{ \AA}$), voltage: 40 kV, current: 30 mA, scan rate: 5°/min, scan range: $2\theta = 10\text{--}80^\circ$ was used to analyze the phase of vanadium slag, roasting slag, and leaching residue as well as vanadium precipitation products. A field emission scanning electron microscope (SEM-EDS, EDAX, Portland, USA) and its energy spectrum analysis are used to analyze the surface morphology of vanadium slag, roasting slag, and leaching residue. And element distribution, X-ray photoelectron spectroscopy (XPS) was used to characterize the valence states of major elements in vanadium slag, roasting slag, and residue.

3. Results and Discussion

3.1. Effect of Conditions of Roasting with Sodium on The Leaching Rate of Vanadium and Silicon

Figure 2 shows the effects of Na_2CO_3 addition, roasting temperature, and roasting time on the leaching rate of V and Si. The roasted sample is leached with water at 90 °C for 60 min, the ratio of liquid to solid is 5 to 1, and the stirring speed is 300 rpm. In Figure 2a,

the vanadium leaching rate increases at first and then decreases with the increase of Na_2CO_3 content. When the mass fraction of Na_2CO_3 is 20%, the maximum leaching rate of vanadium is 89.54%, which is due to the formation of soluble sodium salts such as NaVO_3 , Na_3VO_4 and $\text{Na}_4\text{V}_2\text{O}_7$. When the amount of sodium carbonate is more than 20%, the leaching rate of vanadium decreases, mainly because too much Na_2CO_3 is easy to form a substance ($\text{NaFeSi}_2\text{O}_6$) with a low melting point with vanadium slag, which leads to melting and sintering of the sample, wrapping on the surface of roasting slag and reducing the leaching of vanadium. For the leaching behavior of Si, the results show that the leaching rate of Si increases gradually with the increase of Na_2SiO_3 content, this is because part of excess Na_2CO_3 is easy to combine with SiO_2 in vanadium slag to form Na_2SiO_3 , When the leaching solution is alkaline, Na_2SiO_3 is retained in the leaching solution, so that the leaching rate of Si in the leaching solution gradually increases. When the leaching rate of vanadium reaches the highest, the leaching rate of Si is 1.96%.

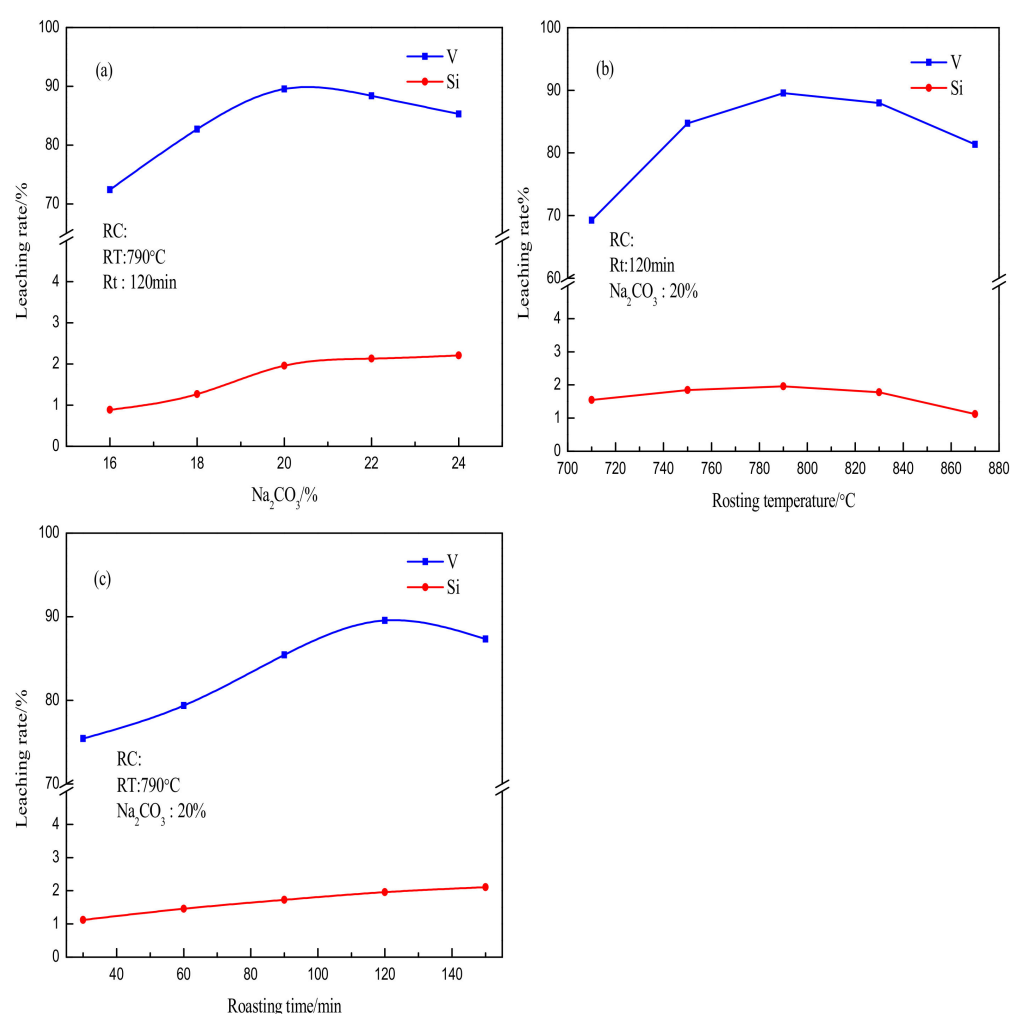


Figure 2. Effects of Na_2CO_3 addition (a), roasting temperature (b), and roasting time (c) on leaching rate of vanadium and silicon.

In Figure 2b, when the roasting temperature of vanadium slag is 710 °C, 69.25% of V is leached. It can be inferred that most of the vanadium in the vanadium slag has undergone sodiumization and oxidation at 710 °C, forming soluble sodium vanadate. When the temperature rises to 790 °C, the highest vanadium leaching rate is 89.54%. When the temperature exceeds 790 °C, the vanadium leaching rate decreases gradually, This is since the high roasting temperature leads to the appearance of the glass phase in the roasted sample, which makes the material denser and reduces the vanadium leaching. However,

the leaching rate of Si is opposite to that of V, which is attributed to the insoluble $\text{NaFeSi}_2\text{O}_6$ and $\text{NaTiSi}_2\text{O}_6$ in the phase of vanadium slag when the roasting temperature is higher than 710°C , which reduces the leaching rate of Si. The leaching rate of silicon is 1.96% at 790°C .

The effect of roasting time on the leaching rate of V and Si is shown in Figure 2c. With the extension of roasting time, the leaching rate of vanadium increases gradually, mainly because the trivalent vanadium in vanadium slag is fully oxidized and natrified with the extension of roasting time. When the roasting time exceeds 120 min, the leaching rate of vanadium decreases, which is mainly due to the long residence time of vanadium slag in the high-temperature zone and the caking of vanadium slag samples. It is not conducive to the oxidation and natrification of low-valent vanadium. At the same time, with the extension of roasting time, the leaching rate of Si increased slightly, and when the roasting time was 120 min, the leaching rates of vanadium and Si were 89.54% and 1.96%, respectively. Through the single factor roasting experiment, the optimum roasting conditions are determined as follows: the roasting temperature is 790°C , the roasting time is 120 min and the amount of Na_2CO_3 is 20%.

3.2. Effect of Leaching Conditions on The Leaching Rate of Vanadium and Silicon

Figure 3 shows the effects of leaching liquid-solid ratio, leaching time, and leaching temperature on the leaching rate of V and Si. The roasting sample was obtained under the conditions of 20% Na_2CO_3 addition, roasting temperature 790°C , roasting time 120 min, and leaching solution stirring speed 300 r/min. In Figure 3a, the leaching rate of vanadium increases gradually with the increase of the liquid-solid ratio, and the maximum vanadium leaching rate reaches 89.54% when the liquid-solid ratio is 5 to 1. This is mainly because the viscosity of the leaching solution decreases gradually with the increase of liquid-solid ratio, and the diffusion resistance of soluble sodium vanadate into the solution decreases gradually, which makes the soluble sodium vanadate can be leached more easily. Meanwhile, with the increase of solid-liquid ratio, the alkalinity of vanadium leaching solution also decreases, which is harmful to the leaching of vanadium (sodium vanadate is the salt of strong alkali weak acid, the vanadate ion is easily hydrolyzed, making the solution alkaline. The higher the alkalinity, the more it can inhibit the hydrolysis of vanadate ion, which is beneficial to the leaching of vanadium.), This explains why the leaching rate of vanadium will decrease when the liquid-to-solid ratio is greater than 5:1. When the leaching rate of vanadium reaches the maximum, the leaching rate of Si is 1.96%.

Figure 3b shows the effect of leaching time on the leaching rate of V and Si. With the increase of leaching time, the leaching rate increases gradually. When the leaching time is 60min, the leaching rate of vanadium reaches 89.54%. This is due to the physical dissolution of soluble sodium vanadate in the roasted sample and increasing the leaching time can effectively increase the leaching rate. When the leaching time exceeds 60min, the leaching rate of vanadium increases slightly. Therefore, the suitable leaching time is 60min. The leaching rate of Si is the same as that of vanadium. When the leaching time is 70min, the maximum leaching rate of Si is 2.18%.

Figure 3c shows the effect of leaching temperature on the leaching rate of V and Si. With the increase of leaching temperature, the leaching rate of vanadium increases gradually. When the Leaching temperature is 50°C , the leaching rate of vanadium is only 62.45%. When the temperature rises to 90°C , the leaching rate of vanadium is 89.54%. This is mainly since increasing temperature can improve the solubility of soluble sodium vanadate, on the other hand, the increasing temperature can improve the movement ability of water molecules, reduce the viscosity of the solution and gradually increase the leaching rate of vanadium. When the temperature of the leaching solution rises to 99°C , the leaching rate of vanadium is 90.13%, which indicates that when the leaching temperature is higher than 90°C , the contribution of temperature to the leaching rate of vanadium becomes very small. The leaching trend of Si is consistent with that of vanadium. Increasing temperature will increase the leaching rate of Si. When the temperature is 99°C , the maximum leaching

rate of Si is 2.01%. Through the single factor leaching method, the optimum leaching conditions can be determined as follows: the ratio of liquid to solid is 5 to 1, the leaching time is 60 min and the leaching temperature is 90 °C.

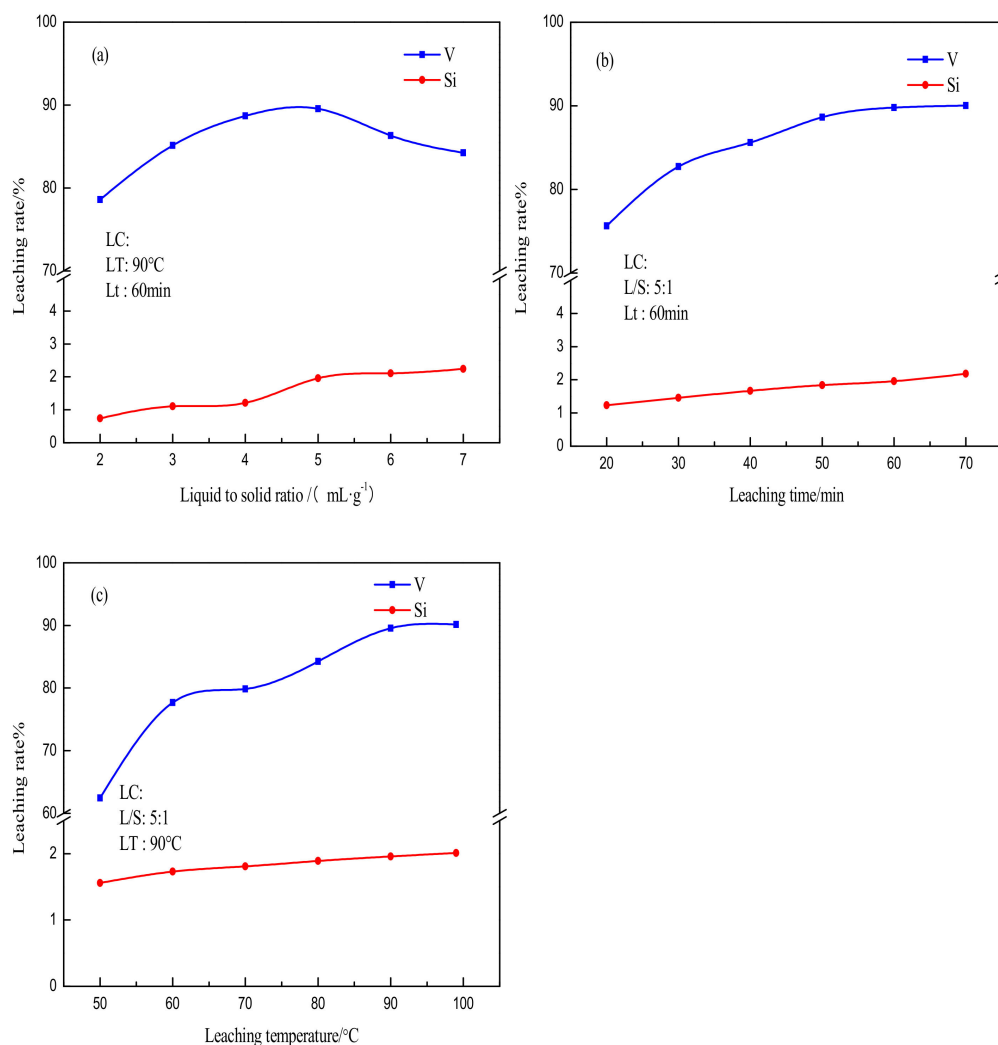


Figure 3. Effects of leaching liquid-solid ratio (a), leaching time (b), and leaching temperature (c) on vanadium leaching rate.

Besides, the concentration of the main ions in the vanadium leaching solution under the optimal conditions is shown in Table 2. The results show that the concentration of impurities is far less than that of vanadium ion, which indicates that the vanadium-containing leaching solution can be directly used as a vanadium source without purification.

Table 2. Concentration of main ions in vanadium leaching solution.

Ion Species	V	Na	Si	P	Cr	Ti	Mn	Fe
Concentration (g/L)	8.23	12.8	0.251	0.018	0.0013	0.0021	0.001	0.012
Concentration ratio of V/impurity elements	1	0.642	32.78	457.22	6330.77	3919.05	8230	685.83

Figures 4 and 5 show the phase, surface morphology, and element distribution of vanadium slag, roasting slag, and residue. It can be seen from Figure 4 that vanadium slag is mainly composed of vanadium iron spinel phase (FeV_2O_4), silicate phase (Fe_2SiO_4), and titanium spinel phase ($\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$). Combined with Figure 5a, it can be seen that most

of the surface distribution of vanadium and titanium elements coincide with each other, mainly because the chemical properties of titanium and vanadium are similar and often associated. It can be seen from Figure 4 that the spinel and silicate phases in vanadium slag have been decomposed after roasting, which can be observed from the disappearance of the peaks of these phases in the roasting slag, and replaced by new phases such as Fe_2O_3 , Na_2SiO_3 , $\text{Na}_4\text{V}_2\text{O}_7$, and NaVO_3 , the main reactions of sodium vanadate formation in Equations (3) and (4). The distribution of vanadium and sodium in Figure 5b is almost the same, which proves the existence of sodium vanadate and the repeated distribution of Na, Fe, and Si, which proves the existence of $\text{NaFeSi}_2\text{O}_6$. This corresponds to the diffraction peak of $\text{NaFeSi}_2\text{O}_6$ in Figure 4. After the roasting slag was leached by water, the soluble $\text{Na}_4\text{V}_2\text{O}_7$, NaVO_3 , and NaSiO_3 phases disappeared and transferred into the vanadium leaching solution, and the insoluble Fe_2O_3 , $\text{NaFeSi}_2\text{O}_6$, and $\text{NaTiSi}_2\text{O}_6$ remained in the residue. At the same time, combined with Figure 5c, it is known that the V in the residue is uniformly distributed and the content is greatly reduced, which is different from the segregation behavior in the roasting slag, which is a typical manifestation of vanadium water leaching. At the same time, the surface distributions of Fe, Si, and Na are also highly overlapping, which shows that silicon is retained in the residue mainly in the form of $\text{NaFeSi}_2\text{O}_6$:

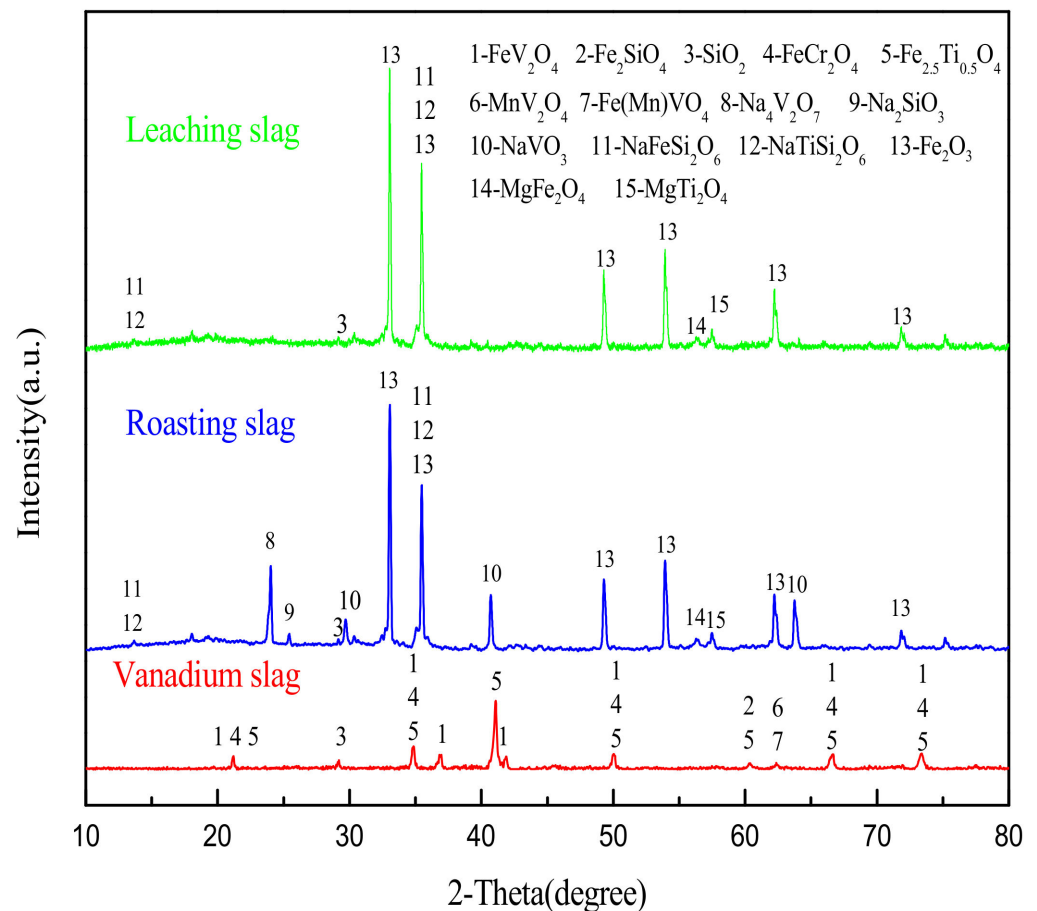
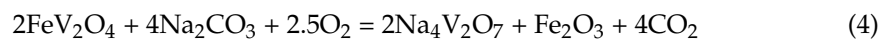
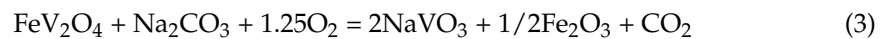
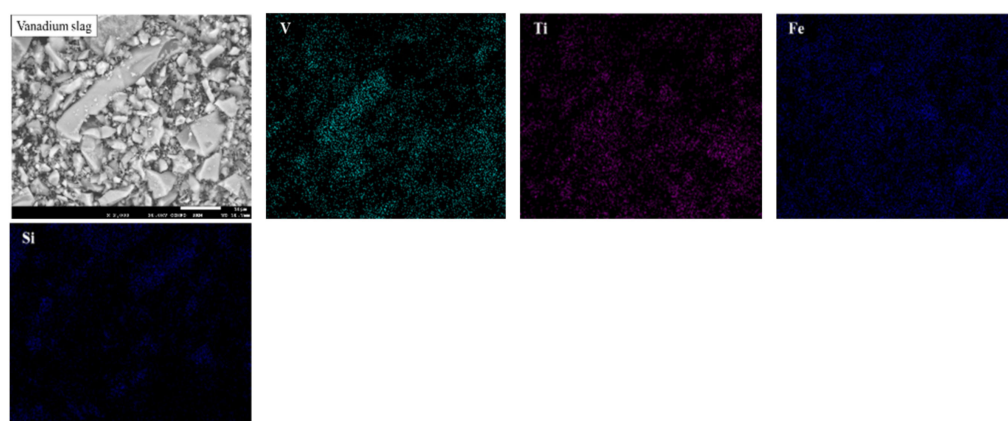
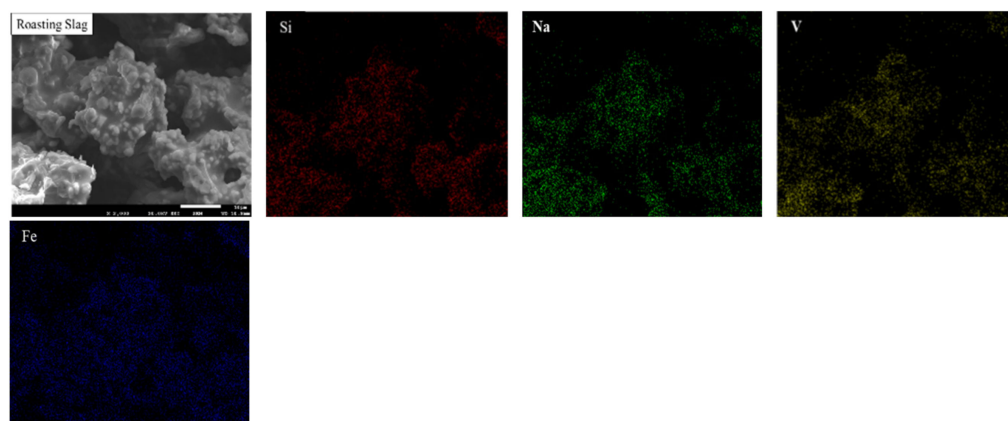


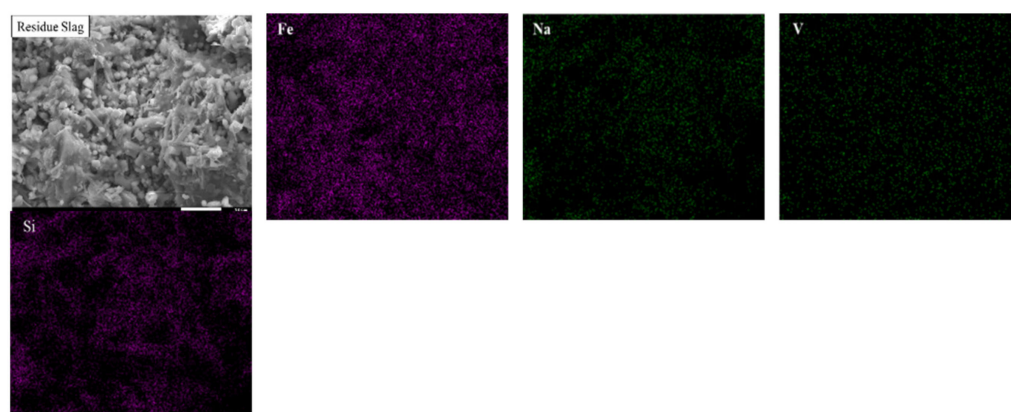
Figure 4. XRD patterns of Vanadium slag and the samples after roasting and leaching.



(a) Areal distribution of different elements in vanadium slag



(b) Areal distribution of different elements in roasting slag

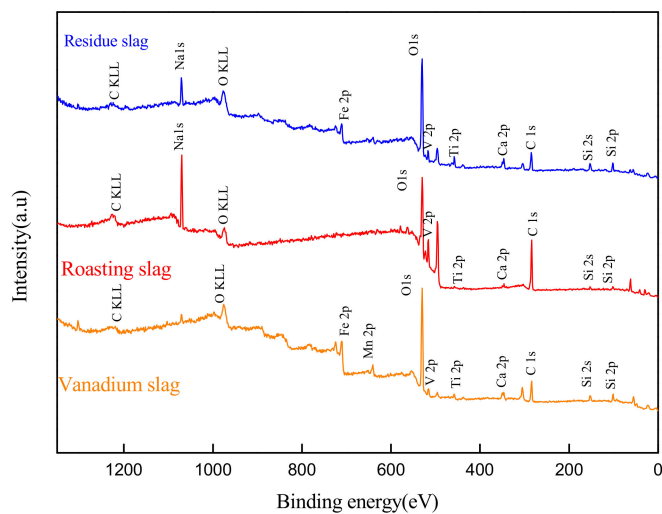


(c) Areal distribution of different elements in residue slag

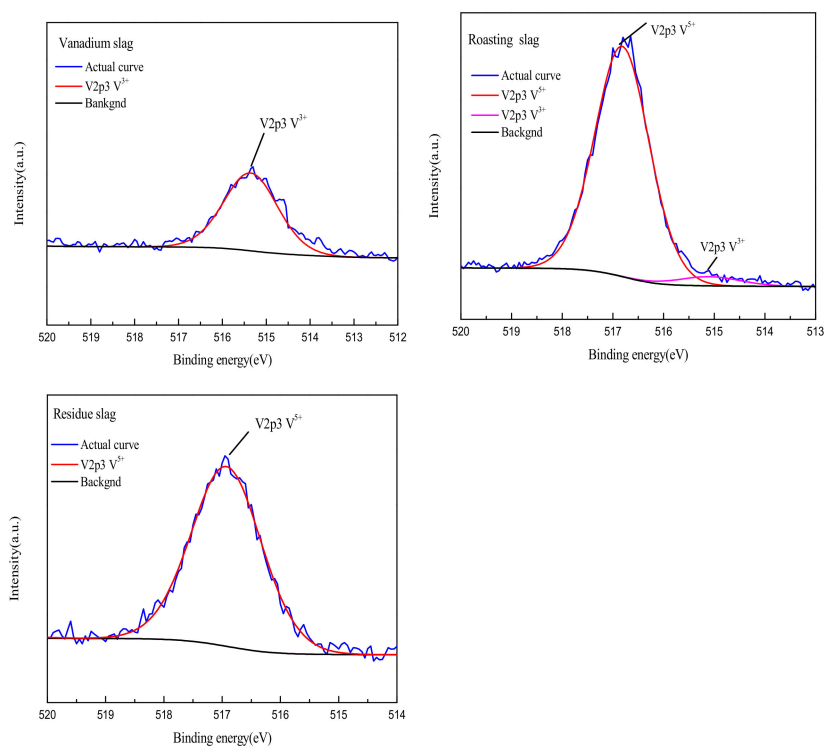
Figure 5. Microstructure and elements distribution of vanadium slag and during roasting and leaching.

Figure 6 shows the X-ray photoelectron spectroscopy of vanadium slag, roasted slag, and residue samples (a) global XPS; (b) the valence change of V; and the valence change of Fe. It can be seen from Figure 6 that vanadium slag mainly contains Fe, Mn, V, Si, O, Ca, and C elements; roasting slag mainly contains C, Na, O, V, Ca, C and Si, but Fe element peak is very small, this is because XPS is a surface analysis technique, the formed sodium

vanadate covers the surface of vanadium slag, resulting in the annihilation of Fe peak; the residue mainly contains C, Na, O, Fe, V, Ti, Ca and Si.

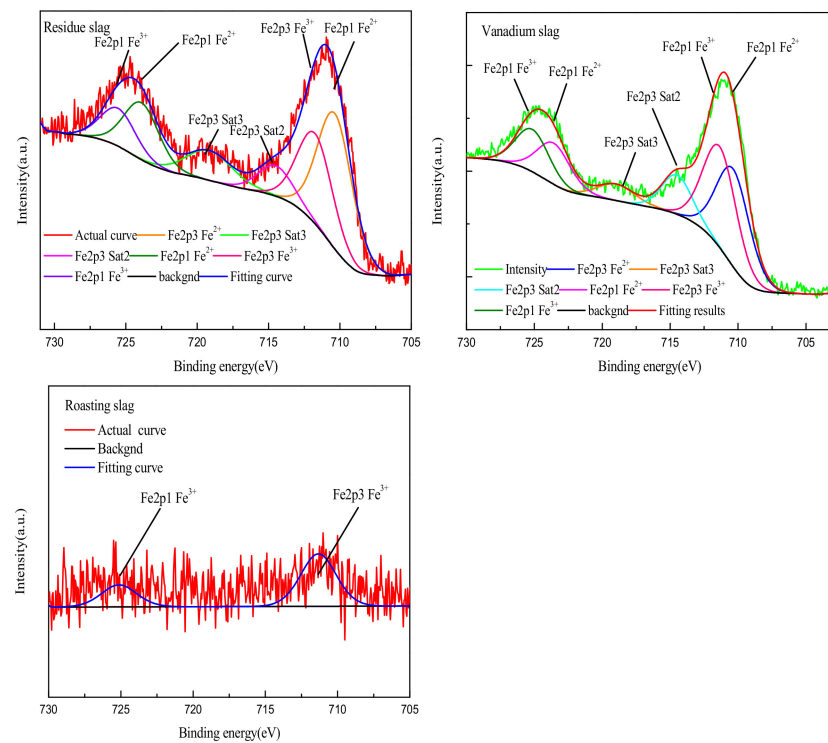


(a) XPS analysis of vanadium slag, roasting slag and residue

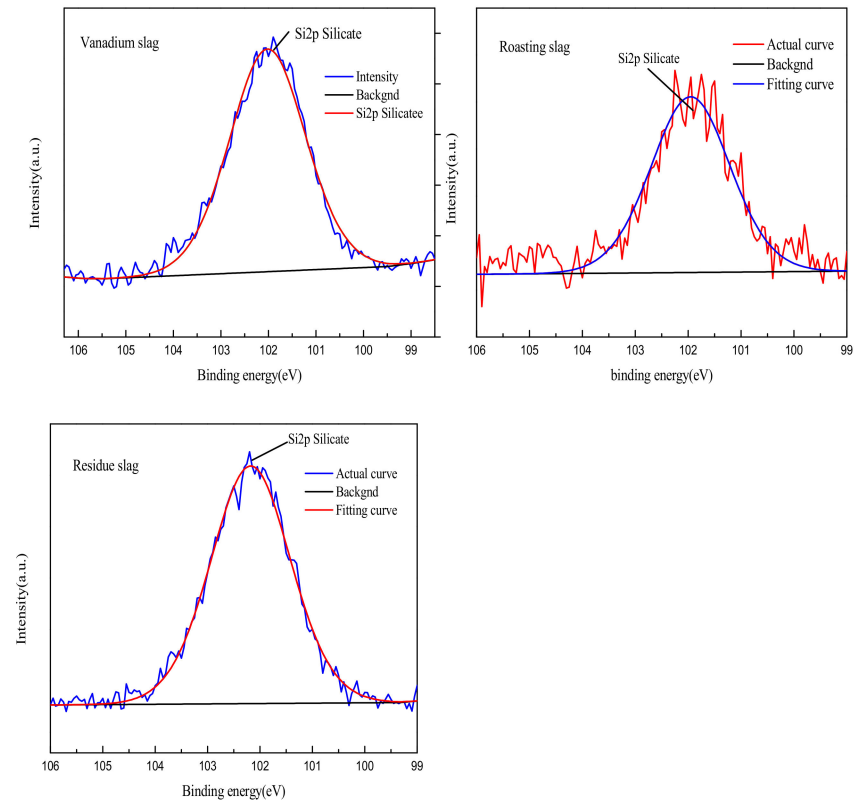


(b) High resolution spectrum characterization of different elements in vanadium slag

Figure 6. Cont.



(c) High resolution spectrum characterization of different elements in roasting slag



(d) High resolution spectrum characterization of different elements in residue slag

Figure 6. XPS analysis of vanadium slag, roasting slag and residue (a) Global XPS; (b) valence states change of V; (c) valence states change of Fe.

The vanadium on the surface of vanadium slag mainly exists in the form of trivalent vanadium, and the binding energy of trivalent vanadium is 515.5 eV, which is consistent with the reference [17] this is the characteristic valence state of vanadium in Spinel of vanadium slag. The Fe element is in the state of coexistence of trivalent iron and bivalent Fe, in which the proportion of bivalent Fe^{2+} is 52.89%. The proportion of Fe^{3+} is 47.11%, such as bivalent $\text{Fe}2p_{3/2}$ near 710 eV and trivalent $\text{Fe}2p_{3/2}$, near 711 eV, bivalent $\text{Fe}2p_{1/2}$ near 723 eV and trivalent $\text{Fe}2p_{1/2}$, near 725 eV, which corresponds to Fe_2SiO_4 and FeV_2O_4 in vanadium slag. It can be seen from Figure 6, When the vanadium slag is roasted by sodiumization, the valence state of vanadium is mainly 5, and the binding energy of the V element in the roasted slag increases from about 515.5 eV to near 517 eV, which is due to the oxidation of spinel. Among them, the proportion of V^{5+} is 95.6% and the proportion of V^{3+} is 4.4%, which shows that vanadium has been transformed from trivalent vanadium to pentavalent vanadium after roasting at 790 °C for 120 min, which achieves the purpose of sodium roasting. The Fe element mainly exists in the form of Fe^{3+} , which indicates that Fe^{2+} has been oxidized to Fe^{3+} . It is worth noting that the Fe and high-resolution peaks are so weak that they cannot be shown on the full spectrum peak. This is because the sodium vanadate formed during roasting is mostly distributed on the surface of the roasting slag, and the formation of sodium vanadate benefits from the decomposition of vanadate spinel. Under this condition, the material interdependent with sodium vanadate must be the Fe^{3+} ion after oxidation. Therefore, the roasting slag can only detect Fe^{3+} with low peak strength during XPS scanning but cannot detect oxidized Fe^{2+} .

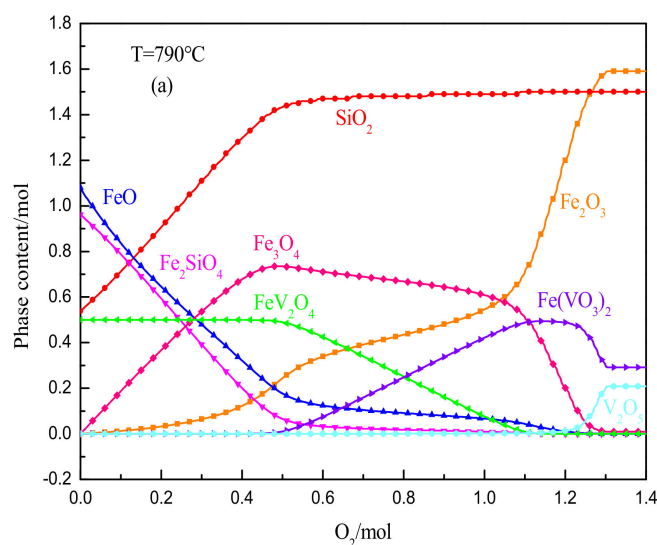
The high-resolution characterization of different elements in the leaching residue shows that the V element mainly exists in the form of pentavalent vanadate, which indicates that some vanadates of pentavalent V ions are not leached, and the distribution of Fe elements shows the coexistence of bivalent Fe and trivalent Fe, which is because the naked leakage of internal unoxidized Fe^{2+} was detected by XPS after the leaching of roasting slag.

For silicon element, its XPS analysis shows that the binding energy of silicon element in three kinds of slag is all near 102 eV in Figure 6, indicating that Si element mainly shows the chemical state of silicate, which is consistent with the corresponding XRD diagram. Silicon exists in the form of Fe_2SiO_4 in vanadium slag and in roasting slag and residue in the form of $\text{NaFeSi}_2\text{O}_6$ and $\text{NaTiSi}_2\text{O}_6$.

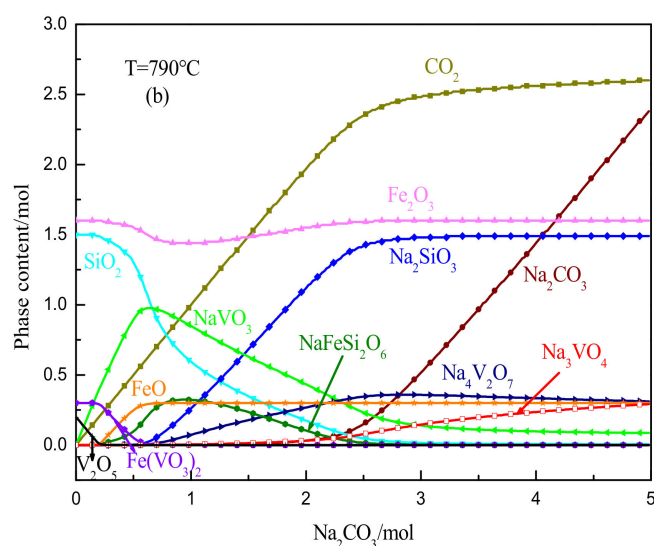
3.3. Thermodynamic Simulation

The thermodynamic simulation is carried out by Factsage software (Montreal, Canada and, Aachen, Germany). According to the composition and phase of vanadium slag, vanadium in vanadium slag mainly exists in the form of FeV_2O_4 and silicon mainly in the form of Fe_2SiO_4 . According to the calculation of Table 1, in the balance module of Factsage software, the relative amount of initial FeV_2O_4 is simplified to be 0.5 mol and the relative amount of Fe_2SiO_4 is 1.5 mol. The effects of the amount of oxygen and sodium carbonate on the phase transformation of Si and V elements in vanadium slag were simulated.

As shown in Figure 7a, when the initial Fe_2SiO_4 and FeV_2O_4 with an initial content of 1.5 mol and 0.5 mol were oxidized at 790 °C, 0.538 mol of Fe_2SiO_4 was decomposed into 1.076 mol of FeO and 0.538 mol of SiO_2 . After that, the oxidation reaction began, 0.962 mol of Fe_2SiO_4 was oxidized into Fe_2O_3 , Fe_3O_4 , and SiO_2 . With the formation of Fe_2O_3 FeO and oxidation and Fe_3O_4 , which is given priority to with oxidation for Fe_3O_4 , this suggests that the affinity of Fe and O 8/3 valence than the valence of 3 Fe affinity, and FeV_2O_4 oxidation decomposition, until the O_2 consumption came to 0.42 mol, FeV_2O_4 oxidative decomposition of the beginning of the formation of $\text{Fe}(\text{VO}_3)_2$ and V_2O_5 , and after that with the increase of oxygen consumption, SiO_2 content remains the same, gradually transforms the Fe_3O_4 Fe_2O_3 , As a result, the Content of Fe_2O_3 gradually increases. When the oxygen consumption is 1.4 mol, the content of each phase remains constant. At this time, V_2O_5 is 0.2 mol, $\text{Fe}(\text{VO}_3)_2$ is 0.3 mol, SiO_2 is 1.5 mol, and Fe_2O_3 is 1.6 mol.



(a) Oxidation phase transition of spinel and silicate



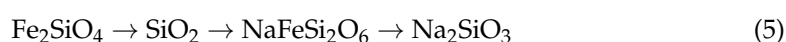
(b) Phase transformation process of vanadium slag sodium reaction

Figure 7. Phase transformation of vanadium slag during sodium roasting.

It can be seen from Figure 7b that V_2O_5 first consumes 0.2 mol of Na_2CO_3 to form $NaVO_3$, while Fe_2O_3 and SiO_2 , which are reaction pairs of reaction substances, also react with Na_2CO_3 to form $NaFeSi_2O_6$. When Na_2CO_3 consumption exceeded 0.2 mol, $Fe(VO_3)_2$ also began to participate in the reaction with Na_2CO_3 to form $NaVO_3$ and FeO . When Na_2CO_3 consumption was 0.5 mol, all V in V_2O_5 and $Fe(VO_3)_2$ were transferred to V of $NaVO_3$, and the environment of V atoms was changed. Later, with the continuous increase of consumption of Na_2CO_3 , $NaVO_3$ combined with Na_2CO_3 to form Na_3VO_4 and $Na_4V_2O_7$. As an intermediate product, $NaFeSi_2O_6$ shows a tendency to increase first and then decrease. This is due to the combination of Na_2CO_3 and $NaFeSi_2O_6$ to form more stable Na_2SiO_3 and Fe_2O_3 , at the same time, the formation of $NaFeSi_2O_6$ also proves that when vanadium slag is roasted at 790 °C, 20% Na_2CO_3 is appropriate. In the phase region

of $\text{NaFeSi}_2\text{O}_6$, the main soluble sodium vanadate salts formed are NaVO_3 and $\text{Na}_4\text{V}_2\text{O}_7$, which are consistent with the experimental results.

It can be seen that Fe_2SiO_4 in vanadium slag is transformed into insoluble substances such as $\text{NaFeSi}_2\text{O}_6$ (acmite) in the case of consumption of sodium salt. due to the limited content of sodium carbonate, it is difficult for conopyroxene to be retained in roasting slag. when leaching experiments are carried out, acmite is insoluble, so the leaching rate of silicon is low, which achieves the purpose of separation of silicon and vanadium. At the same time, from the effect of the addition of sodium carbonate on the leaching rate of silicon, it can be seen that the increase of sodium carbonate is beneficial to the leaching of silicon, which is consistent with the thermodynamic analysis in Figure 7b. When excessive sodium carbonate is added, the silicon-containing phase changes from conopyroxene sodium silicate, while sodium silicate is easily soluble in water, which increases the leaching rate of silicon. Therefore, in the case of excessive sodium carbonate, the migration mode of silicon in the whole process is as follows:



3.4. Precipitation of Vanadium by Calcification

To prepare CaV_2O_6 and ensure the precipitation of vanadium under weak acid conditions, the reaction system must be within the range of the red dotted line in Figure 8 [18], so the pH of the precipitation of vanadium is 6.7 ± 0.1 .

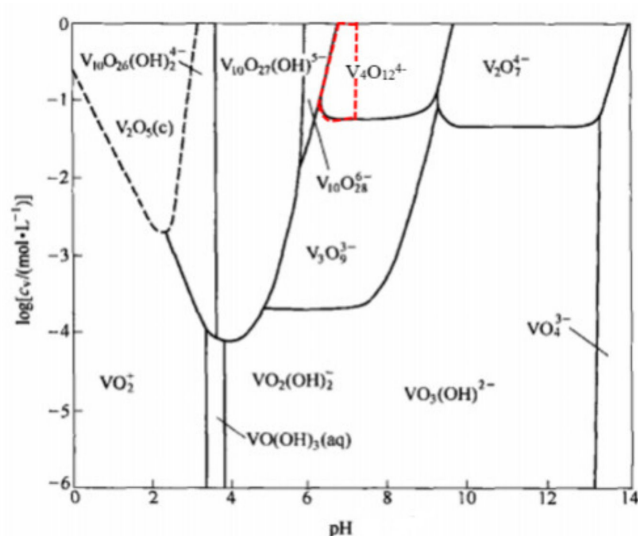
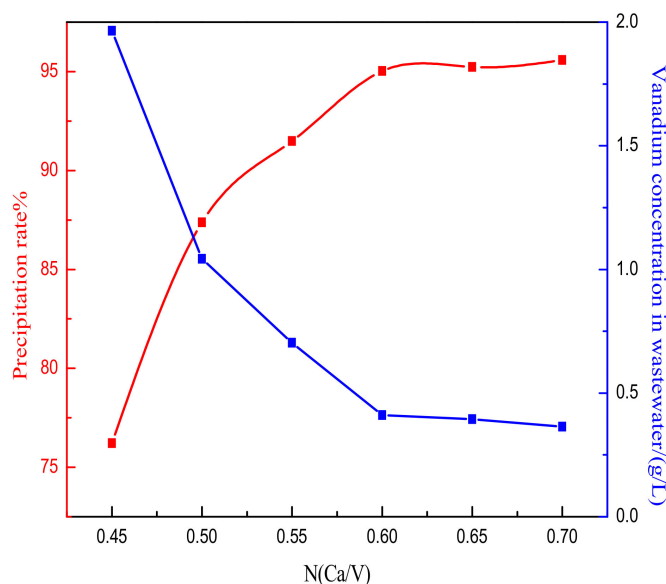


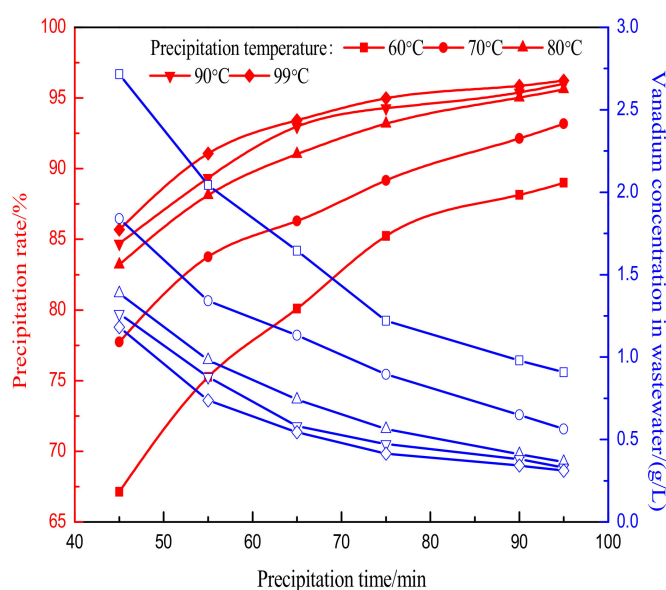
Figure 8. Morphology of pentavalent vanadate ions in aqueous solution.

The molar ratio of calcium to vanadium N refers to the effect of $n(\text{Ca}) / n(\text{V})$, on the precipitation rate of vanadium under the conditions of vanadium precipitation temperature 90°C , vanadium precipitation time 90 min and vanadium precipitation pH 6.7 ± 0.1 . the effect of calcium-vanadium molar ratio N on vanadium precipitation ratio was investigated. The results are shown in Figure 9. It can be seen from the figure that with the increase of N , the precipitation rate of vanadium increases gradually. When the ratio of calcium to vanadium is 0.45, the precipitation ratio of vanadium is only 76.21%. When the molar ratio of calcium to vanadium N increases to 0.6, the precipitation ratio of vanadium reaches 95.03%. With the continuous increase of N , the precipitation ratio of vanadium increases very slowly. In the process of calcium precipitation of vanadium, the increase of the molar ratio of calcium to vanadate greatly promoted the positive precipitation of calcium vanadate. at the same time, under the acidic condition, it greatly inhibited the hydrolysis of CaO and increased the concentration of effective Ca in the solution system. Compared with precipitation at alkaline conditions of vanadium, the concentration of available calcium

in the solution is lower, the reaction is slow and there are more impurities. Therefore, the suitable molar ratio of calcium to vanadium is 0.6, and the vanadium concentration of the supernatant of precipitated vanadium under this condition is 0.41 g/L.



(a) Effect of molar ratio of calcium to vanadium on precipitation rate of vanadium



(b) Effect of precipitation temperature and time on precipitation rate of vanadium

Figure 9. The effects of $N(\text{Ca})/n(\text{V})$, precipitation temperature, and precipitation time on the vanadium precipitation ratio and vanadium concentration in the vanadium wastewater.

It can be seen from the diagram that temperature and reaction time have a significant effect on the vanadium precipitation rate. Increasing vanadium precipitation temperature and reaction time can effectively increase the vanadium precipitation rate. When precipitation temperature is the same, increasing vanadium precipitation time can increase the vanadium precipitation rate. When precipitation time is the same, the higher the vanadium precipitation temperature is, the higher the vanadium precipitation rate is.

The precipitation rate of vanadium at 80 °C, 90 °C, and 99 °C is much higher than that at 60 °C and 70 °C, because the calcification reaction is endothermic, the reaction is positive, which is beneficial to the formation of vanadium precipitation. When the vanadium precipitation temperature is 60 °C and the vanadium precipitation time is 45 min, the vanadium precipitation ratio is only 67.13%, and the residual V concentration in the solution is 2.71 g/90 min. When the vanadium precipitation time is 90 min, the vanadium precipitation ratio increases to 88.14%, while the residual vanadium concentration in the solution decreases to 0.97 g/L. When the vanadium precipitation temperature is 90 °C and the vanadium precipitation time is 45 min, the vanadium precipitation ratio is 84.71%, the concentration of residual vanadium in the supernatant of vanadium precipitation is 1.26 g/L when the vanadium precipitation time is 90 min, the vanadium precipitation ratio is 95.03%, and the residual vanadium concentration in the vanadium precipitation supernatant is 0.41 g/L; when the vanadium precipitation temperature is 99 °C, the increase of vanadium precipitation rate will become very small.

Through this comparative analysis, it can be seen that time has a great influence on the vanadium precipitation rate when the vanadium is precipitated at low temperatures, and the effect of time on the vanadium precipitation rate will be greatly reduced when the temperature is beyond 80 °C. Therefore, the suitable temperature and time for depositing vanadium is 90 °C and 90 min.

3.5. Kinetic Analysis of Vanadium Precipitation

The process of calcium precipitation of vanadium is a process of isothermal crystallization, so the isothermal crystallization kinetics of vanadium precipitation can be described with Avrami kinetic model [19–21], the equation is as follows:

$$\varphi = \varphi_{\infty} [1 - \exp(-kt^n)] \quad (6)$$

Among them, φ is the volume fraction of calcium vanadate crystallized at t time (%), φ_{∞} is the volume fraction of grains in the total sample for an infinitely long time (%), k is the crystallization rate constant (min⁻ⁿ), n is the Avrami index, which is related to the nucleation mechanism and growth mode. Avrami model assumes that the nuclei are irregularly distributed and each nucleus forms a grain.

Use η to represent relative crystallinity, that is, $\eta = \varphi / \varphi_{\infty}$, then (6) can be rewritten as:

$$1 - \eta = \exp(-kt^n) \quad (7)$$

Taking the logarithm of both sides of (4) we get:

$$\ln [-\ln (1 - \eta)] = \ln k + n \ln t \quad (8)$$

Using $\ln [-\ln (1 - \eta)]$ as the y-axis and $\ln t$ as the x-axis, draw the graph. According to the slope and intercept of the straight line obtained, the Avrami index n and the reaction kinetic rate constant k can be obtained.

The Avrami index n is theoretically an integer 1, 2, 3, etc., n is 1, 2, 3 representing needle-shaped crystals, disc-shaped crystals, and spherical crystals, respectively. Practice has shown that most of the reaction crystallization processes are complex, will not form a single crystal grain, and the way of nucleation is not a single, so the Avrami index is generally a decimal number, usually not an integer.

The Avrami kinetic equation was used to fit the precipitation rate of vanadium at different temperatures and times in Figure 10. The relative crystallinity is the precipitation rate of vanadium. From Figure 10, it can be seen that the growth process of calcium vanadate crystals can be determined by Avrami at 60~80 °C. The equation is well described, and the reaction kinetic parameters can be solved from the intercept and slope of each curve. It can be seen from Table 3 that as the temperature increases from 60 °C to 99 °C, the crystallization rate constant increases from 0.035 to 0.16, and the crystallization index

decreases from 0.915 to 0.671. When the temperature is 60 °C, the crystallization index is close to 1.0, and the crystal grows in one dimension and is a needle-like crystal. As the temperature increases, the crystallization will become complicated, and the crystallization index will gradually decrease. Under these temperature gradients, the crystallization index is low (less than 1), which may be a result of the combined effect of experimental deviation, temperature factors, and the complexity of the crystallization process, but it can be seen that the crystallization rate constant is more affected by temperature. Obviously, the higher the temperature, the higher the crystallization rate constant, which also proves that the calcification reaction is endothermic.

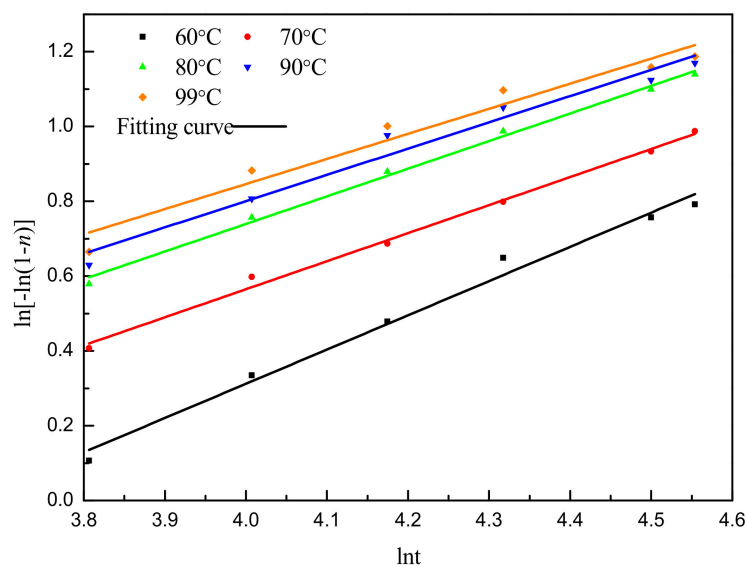


Figure 10. Relationship between $\ln [-\ln (1 - \eta)]$ and $\ln t$ at different temperatures.

Table 3. Dynamic parameters at different temperatures.

Temperature/°C	Pearson's r	R-Square	Avrami Index n	Crystallization Rate Constant K
60	0.994	0.985	0.915	0.035
70	0.997	0.994	0.750	0.082
80	0.997	0.994	0.738	0.110
90	0.985	0.964	0.702	0.135
99	0.979	0.949	0.671	0.160

According to the Arrhenius formula, the linear relationship between the reaction rate constant K and temperature is as follows:

$$\ln K = \ln A - E_a/(RT) \quad (9)$$

Plot $\ln K$ and T^{-1} to get Figure 11, whose fitting equation is:

$$\ln K = 11.818 + 5028.835T \quad (10)$$

By comparing Equations (9) and (10), we can get:

Pre-referential factor $A = 1.35 \times 10^5$, apparent activation energy $E_a = 41.81$ kJ/mol.

The phase and surface morphology of the calcium vanadate product under the conditions of a reaction time of 90 min, a reaction temperature of 90 °C, and a calcium-vanadium molar ratio of 0.6 are shown in Figures 12 and 13.

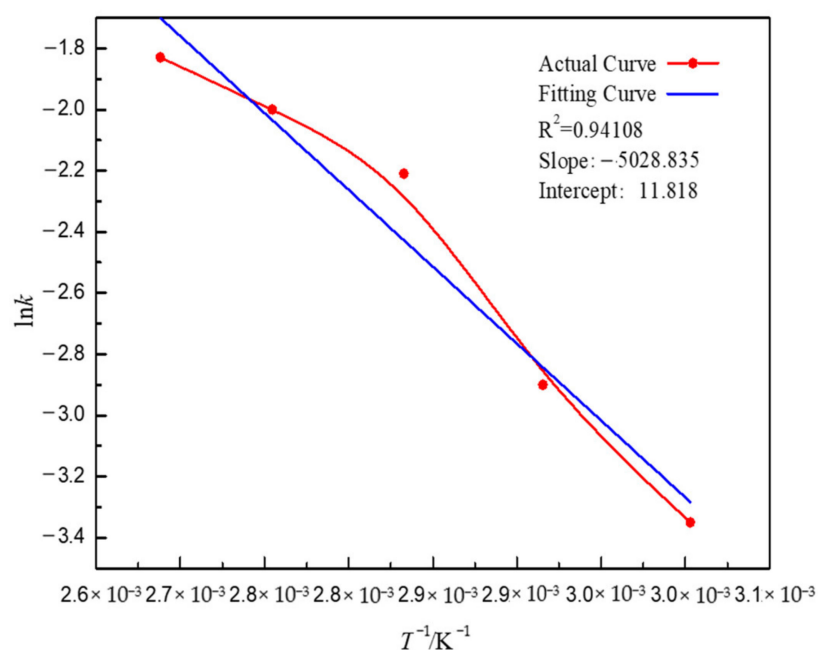


Figure 11. Relationship between $\ln K$ and T^{-1} .

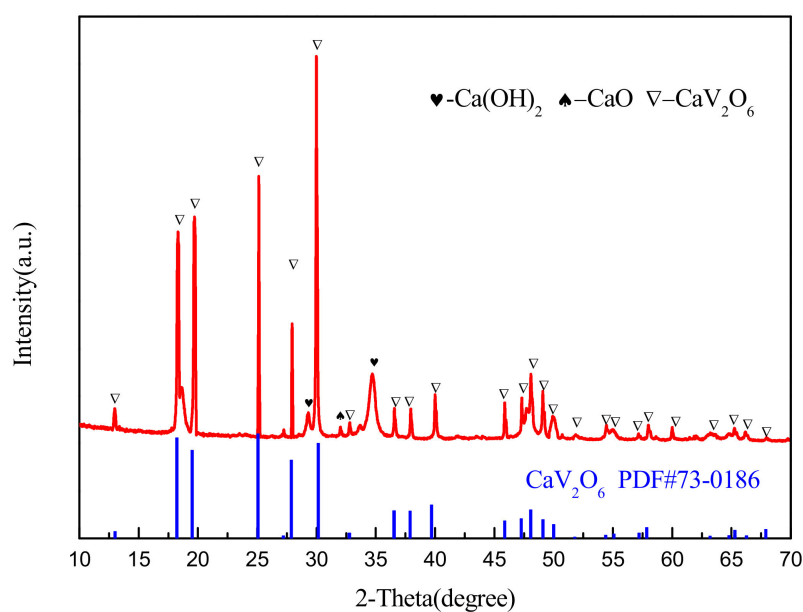


Figure 12. XRD pattern of calcification products.

It can be seen from Figure 12 that the precipitation products are mainly CaV_2O_6 and a small amount of CaO and Ca(OH)_2 . From Table 4, it is calculated that CaV_2O_6 in the calcium method product accounts for about 95.69%, and the molar ratio of calcium to vanadium is 0.58, which is greater than that of CaV_2O_6 .

Table 4. Chemical composition of calcific product.

Component	Ca	V	CaO	V_2O_5	Ca: V(mol)
Content(%wt)	19.66	43.92	20.61	78.41	0.56

Figure 13 shows the microscopic morphology of the precipitated product. It can be seen from Figure 13 that the synthesized CaV_2O_6 crystals are dendritic needle-like crystals.

Combined with thermodynamic and kinetic analysis, it can be seen that the formation of calcium vanadate is dependent on other impurity points. The nucleus grows up, and this non-uniform nucleation point should be calcium oxide or calcium hydroxide. At the beginning of the reaction, even under acidic conditions, calcium oxide combines with water to form a large amount of $\text{Ca}(\text{OH})_2$. Calcium provides nucleation sites for the formation of calcium vanadate. As the reaction time increases, the action of calcium hydroxide and hydrochloric acid in the solution is “eroded”, and as the outer Ca^{2+} is “eroded”, the internal Ca^{2+} gradually Migrate to the surface of the formed calcium vanadate, and further contact with the Vanadate ion in the solution, the calcium vanadate crystals will continue to grow. Because the reaction of preparing calcium vanadate by calcium precipitation of vanadium is an endothermic reaction, it tends to grow higher. As shown in Figure 13, the morphological structure of calcium vanadate is needle-like, and it is attached to the nucleation site to expand in three dimensions. The energy-dispersive X-ray spectroscopy (EDS) matched with the scanning electron microscope measured the elemental composition of the sample. The Ca, V and O element signal peaks appeared in the spectrum. The calculated average Ca/V ratio was 0.521, which is close to the atomic ratio of calcium to vanadium in CaV_2O_6 . The theoretical stoichiometric value of the chemical formula.

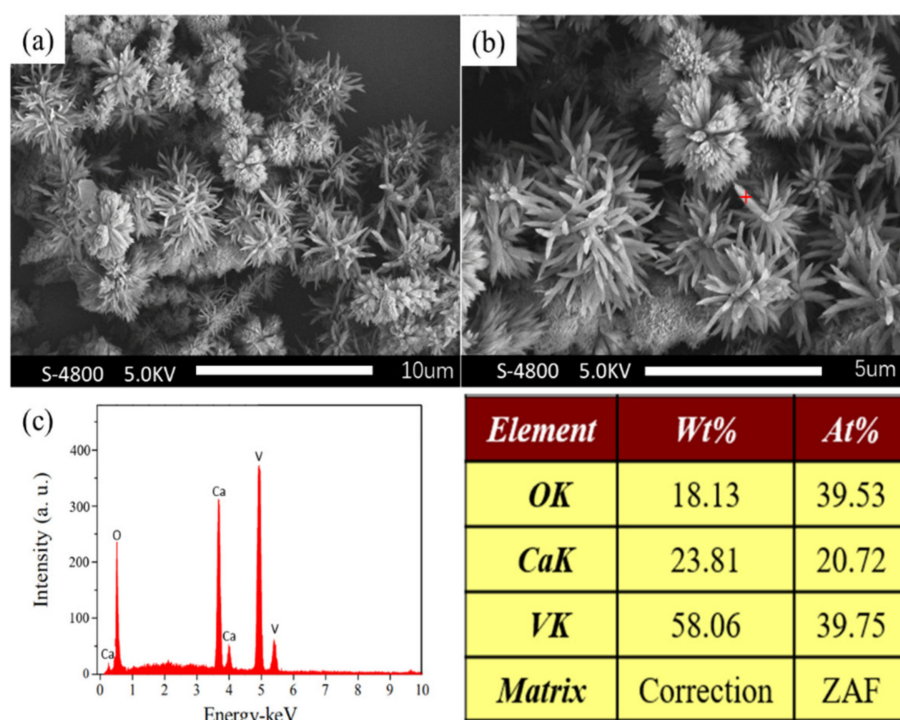


Figure 13. Surface morphology and energy spectrum analysis of calcification products ((a,b) CaV_2O_6 surface morphology under different magnifications; (c) analysis of the energy spectrum points in the Figure 13(b)).

4. Conclusions

A simple schematic diagram of the whole process is shown in Figure 14. The main conclusions of this research are as follows: The experimental study of vanadium slag single-factor sodiumization roasting shows that with the increase of the roasting temperature and the extension of the roasting time, the vanadium leaching rate increases first and then decreases; during the roasting process, increasing the amount of Na_2CO_3 within a certain range can be effective Improve the leaching rate of vanadium, but if it is too high, it will decrease the leaching rate of vanadium. The best calcination conditions under the experimental conditions are calcination time 120 min, calcination temperature 790 °C, and Na_2CO_3 addition amount is 20%.

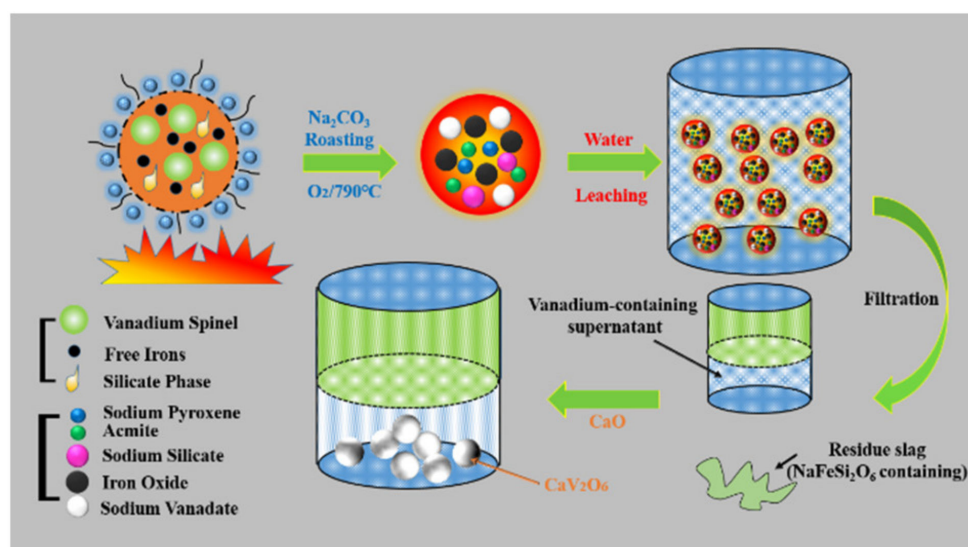


Figure 14. Process diagram.

The single-factor leaching experiment of vanadium slag roasting clinker shows that the leaching rate of vanadium increases with the increase of leaching temperature and leaching time, and it first increases and then decreases with the increase of solid-liquid ratio; vanadium leaching The process is controlled by diffusion and conforms to the shrinking core model with reduced particle size. The optimum leaching conditions were as follows: leaching temperature 90 °C, leaching time 90 min, leaching liquid-solid ratio 5:1, and vanadium leaching solution can be used for calcification and vanadium deposition without purification.

After sodium roasting-water leaching of vanadium slag, vanadium and silicon can be effectively separated. Under the optimum roasting and leaching conditions, the leaching rate of vanadium is 89.54%, and the leaching rate of silicon is 1.96%, which achieves the effective separation of vanadium and silicon. Vanadium combines with sodium to form sodium vanadate. Silicon is easy to combine with iron, sodium, and titanium to form acmite and sodium pyroxene.

The experimental study on calcium precipitation of vanadium shows that the precipitation time of vanadium is 90 min, the temperature of precipitation of vanadium is 90 °C, the molar ratio of calcium to vanadium is 0.6, the best precipitation ratio of vanadium is 95.03%, and the concentration of residual vanadium in the supernatant of precipitated vanadium is 0.41 g/L. The process of calcium precipitation of vanadium can be described by Avrami isothermal crystallization kinetic model. Under the experimental conditions, the apparent activation energy of the reaction is 41.81 kJ/mol. the main phase of the calcification product is CaV_2O_6 , which is a dendritic needle crystal.

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