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Study on Deep Vanadium Extraction and Calcified Dealkalinization of Vanadium Extraction Residue

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Abstract

Vanadium extraction tailings, as a highly alkaline and hazardous solid waste, pose not only serious environmental risks but also severely hinder the large-scale recycling of secondary iron resources. This study proposes an innovative process of "mild alkali leaching for vanadium extraction coupled with deep calcification and dealkali removal". The vanadium extraction slag from a steel plant in China was used as a raw material to carry out the experimental and pilot study of alkali leaching of vanadium and calcification dealkalization. Experimental results show that under the conditions of 120 °C, 1% NaOH solution, liquid-solid ratio of 4:1 to 6:1, and reaction time of 1 h, vanadium leaching rate can reach 50%, which can be effectively used as a high-value-added economic hedge. Subsequently, under the conditions of 200 °C, calcium oxide concentration of 19.29%, stirring speed of 800 rpm, liquid-solid ratio of 4:1, and reaction time of 1 h, the Na_2O content in the tailings was successfully reduced to below 1%. A large number of tailings can be converted into high-quality secondary iron ore resources, which are suitable for subsequent iron-bearing briquette preparation and blast furnace ironmaking. Furthermore, pilot-scale testing in a 200 L reactor verified the engineering scalability of this combined process, maintaining a vanadium extraction rate of over 50% and an alkali removal rate of over 80%. This study provides a robust, scalable, and highly profitable pathway for the comprehensive utilization of high-alkali metallurgical solid waste.

Keywords: vanadium extraction residue; alkali immersion; calcified dealkalinization; pilot test

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1. Introduction

Vanadium is a strategically important transition metal widely used in steel production, aerospace alloys, catalysts, and emerging energy storage technologies such as vanadium redox flow batteries [1]. Its consumption in the iron and steel industry accounts for approximately 85% of total vanadium-bearing products produced worldwide [1]. As high-grade primary vanadium ore reserves become increasingly scarce globally, secondary vanadium resources—particularly metallurgical slags—have attracted growing international attention [2]. Petranikova et al. emphasized that vanadium was formally recognized as a Critical Raw Material by the European Commission in 2017, and the United States and Canada

have similarly prioritized its sustainable recovery from secondary sources, including metallurgical slags and petroleum residues [2].

The residue generated from vanadium slag after sodium oxide roasting and water leaching is referred to as vanadium extraction residue. Currently, the primary method of disposal is open-air storage [3]. As a solid waste, vanadium extraction residues not only occupy large areas of land but, when exposed to long-term rain erosion, release pentavalent vanadium and hexavalent chromium ions into rivers or groundwater, contaminating water resources and posing environmental and health risks [4]. More than 1.2 million tons of vanadium extraction tailings are generated annually in China alone, making their environmentally sound treatment a matter of urgent global concern [5].

Vanadium extraction residue contains more than 30% iron, making it highly valuable for recycling [6]. However, its high alkalinity and complex mineral phases and composition hinder its comprehensive utilization [7,8]. As China's industrial development drives an increasing demand for iron ore, vanadium residue, being a secondary iron ore resource and rich in vanadium, chromium, gallium, and other rare metals, has regained attention for its potential value [9–11]. The tailings have a fine particle size, with more than 80% being smaller than 0.2 mm. It serves as an excellent raw material for pellet production via cold consolidation. Therefore, vanadium extraction residue can be incorporated into the sinter in specific proportions and reintroduced into the steelmaking process to recover iron and other valuable metals [12]. However, the high sodium content in vanadium extraction residue increases the risk of sinter entering the blast furnace, raising the alkali load, which severely affects the stable operation and lining of the furnace [13]. Thus, efficient dealkalization of vanadium extraction residue is crucial to enable its large-scale utilization.

Moskalyk and Alfantazi [1] conducted a comprehensive review of vanadium processing routes and highlighted that both acid and alkaline leaching pathways are viable for extracting vanadium from metallurgical slags, with alkaline systems offering superior selectivity when managing co-dissolution of chromium and silicon. More recently, Sadeghi and Alamdari [14] proposed an innovative two-stage recovery approach for vanadium and other valuable materials from high-lime steelmaking slag, combining alkaline roasting at 900 °C with sodium bicarbonate leaching, demonstrating that process parameters such as reagent concentration, temperature, and particle size can be optimized to significantly improve vanadium recovery efficiency from complex slag matrices. On the question of calcium–vanadium interactions in slag systems Kokko et al. [15] proposed an innovative two-stage process for high calcium basic oxygen furnace slag, in which calcium was first selectively removed at low temperature, followed by ammonium carbonate leaching of the vanadium-rich residue, demonstrating that prior calcium removal can substantially enhance subsequent vanadium leaching efficiency. In parallel, Liu et al. [16] systematically investigated water leaching of sodium-roasted vanadium slag, establishing optimal conditions for desiliconization and precipitation of high-purity ammonium vanadate, achieving an overall vanadium recovery efficiency of 96.9%. These international studies underscore the technical feasibility of alkaline leaching as an environmentally preferable alternative to conventional sodium roasting processes, and collectively demonstrate that the coupled management of calcium, sodium, and silicon impurities is a central challenge in vanadium recovery from steelmaking slag.

Currently, the development and application of vanadium extraction residues focus on three main areas. The first is the secondary extraction of vanadium. Fan and Ge [17] employed atmospheric or pressurized acid leaching processes to extract vanadium, yielding positive results. The second approach involves the direct or indirect utilization of tailings after processing. Xiu [18] developed new black materials from vanadium extraction residue, which demonstrated excellent properties as photothermal conversion materials and ce-

ramics. The third method involves coal-based direct reduction in vanadium extraction residue, followed by magnetic separation to convert non-magnetic Fe_2O_3 into magnetic substances for iron recovery [19,20]. Generally, whether operating at atmospheric pressure or within high-pressure autoclaves, wet acid processing primarily focuses on vanadium extraction, though balancing the leaching rate and severe acid consumption remains a universal challenge. Pyrometallurgical processes are mainly used for iron extraction. Bi Xiurong studied the calcification roasting-magnetic separation process. While iron recovery from slag was effective, the sodium removal rate was only 60%, and vanadium remained in the slag. To reduce the sodium content to below 0.5%, electric furnace melting separation must be employed. The process is lengthy, requires significant investment, and generates environmental pollution from HCl and Cl_2 emissions [21].

Outside of China, vanadium recovery from secondary metallurgical resources has largely been pursued via carbothermal reduction methods [22]. Additionally, vanadium is recovered by producing a vanadium-bearing pig iron, in which V_2O_5 is reduced and enriched from vanadium-bearing converter slag into hot metal in a submerged arc furnace, and vanadium is subsequently oxidized to slag in an induction furnace to yield high-content vanadium slag. Despite these advances, a unified process integrating efficient vanadium recovery with effective dealkalization of the residue—directly enabling reuse in blast furnace burdens—remains lacking in the global literature [2,4].

Building on the wet process of vanadium extraction via water leaching and the selective replacement mechanism of calcium for sodium and potassium, and drawing upon both domestic research experience and the broader international hydrometallurgical literature reviewed above, this paper proposes a novel integrated approach: 'wet calcification and dealkalization' coupled with 'deep vanadium extraction through an alkaline process combined with calcification and dealkalization.' This process does not require high costs to pursue the ultimate vanadium extraction rate. Instead, it uses extremely mild alkaline leaching conditions to recover about 50% of the vanadium as a high-value-added byproduct to offset operating costs. Subsequently, deep dealkali removal was carried out at 200 °C using inexpensive calcium sources and the waste heat from the steel plant's existing low-grade waste steam. The tailings after alkali metal removal completely eliminate the threat of the alkali load to the blast furnace lining, thus enabling them to be fully returned to the iron and steel smelting process as a high-quality secondary iron ore resource. This approach offers a feasible solution for the large-scale utilization and consumption of sodium vanadium extraction residue.

2. Materials and Methods

2.1. Materials

As shown in Table 1, the main components of vanadium extraction residue are 41.9% Fe_2O_3 and 21.9% SiO_2. Additionally, Na_2O content is 5.30%, and V_2O_5 content is 1.29%. The vanadium content is significantly higher than that of vanadium-titanium magnetite (V_2O_5 at 0.3%), highlighting its substantial recycling potential. As shown in Table 2 and Figure 1, the average particle size of vanadium extraction residue is 72.02 μm (D50).

As shown in Figure 2, the primary phases of vanadium extraction residue include hematite, ilmenite, silicate, limonite, and spinel phases. The iron-bearing phases in the vanadium extraction residue remain unchanged compared to vanadium slag. Chromium (Cr) in the vanadium extraction residue is primarily found in the spinel phase, while vanadium (V) is predominantly located in the silicate phase. The silicate phase is rigid and resistant to complete leaching. Sodium primarily exists as sodium aluminosilicate, in combination with aluminum and silicon, which is similar to the form of sodium in red mud.

Table 1. Composition analysis of vanadium extraction residue (wt.%).

Element	Fe_2O_3	SiO_2	TiO_2	MnO	Na_2O	Al_2O_3	Cr_2O_3	MgO	CaO	V_2O_5
Content	41.9	21.9	8.61	8.13	5.30	4.15	3.93	2.27	1.86	1.29

Table 2. Particle size analysis of vanadium extraction residue.

D	Particle Size
3%	2.245 μm
6%	4.443 μm
10%	7.620 μm
16%	12.93 μm
25%	23.92 μm
50%	72.02 μm
75%	137.5 μm
84%	179.3 μm
90%	224.7 μm
97%	342.3 μm

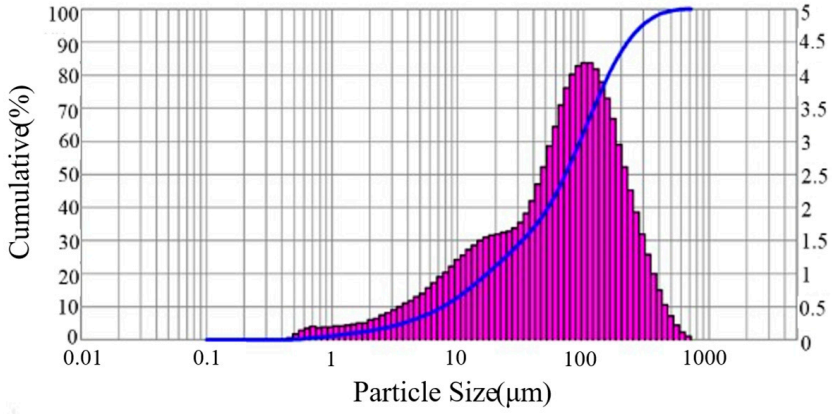


Figure 1. Particle size distribution of vanadium extraction residue.

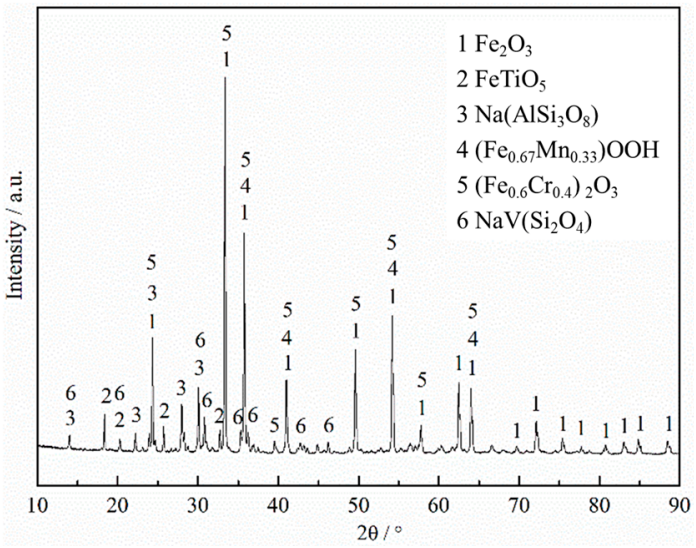


Figure 2. XRD analysis of vanadium extraction residue.

2.2. Methods

Experimental process of alkali leaching vanadium: The vanadium extraction residue, collected from the site, was directly added to a reactor with sodium hydroxide and water,

following the liquid-solid ratio, then sealed and stirred. The mixture was heated to a predetermined temperature, maintained for a set duration, cooled to atmospheric pressure, and then the slurry was removed for suction filtration to separate the solid and liquid phases. The weight of the solid slag and the volume of the leachate were recorded. Each group of experiments was repeated three times, and the results were averaged. The primary reactions involved in deep vanadium extraction are as follows:

$$V_2O_5 + 6NaOH = 2Na_3VO_4 + 3H_2O$$

The experimental process of calcification dealkalization: The vanadium extraction residue, collected from the site, was directly added to a reactor along with calcium oxide and water, following the liquid-solid ratio, then sealed and stirred. After heating to the predetermined temperature and maintaining it for a set time, the slurry was cooled to atmospheric pressure, then removed for filtration and solid–liquid separation. The weight of the solid slag and the volume of the leachate were recorded. The experimental equipment is shown in Figure 3. The primary reactions involved in calcification are as follows:

$$Na_2O{\cdot}Al_2O_3(Fe_2O_3){\cdot}xSiO_2{\cdot}6 - 2x)H_2O + 3CaO \rightarrow 3CaO{\cdot}Al_2O_3(Fe_2O_3){\cdot}xSiO_2{\cdot}(6 - 2x)H_2O + Na_2O$$



Figure 3. High-temperature reaction kettle and filtration device.

The high-temperature reactor used is FJHJX-1000 from Fujing, Shanghai, China. The chemical composition of the leaching solution was determined by Agilent 5110 (Agilent Technologies, Santa Clara, CA, USA) inductively coupled plasma optical emission spectrometer (ICP-OES). The typical emission wavelengths used to analyze the key elements are: V (292.402 nm), Na (589.592 nm), Si (251.611 nm), Cr (267.716 nm), and P (213.618 nm).

3. Result and Discussion

3.1. Effect of Vanadium Extraction by Alkaline Leaching

3.1.1. Effect of Concentration on Vanadium Extraction

As shown in Figure 4, the dissolution rate of vanadium exhibits an overall upward trend with increasing alkali concentration. The leaching rate of vanadium increased from 50.99 to 66.73% as the alkali concentration rose from 10 to 40%. In the low-alkali concentration region of a conventional aqueous solution, the dissolution rate of vanadium increases linearly. However, as the alkali concentration further increases, the reaction system transitions to a sub-molten salt medium, as defined by Zhang et al. from the Institute of Process Engineering, Chinese Academy of Sciences [5]. The sub-molten salt region lies between the molten salt and conventional electrolyte aqueous solution regions, providing a medium with high chemical and ionic activity for alkali metal salts and oxidizing ions. The dissolution rate of vanadium in this region also increases linearly, but at a slower rate than in the low-alkalinity region. This occurs because, as the alkali concentration enters the sub-molten salt region, the viscosity of the NaOH solution increases rapidly, hindering mass transfer between the vanadium residue and NaOH, which in turn reduces vanadium leaching efficiency. Overall, the vanadium leaching rate increases linearly in two stages as alkali concentration rises. As shown in Table 3. The leaching rate of Si gradually increased with increasing NaOH concentration. At a NaOH concentration of 40%, the Si leaching rate reached as high as 13.46%.

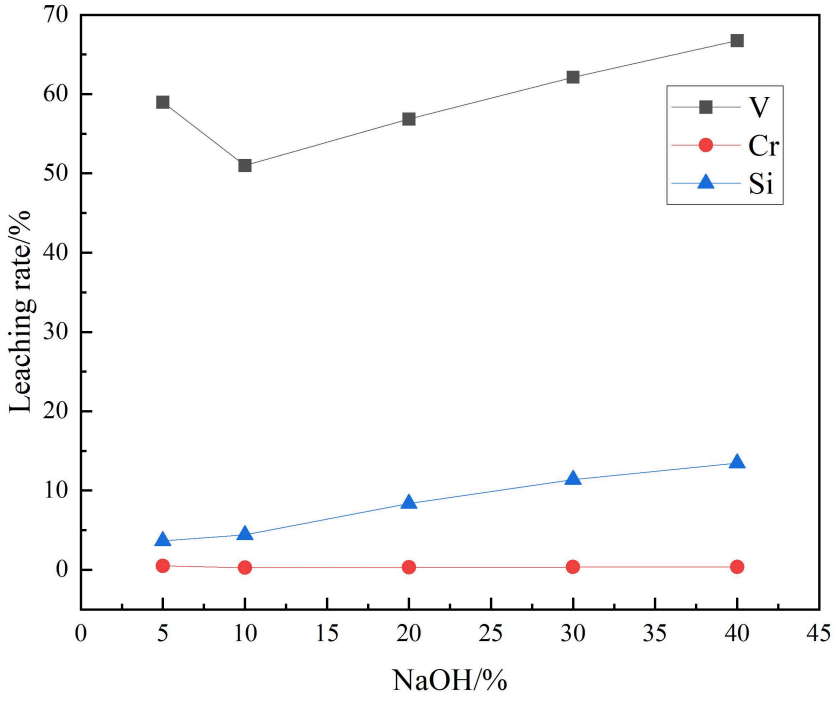


Figure 4. Effect of sodium hydroxide concentration on vanadium extraction (120 °C).

Table 3. Effect of sodium hydroxide concentration on leaching of vanadium, chromium and silicon (120 °C, wt.%).

NaOH %	V/%	Cr/%	Si/%
5	58.96	0.50	3.65
10	50.99	0.26	4.42
20	56.85	0.31	8.34
30	62.13	0.34	11.37
40	66.73	0.36	13.46

At 120 °C, the chromium leaching rate remains between 0.26 and 0.50%. As the alkali concentration increased, the dissolution rate of chromium exhibited a linear rise, but remained below 1%. The dissolution rate of silicon increased linearly as alkali concentration rose, with the leaching rate of silicon increasing from 3.65 to 13.46%.

3.1.2. Effect of Temperature on Vanadium Extraction

When the temperature ranges from 30 °C to 90 °C, the leaching rate of vanadium remains below 50%. The vanadium leaching rate exceeds 50% between 120 °C and 250 °C. The chromium leaching rate increased from 0.14 to 2.83%, while the silicon leaching rate rose from 2.76 to 24.47%, as shown in Figure 5 and Table 4. Overall, the temperature promotes the dissolution of vanadium, chromium, and silicon. The higher the temperature, the higher the dissolution rate.

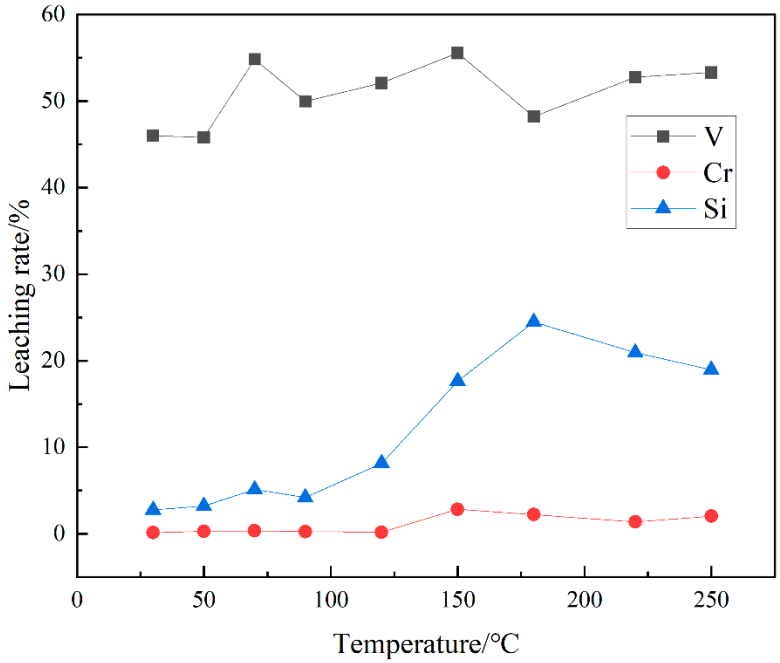


Figure 5. Effect of different reaction temperatures on vanadium extraction.

Table 4. Effect of different reaction temperatures on the leaching of vanadium, chromium and silicon (wt.%).

Temperature/°C	V/%	Cr/%	Si/%
30	46.01	0.14	2.76
50	45.82	0.30	3.23
70	54.83	0.35	5.11
90	49.98	0.26	4.22
120	52.09	0.18	8.16
150	55.55	2.83	17.64
180	48.21	2.22	24.47
220	52.75	1.39	20.96
250	53.30	2.04	18.95

In summary, under a pure NaOH system, the leaching rate of vanadium reaches a plateau at around 50%. This is not due to secondary precipitation within the reaction system, but rather due to the mineralogical characteristics of the tailings. Based on the XRD analysis results in Figure 2, it can be seen that about half of the vanadium in the tailings is deeply embedded in a solid silicate phase. Because silicate phases are highly rigid and

difficult to leach completely, the reagents cannot completely destroy their lattice to release the remaining vanadium under mild conditions of 120 °C and low-concentration alkali. For the sake of the overall technical and economic efficiency of this joint process, we did not use more extreme conditions to break this mineralogical encapsulation limitation.

It is worth noting that direct microstructural characterization (e.g., XRD or XPS) of the newly formed calcium vanadates in the residue is highly constrained, as the residual vanadium concentration drops below 0.6 wt.%, falling well beneath the inherent detection limits of these instruments. However, according to hydro-metallurgical thermodynamics and established literature [23], in a calcium-rich alkaline hydrothermal medium, highly reactive dissolved vanadium species spontaneously undergo irreversible chemical immobilization with Ca^{2+} ions to form ultra-low solubility precipitates (such as CaV_2O_6). This profound chemical precipitation securely binds the remaining 50% of vanadium within the matrix. Crucially, this retention is highly advantageous for the overall process closure: when the deeply detoxified residue ($Na_2O < 1\%$) is subsequently utilized in its entirety as iron-containing briquettes in the blast furnace, this immobilized vanadium will serve as a valuable micro-alloying element for steelmaking.

3.1.3. Effect of Reaction Time on Vanadium Extraction

At 120 °C, the leaching rate of vanadium remains between 50 and 53% over a period of 10 min to 3 h. Increasing the reaction time has minimal effect on the vanadium leaching rate. The chromium leaching rate increased from 0.17 to 0.42%, while the silicon leaching rate rose from 1.8 to 7.39%, as shown in Figure 6 and Table 5.

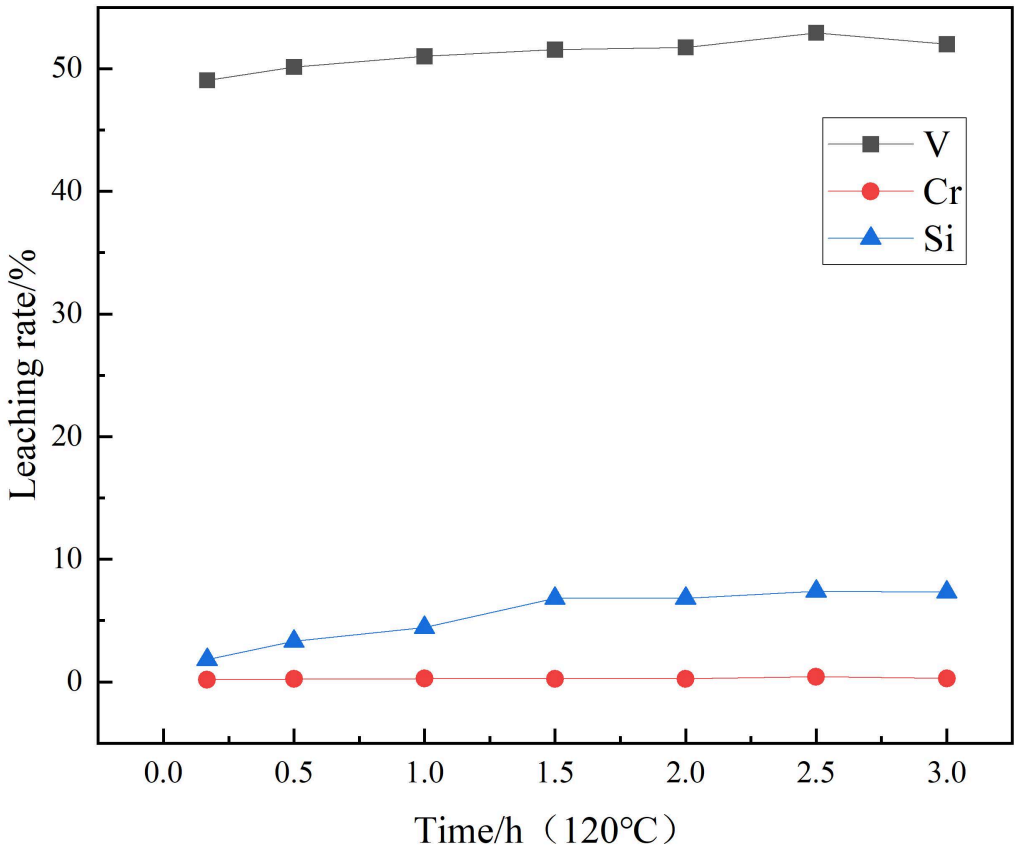


Figure 6. Effect of different reaction time on vanadium extraction (120 °C).

Table 5. Effect of different reaction time on leaching of vanadium, chromium and silicon (120 °C, wt.%).

Time/h	V/%	Cr/%	Si/%
0.167	49.04	0.17	1.81
0.5	50.24	0.23	3.30
1	50.99	0.26	4.42
1.5	51.53	0.25	6.81
2	51.72	0.24	6.80
2.5	52.92	0.42	7.39
3	51.98	0.28	7.32

3.1.4. Effect of Liquid-Solid Ratio on Vanadium Extraction

Figure 7 and Table 6 show that increasing the liquid-solid ratio has minimal impact on the leaching rates of vanadium, chromium, and silicon. As the liquid-solid ratio increased from 1:1 to 10:1, the vanadium leaching rate fluctuated between 50.99 and 58.23%, first decreasing, then increasing. The chromium leaching rate varied between 0.20 and 0.50%, while the silicon leaching rate increased from 2.19 to 5.95%.

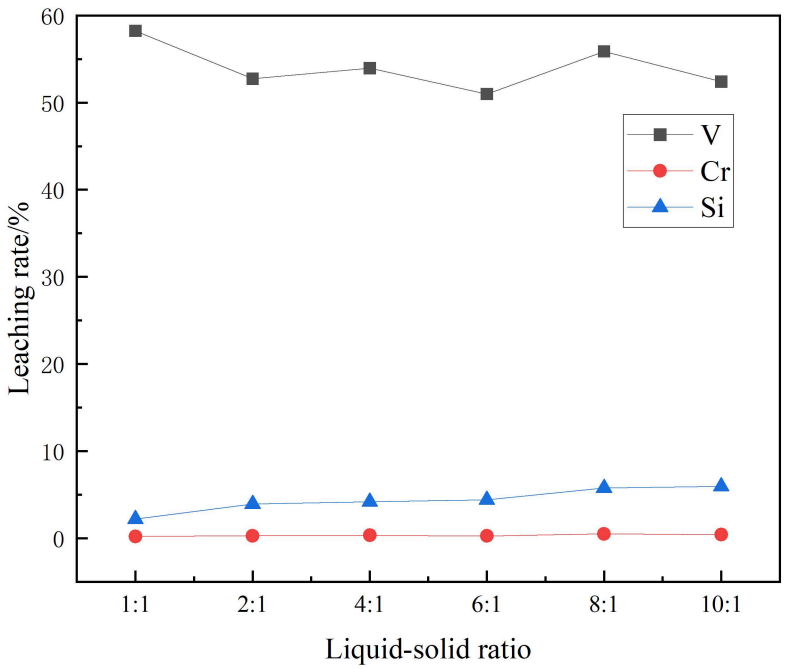


Figure 7. Effect of different liquid-solid ratio on vanadium extraction (120 °C).

Table 6. Effect of different liquid-solid ratios on the leaching of vanadium, chromium and silicon (120 °C, wt.%).

Liquid-Solid Ratio	V/%	Cr/%	Si/%
1:1	58.23	0.20	2.19
2:1	52.73	0.28	3.93
4:1	53.95	0.34	4.17
6:1	50.99	0.26	4.42
8:1	55.88	0.50	5.77
10:1	52.41	0.41	5.95

3.1.5. Effect of Mixing Speed on Vanadium Extraction

When the concentration of sodium hydroxide is 1%, and the stirring speed varies between 400 rpm and 100 rpm, the leaching rates are as follows: vanadium (49.08 to

49.43%), chromium (0.53 to 0.55%), silicon (2.03 to 2.10%), and phosphorus (2.09 to 2.65%), as shown in Figure 8 and Table 7. The stirring speed has minimal effect on the leaching of vanadium, chromium, silicon, and phosphorus. Their co-leaching is suppressed by a strict thermodynamic threshold. In a 1% dilute alkaline medium, the silicate phase lacks the thermodynamic driving force for structural transformation. Similarly, the Cr in the residue exists primarily in the extremely stable form of iron-chromium spinel. Without high-temperature oxidation calcination, it is thermodynamically impossible to convert inert Cr(III) into soluble Cr(VI) in such a mild hydrothermal system. The shorter reaction time (1 h) further restricts their dissolution kinetically. Moreover, the silicate and iron spinel matrix in the residue provides essential structural strength for its subsequent use as iron-containing briquettes.

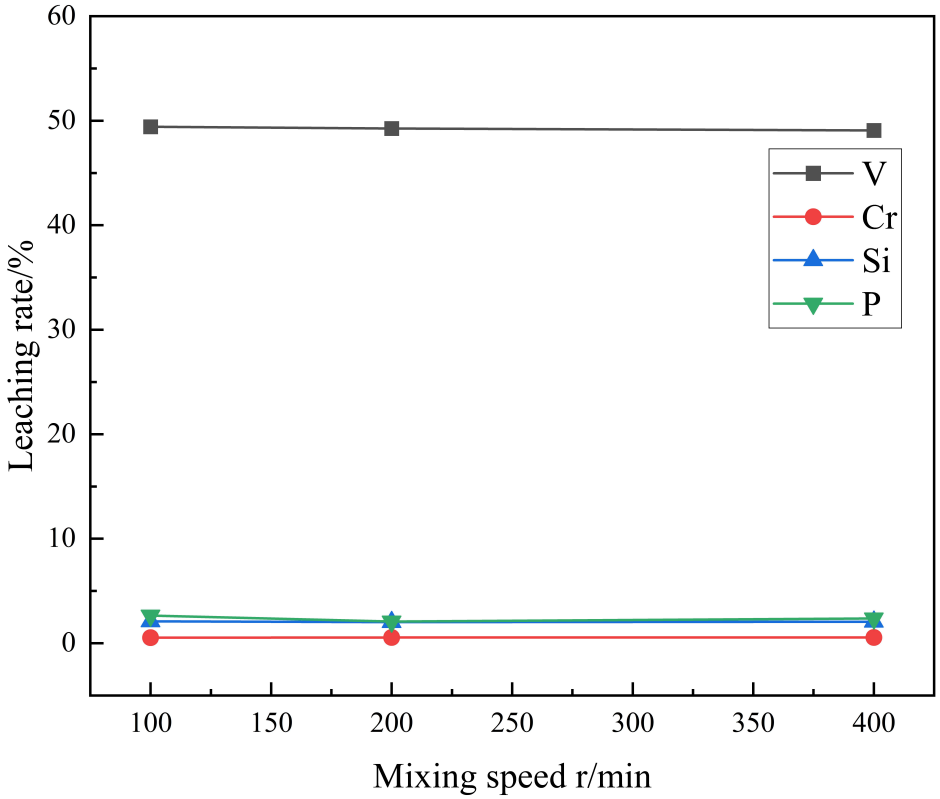


Figure 8. The effect of stirring speed on vanadium extraction when the alkalinity is 1% (120 °C).

Table 7. The effect of stirring speed on the leaching effect of vanadium, chromium and silicon when the alkalinity is 1% (wt.%).

Mixing Speed/rpm	V/%	Cr/%	Si/%	P/%
400	49.08	0.55	2.07	2.37
200	49.26	0.55	2.03	2.09
100	49.43	0.53	2.10	2.65

In summary, although the leaching of impurities such as silicon and chromium was effectively suppressed under optimized mild conditions of 120 °C and 1% NaOH, a certain concentration of soluble silicates will still inevitably be present in the alkaline leaching solution in actual industrial applications. From the perspective of the integrity of the entire process chain, in order to obtain V_2O_5 products that meet commercial-grade standards, the deep removal of impurities downstream is an essential step. Currently, silicon removal technology using alkaline vanadium-containing solutions is highly mature in the metallurgical industry. For example, using traditional calcium or magnesium salt precipitation methods,

free silicate ions can be rapidly converted into highly insoluble calcium or magnesium silicate and removed as solid filter residue, thus achieving deep separation of vanadium and silicon. The high-purity vanadium-containing solution after standard silicon removal can then be seamlessly integrated into conventional commercial purification processes such as ammonium salt precipitation of vanadium.

3.2. Effect of Calcified Dealkalinization

3.2.1. Effect of Concentration on Dealkalization Effect

Under the conditions of a temperature of 220 °C and a stirring speed of 200 rpm. As the amount of CaO increased from 4.83 to 19.29%, the alkali removal rate rose from 47.98 to 74.97%, while the Na_2O content in the slag decreased from 2.57 to 0.995%. The vanadium leaching rate remained between 6.58 and 7.39%, and the chromium leaching rate ranged from 0.52 to 0.61%.

Figure 9 shows that as the CaO dosage increased from 4.83 to 19.29%, the sodium removal rate of the vanadium extraction residue consistently increased. Between 5 and 10%, the removal rate exhibited rapid growth, while from 10 to 20%, the growth rate slowed significantly but remained positive. When CaO constituted 20% of the vanadium extraction residue, the sodium leaching rate reached a maximum of 74.97%. This is attributed to the continuous consumption of calcium ions as the substitution of sodium ions by calcium ions progresses, promoting the reaction between calcium oxide and water, leading to the ionization of calcium hydroxide. Owing to the low solubility of calcium hydroxide in water, the reaction eventually reaches equilibrium as the CaO dosage increases under a fixed water volume. Beyond this point, as the CaO dosage continues to increase, the calcium hydroxide formed in the reaction can no longer ionize, leading to the formation of a lime suspension, which blocks the ion exchange channels between calcium and sodium, ultimately reducing the sodium leaching rate.

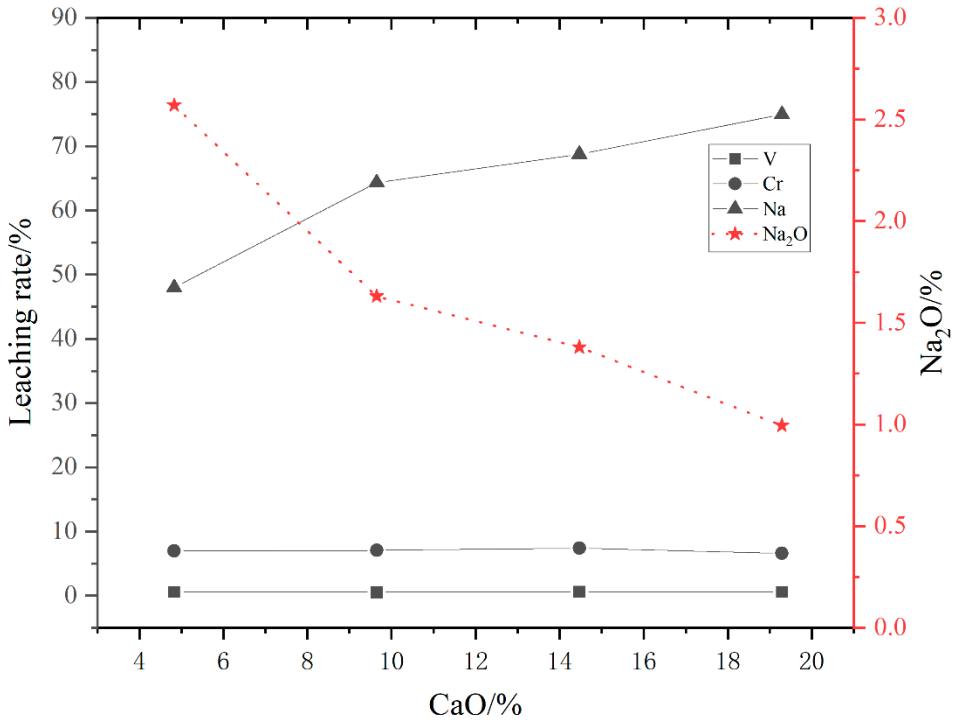


Figure 9. The effect of CaO addition on alkali removal and vanadium/chromium leaching.

As shown in Table 8. During the dealkali removal process with the addition of CaO, it was observed that the vanadium leaching rate was significantly suppressed and maintained

at 6.58%~7.39%. From a thermodynamic perspective, this is due to the introduction of a large number of Ca^{2+} ions into a highly alkaline environment. Once a trace amount of vanadium dissolves in the system, it will rapidly react with calcium ions under thermodynamic drive to form highly insoluble calcium vanadate, which will then redeposit in the solid residue. This thermodynamic spontaneous precipitation mechanism is extremely advantageous to this process. It not only retains residual vanadium to avoid secondary pollution of the dealkali wastewater, but also ensures that the iron-containing tailings can carry the remaining useful components back to the metallurgical process in full.

Table 8. Effect of different CaO additions on alkali removal and vanadium/chromium/phosphorus leaching (wt.%).

CaO Addition Amount %	V/%	Cr/%	Na/%	Na_2O/%	P/%
4.83	6.94	0.57	47.98	2.57	20.31
9.65	7.06	0.52	64.32	1.63	23.59
14.47	7.39	0.61	68.75	1.38	27.62
19.29	6.58	0.57	74.97	0.995	30.82

3.2.2. Effect of Temperature on Dealkalization Effect

As the temperature rises from 150 °C to 250 °C, the alkali removal rate increases from 55.31 to 70.13%, the Na_2O content in the slag decreases from 2.05 to 1.38%, the vanadium leaching rate ranges from 6.25 to 11.48%, and the chromium leaching rate ranges from 0.52 to 0.87%.

Temperature significantly influences the key thermodynamic and kinetic steps in this highly alkaline system, such as the Ca^{2+}/Na^{+} ion-exchange rate within the aluminosilicate lattice, the thermodynamic precipitation of calcium vanadate, and the overall mass transfer efficiency. Consequently, an experimental study was conducted to investigate the effect of temperature on sodium removal from vanadium extraction residue.

Figure 10 and Table 9 show that as temperature rises, the sodium removal rate of the vanadium extraction residue increases progressively. At 150 °C, the sodium removal rate is 55.31%. As the temperature rises from 150 °C to 200 °C, the removal rate increases to 70.13%, a 15-percentage point improvement, demonstrating a significant effect. However, excessively high temperatures can lead to a slight decrease in the Na leaching rate. Thus, increasing the reaction temperature within an optimal range is advantageous for sodium removal from the tailings. The solubility of calcium hydroxide decreases with increasing temperature. As ion exchange progresses, calcium ions are continuously consumed and calcium hydroxide is dissolved. The solution remains saturated with calcium hydroxide. As temperature rises, the viscosity of the slurry decreases, enhancing the contact between calcium ions and the tailings. Consequently, during the initial stage, the ion exchange rate is rapid, facilitating calcium hydroxide dissolution and improving the overall sodium removal rate. From a kinetic perspective, this dealkali removal process is not a single rate-controlled step. In the initial stage of the reaction and at lower temperatures, the system exhibits clear chemical reaction control characteristics. Increasing the temperature can significantly increase the thermodynamic kinetic energy of the reactant molecules in the system, enabling more molecules to overcome the activation energy barrier of the reaction, thereby greatly accelerating the exchange of calcium and sodium ions at the solid–liquid interface and the breaking of old bonds. However, when the temperature is too high or the reaction enters the middle or later stages, as ion exchange progresses, a layer of insoluble calcium silicate or aluminate product will be rapidly generated and covered on the particle surface. At this point, the rate-controlling step of the reaction system gradually shifts towards diffusion control within the product layer. At this stage, the marginal effect of

further increasing the temperature on the diffusion rate diminishes, thus macroscopically manifesting as a slowdown in the rate of dealkali removal and a gradual plateau.

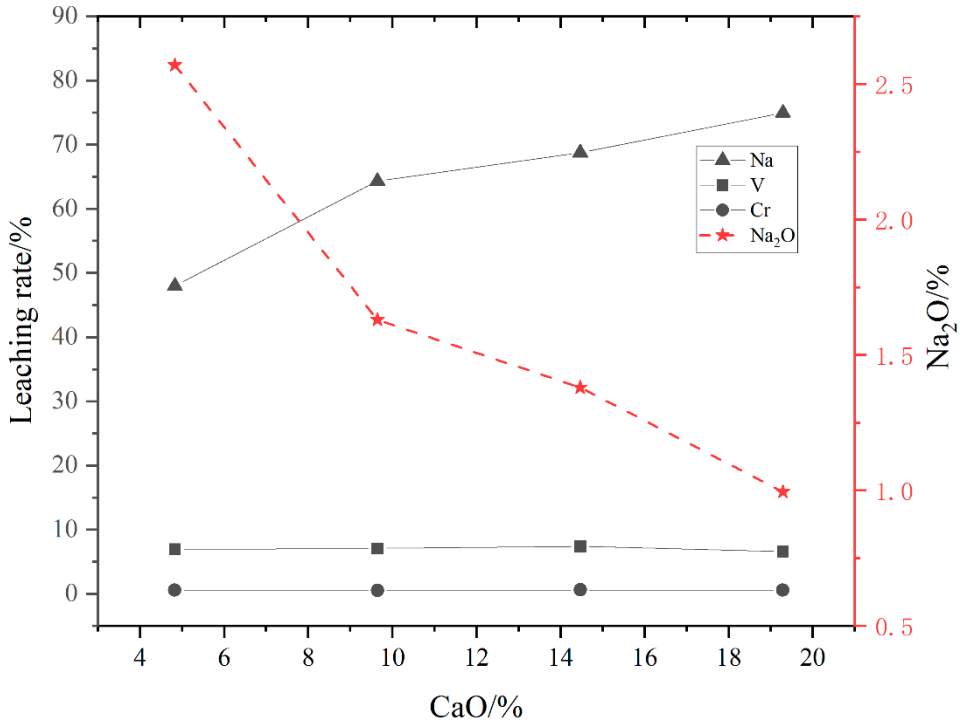


Figure 10. The effect of temperature on the effect of alkali removal and vanadium/chromium leaching (calcium oxide content 9.65%).

Table 9. Effect of temperature on dealkalization and vanadium/chromium/P leaching (CaO content 9.65%, wt.%).

Temperature/°C	V/%	Cr/%	Na/%	Na_2O/%	P/%
150	11.48	0.87	55.31	2.05	19.82
180	7.61	0.74	64.56	1.65	19.22
200	7.13	0.85	70.13	1.38	21.15
220	7.06	0.52	64.32	1.63	23.59
250	6.25	0.65	65.04	1.63	21.62

3.2.3. Effect of Time on Dealkalization Effect

As the reaction time extends from 10 min to 2 h, the alkali removal rate increases from 65 to 74.39%. The Na_2O content in the slag decreases from 1.41 to 1.04%, the vanadium leaching rate ranges from 5.99 to 7.71%, and the chromium leaching rate ranges from 0.57 to 1.55%.

Figure 11 shows that, under constant conditions, the sodium removal rate gradually increases with the extension of reaction time. At 60 min, the sodium removal rate reaches 46.2%. By 120 min, the rate increases slightly to 46.8%, with a small growth rate, indicating a stable state. This trend indicates that reaction time has a minor effect on sodium removal efficiency. With a constant liquid-solid ratio, extending the reaction time leads to continuous consumption of calcium ions, decreasing ion concentration, and a reduced reaction rate. After 60 min, the reaction between calcium oxide and water, as well as the dissolution and ionization of calcium hydroxide, reached equilibrium, maximizing the substitution of calcium ions for sodium ions. As the reaction time extends, soluble silicates enter the slurry, increasing its viscosity. This affects the mass transfer process, leading to a decrease

in the leaching rate and difficulties in filtration. In summary, a reaction time of 60 min is optimal for sodium removal with calcium oxide.

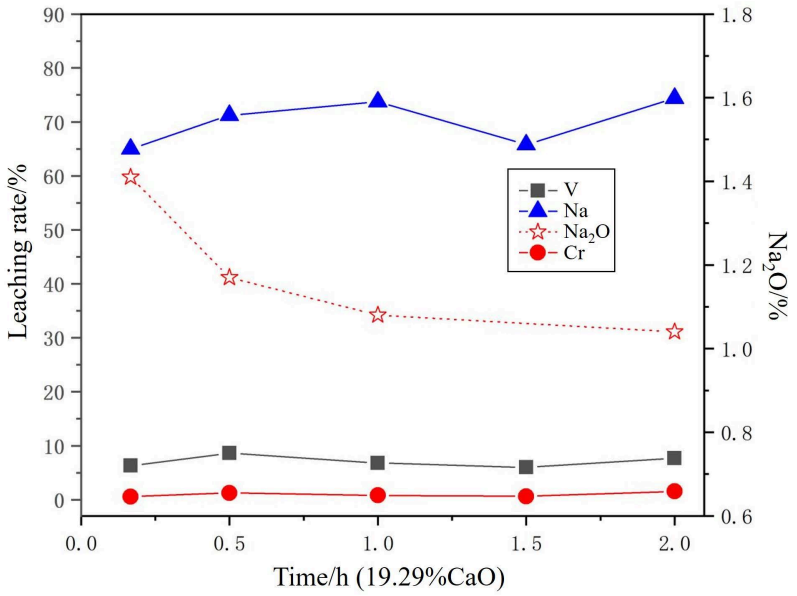


Figure 11. Effect of reaction time on dealkalization and vanadium/chromium leaching (calcium oxide content 19.29%).

Furthermore, the flattening trend of this time curve further confirms the dynamic diffusion resistance mechanism. As the reaction time increases, although Ca^{2+} still exists in the liquid phase, the continuously thickening solid product layer severely hinders the internal and external diffusion and mass transfer of ions, resulting in a significant decrease in the reaction rate. Therefore, 60 min is the optimal engineering balance point to break the chemical reaction phase and reach the bottleneck of diffusion control.

3.2.4. Effect of Liquid-Solid Ratio on Dealkalization Effect

As the liquid-solid ratio increases from 1:1 to 10:1, the alkali removal rate rises from 59.01 to 70.45%. The Na_2O content in the slag decreases from 1.88 to 1.35%, while the leaching rate of vanadium ranges from 1.62 to 10.63%, and the leaching rate of chromium ranges from 0.13 to 0.85%.

Figure 12 and Table 10 illustrate the effect of the liquid-solid ratio on sodium removal from vanadium extraction residue. As shown in the diagram, the sodium leaching rate from the vanadium extraction residue initially increases with the liquid-solid ratio and then levels off. At a liquid-solid ratio of 6:1, the leaching rate of residual Na peaks at 70.14%. As the liquid-solid ratio continues to increase, the Na_2O content in the slag decreases and the Na leaching rate declines. However, the rate of decrease in Na leaching slows with higher liquid-solid ratios. For a given amount of leaching agent, an optimal liquid-solid ratio can reduce the viscosity of the slurry. Additionally, under varying liquid-solid ratios, the specific surface area of contact between solid tailings particles and the solution varies significantly. At lower liquid-solid ratios, there are more tailings particles per unit volume. At higher liquid-solid ratios, the number of tailings particles per unit area decreases, increasing the solid–liquid contact area. This enhances the mass transfer rate between the solid and liquid phases, maintaining high exchange energy between calcium and sodium ions, and improving the sodium leaching rate. However, if the liquid-solid ratio is excessively high, the amount of leaching agent increases, the alkalinity of the solution rises, and equipment requirements become more stringent, complicating subsequent treatment of the leaching solution. Therefore, a liquid-solid ratio of 6:1 is optimal for sodium removal.

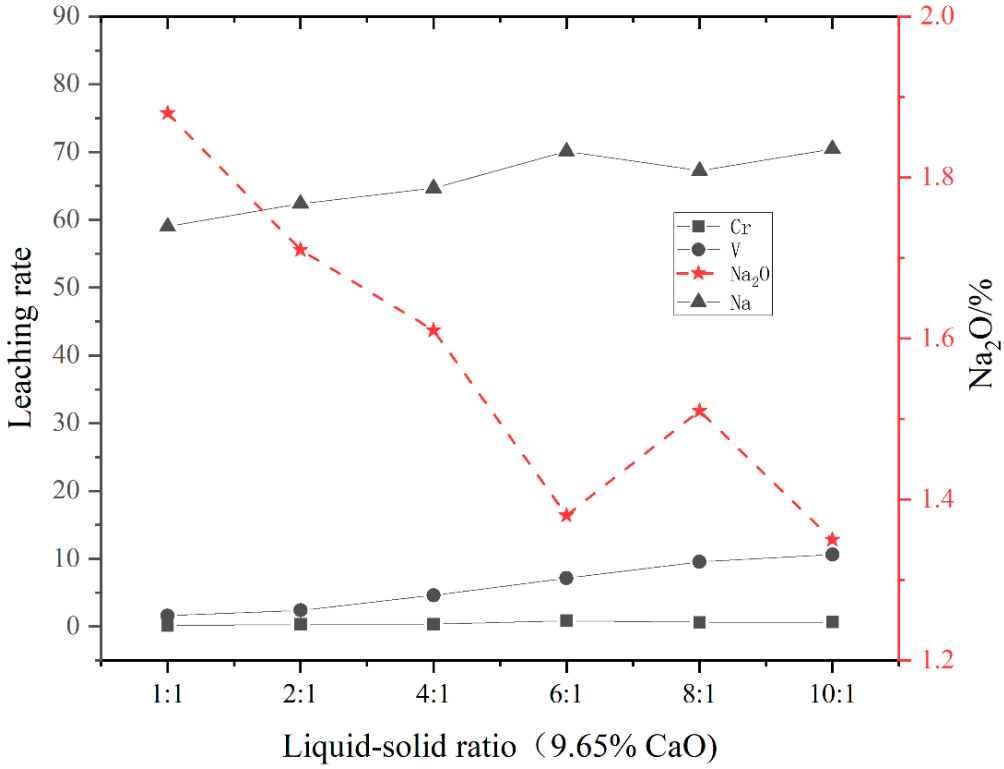


Figure 12. Effect of liquid-solid ratio on dealkalization and vanadium/chromium leaching (CaO content 9.65%).

Table 10. Effect of liquid-solid ratio on dealkalization and vanadium/chromium/P leaching (CaO content 9.65%, wt.%).

Liquid-Solid Ratio	V/%	Cr/%	Na/%	Na_2O/%
1:1	1.62	0.13	59.01	1.88
2:1	2.39	0.32	62.4	1.71
4:1	4.61	0.35	64.67	1.61
6:1	7.13	0.85	70.13	1.38
8:1	9.53	0.61	67.26	1.51
10:1	10.63	0.67	70.45	1.35

3.2.5. Effect of Stirring Speed on Dealkalization Effect

Stirring speed directly influences the mixing efficiency of vanadium tailings with the leaching agent. Higher stirring speeds result in a greater relative motion between vanadium slag particles and the leaching agent, which accelerates the external diffusion during the leaching process and enhances leaching efficiency.

As shown in Figure 13 and Table 11, at a liquid-solid ratio of 1:1, increasing the stirring speed from 400 rpm to 800 rpm raises the alkali removal rate from 71.66 to 79.37% and reduces the Na_2O content in the slag from 1.3 to 0.84%. At a liquid-solid ratio of 2:1, increasing the rotational speed from 400 rpm to 800 rpm increases the alkali removal rate from 72.45 to 86.00% and lowers the Na_2O content in the slag from 1.12 to 0.569%. At a liquid-solid ratio of 4:1, increasing the stirring speed from 400 rpm to 800 rpm raises the alkali removal rate from 72.74 to 79.11% and decreases the Na_2O content in the slag from 1.11 to 0.892%. At a liquid-solid ratio of 6:1, increasing the stirring speed from 400 rpm to 800 rpm increases the alkali removal rate from 73.73 to 82.03% and reduces the Na_2O content in the slag from 1.08 to 0.731%.

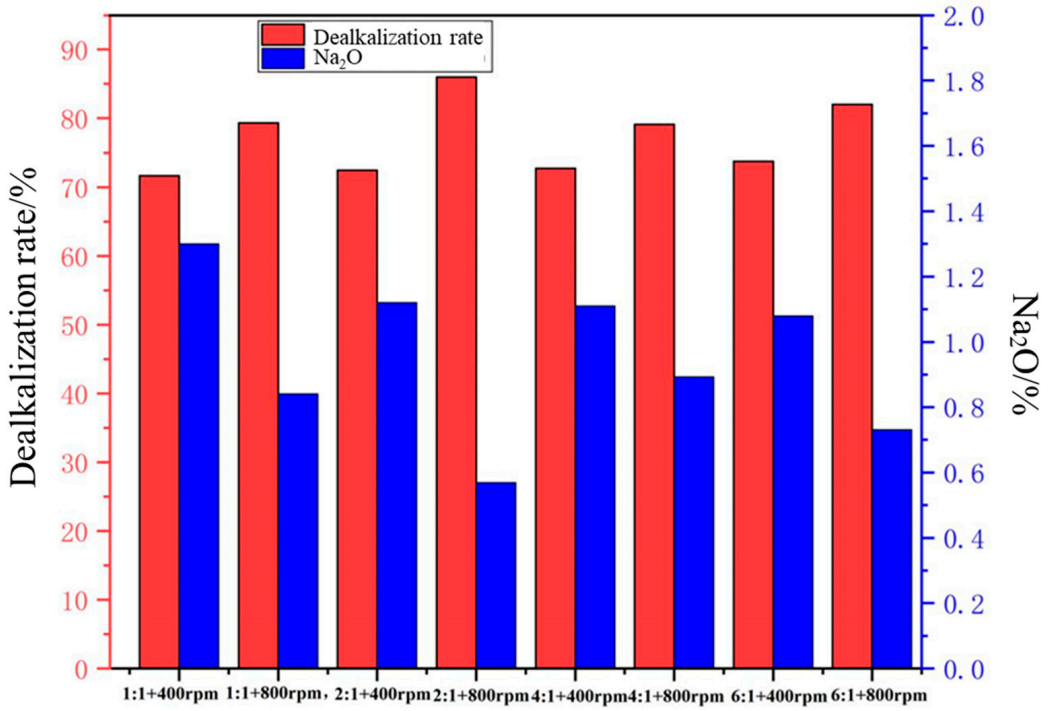


Figure 13. The effect of stirring speed on the effect of alkali removal (calcium oxide content 19.29%).

Table 11. Effect of stirring speed on dealkalization and vanadium/chromium/P leaching (calcium oxide content 19.29%, wt.%).

	V/%	Cr/%	Na/%	Na_2O/%	P/%
1:1 (400 r/min)	1.75	0.18	71.66	1.3	43.63
1:1 (800 r/min)	0.1586	0.0005	79.37	0.84	41.71
2:1 (400 r/min)	2.48	0.37	72.45	1.12	34.67
2:1 (800 r/min)	0.4807	0.0721	86.00	0.569	39.27
4:1 (400 r/min)	4.68	0.36	72.74	1.11	0.4132
4:1 (800 r/min)	0.4757	0.0729	79.11	0.892	0.7786
6:1 (400 r/min)	6.82	0.82	73.73	1.08	32.53
6:1 (800 r/min)	3.0346	0.0233	82.03	0.731	30.07

3.3. Pilot Test

As shown in Figure 14 and Table 12, at 30 °C, the leaching rate of vanadium increased from 34.98 to 43.00% when scaling up from a 1 L to a 200 L kettle. The leaching rate of chromium was negligible, the leaching rate of silicon ranged from 1.16 to 1.63%, and the leaching rate of phosphorus ranged from 4.50 to 9.20%.

At 120 °C, the leaching rate of vanadium ranged from 45.95 to 50.49%, the leaching rate of chromium increased from 0.24 to 0.87%, the leaching rate of silicon ranged from 2.37 to 2.42%, and the leaching rate of phosphorus ranged from 0 to 4.12%.

Applying the optimized dealkalization parameters (time: 1 h, liquid-solid ratio: 6:1, CaO dosage: 19.29%), the hydrothermal reaction was conducted at 200 °C with an autogenous pressure of approximately 1.5 MPa. Under these conditions, the alkali removal rate in the 1 L autoclave (800 rpm) experiment was 82.03%, with a Na_2O content in the slag of 0.82%. In the 200 L kettle experiment (200 rpm), the alkali removal rate was 82.77%, and the Na_2O content in the slag was 0.80%.

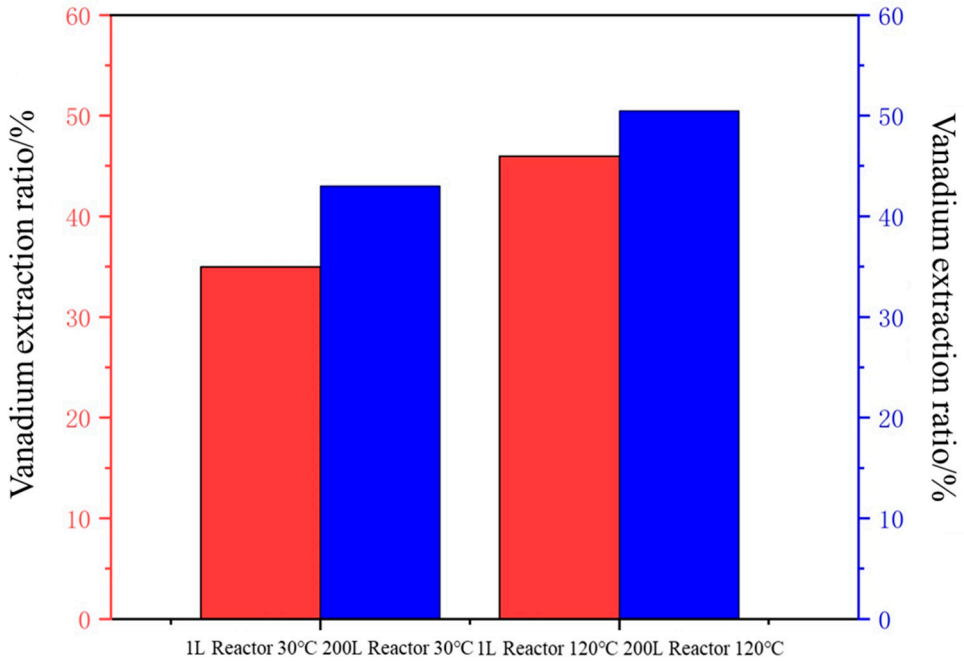


Figure 14. The effect of vanadium extraction in 1 L reactor and 200 L reactor and the analysis of comparison results.

Table 12. The leaching rates of vanadium, chromium, silicon, and phosphorus in 1 L and 200 L autoclaves (wt.%).

	V/%	Cr/%	Si/%	P/%
1 L reactor, 30 °C	34.98	0.00	1.16	9.20
200 L reactor, 30 °C	43.00	0.00	1.63	4.50
1 L reactor, 120 °C	45.95	0.24	2.42	0.00
200 L reactor, 120 °C	50.49	0.87	2.37	4.12

In summary, the successful operation at the 200 L pilot scale strongly underpins the economic and industrial viability of this joint process. In terms of economic feasibility and reagent consumption, the leachate can be recycled. After the second stage of calcification and dealkalization reaction is completed, a large amount of sodium in the tailings is transferred to the liquid phase, making the final dealkalization waste liquid essentially an alkaline solution rich in NaOH, while also containing trace amounts of calcium. Furthermore, since we only need a low concentration of 1% NaOH solution for vanadium extraction in the first stage, the alkali-rich dealkali solution produced in the second stage can be used as a leaching agent after simple solid–liquid separation and directly recycled back to the first stage for vanadium extraction. This reverse circulation drives fresh NaOH consumption to an absolute minimum. Regarding the management of the final residue, the iron-rich matrix ($Na_2O < 1\%$) after deep alkali removal has completely escaped the restrictions of hazardous waste disposal. Conversely, it is ideally suited for complete recycling and consumption in blast furnace smelting in the form of iron-containing briquettes, thus creating a truly closed-loop and highly profitable metallurgical ecosystem.

4. Conclusions

(1) Inthe vanadium extraction process, the concentration of sodium hydroxide and the reaction temperature are the most influential factors, followed by reaction time and liquid-solid ratio. The leaching rate of vanadium increases with higher temperature and alkali concentration, while silicon's leaching rate increases significantly, and

chromium's leaching rate remains relatively stable throughout. The optimal engineering conditions were determined to be: sodium hydroxide concentration of 1%, a reaction temperature of 120 °C, liquid-to-solid ratio of 6:1, and a reaction time of 1 h. Under these optimized conditions, the target economically optimal extraction rate of approximately 50% was achieved.

(2) In the dealkalization process, the effectiveness is significantly influenced by the amount of calcium oxide, reaction temperature, and stirring speed, with reaction time and liquid-solid ratio being secondary factors. Alkali removal increases with higher calcium oxide dosage, reaction temperature, and stirring speed, while vanadium, chromium, and phosphorus are partially leached. At 200 °C, using 19.29% calcium oxide, a stirring speed of 800 rpm, a liquid-solid ratio of 4:1, a reaction time of 1 h, and an alkali concentration of 60 g/L achieves an alkali removal rate of 80%.

(3) The results from the 200 L kettle experiments demonstrate that the vanadium extraction rate exceeds 50% and the alkali removal rate exceeds 80%. Both vanadium extraction and alkali removal experiments show that the scaled-up experiments perform as well as or better than the smaller-scale ones, with improved mixing efficiency. Further engineering scale-up of this process is entirely feasible, with no technical or equipment issues.

(4) From a techno-economic perspective, this process uses low-cost CaO to replace expensive chemical dealkali removal reagents, and the reaction heat source of 120 °C to 200 °C can directly utilize the waste heat steam from the plant. A 200 L pilot test verified the feasibility of this process for engineering scale-up. Its core economic value lies in opening up a path for the full utilization of tailings slag in blast furnace ironmaking through dealkali removal, achieving efficient cascade recovery of vanadium and iron.

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Conflicts of Interest: Author Tianqiu Wang was employed by the company Jianlong Group. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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