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Cyclic metallurgical process for extracting V and Cr from vanadium slag: Part I. Separation and recovery of V from chromium-containing vanadate solution

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Abstract: The separation and recovery of V from chromium-containing vanadate solution were investigated by a cyclic metallurgical process including selective precipitation of vanadium, vanadium leaching and preparation of vanadium pentoxide. By adding $Ca(OH)_2$ and ball milling, not only the V in the solution can be selectively precipitated, but also the leaching kinetics of the precipitate is significantly improved. The precipitation efficiency of V is 99.59% by adding $Ca(OH)_2$ according to Ca/V molar ratio of 1.75:1 into chromium-containing vanadate solution and ball milling for 60 min at room temperature, while the content of Cr in the precipitate is 0.04%. The leaching rate of V reaches 99.35% by adding $NaHCO_3$ into water according to $NaHCO_3$/V molar ratio of 2.74:1 to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for 60 min at room temperature. The crystals of NH_4VO_3 are obtained by adjusting the leaching solution pH to be 8.0 with CO_2 and then adding NH_4HCO_3 according to NH_4HCO_3/$NaVO_3$ molar ratio of 1:1 and stirring for 8 h at room temperature. After filtration, the crystallized solution containing ammonia is reused to leach the precipitate of calcium vanadates, and the leaching efficiency of V is >99% after stirring for 1 h at room temperature. Finally, the product of V_2O_5 with purity of 99.6% is obtained by calcining the crystals at 560 °C for 2 h.

Key words: chromium-containing vanadate solution; calcium salt precipitating vanadium; sodium bicarbonate leaching; ammonium salt precipitating vanadate; cyclic metallurgical process

1 Introduction

Vanadium is an important nonferrous metal element which is widely applied in metallurgical, material and chemical industries [1,2]. Vanadium and chromium are the accompanying elements in the ore of vanadium titano-magnetite [3,4]. During the smelting of the ore, vanadium and chromium are mainly enriched in converter slag. The converter slag is usually called vanadium slag [5], which is the main material of V_2O_5 production [6,7].

The conventional process of V_2O_5 production with vanadium slag includes sodium roasting, leaching and purification, V_2O_5 production, and wastewater purification [8]. V_2O_5 is produced by adding $(NH_4)_2SO_4$ into the purified solution to obtain the precipitate of ammonium polyvanadate under pH 1.8−2.1 at 85−95 °C, and then to calcine the precipitate at about 550 °C for 2−3 h [9]. After vanadium precipitation, a solution containing Cr(VI) and a small amount of V(V) is formed. The contents of Cr(VI) and V(V) are 0.5−5.0 and 0.1−1.0 g/L, respectively, in the solution. Cr(VI) and V(V) are all harmful to lives, and sometimes can be fatal [10]. To protect the environment, many

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methods were used to treat the solution, including solvent extraction [11,12], ion exchange [13], chemical and electrochemical precipitation, membrane filtration and sorption [14]. However, these methods are not suitable for industrial production because of high cost and secondary pollution. For example, the Cr(VI) and V(V) can be completely separated and recovered from the solution using ion exchange resin D314 [13], but the operating life of the resin is shortened as Cr(VI) and V(V) are all strong oxidants in acid solution. Therefore, the solution has no choice but to be reduced with Na_2SO_3 or iron scurf to form the precipitate containing Cr(III), V(IV) and V(III), which is usually called V−Cr-bearing reducing slag [15]. After filtration, the solution containing trace amounts of V and Cr is evaporated to form the mixture of Na_2SO_4 and $(NH_4)_2SO_4$ [16]. The mixture of Na_2SO_4 and $(NH_4)_2SO_4$ and V−Cr-bearing reducing slag are all dangerous solid waste, and the handling of them have become a thorny problem in many plants in China.

In order to avoid the generation of typical solid wastes in the production of V_2O_5 with vanadium slag, researches have been carried out, including adding calcium to precipitate vanadium [6,8]. Although the precipitation of V can reach >99% by adding excessive amount of lime into vanadate solution under stirring [17], the leaching performance of the obtained precipitate of calcium vanadates is not good. Using ammonium carbonate salt solution to leach the precipitate, the leaching efficiency of V was 93.5%−94.3% [17]. Even if the precipitate was leached twice with sodium carbonate solution, the leaching efficiency of V was only 95.0%−96.5% [18]. Moreover, when the leaching solution is used to crystallize NH_4VO_3 by adding ammonium carbonate, and then the crystallized solution is returned to leach V from the precipitate, the escape of ammonia is a difficult problem to overcome. Due to the escape of ammonia, the production site environment is harsh, and the operators cannot accept it. That is why Pangang Group Research Institute Co., Ltd. entrusted the authors to carry out technical research on this problem.

It has been found that adding calcium salt to precipitate V under ball milling not only significantly improved the leaching efficiency of V from calcium vanadate precipitates, but also successfully solved the technical problem of ammonia escape, and developed the cyclic metallurgical process to extract V and Cr from vanadium slag. The so-called cyclic metallurgical process refers to a process that can extract valuable metals from metallurgical materials economically, efficiently, cleanly and environment-friendly, and can also separate and recycle chemical raw materials and water used in the process.

Using the cyclic metallurgical process, can not only V and Cr be separated and recovered from vanadium slag, but also the production of V−Cr-containing reducing slag and ammonia nitrogen wastewater be avoided [19]. In the process, by ball milling, $Ca(OH)_2$ is added into the leaching solution of the vanadium slag roasted with sodium to make V selectively precipitated. After filtering, $PbCO_3$ is added into V precipitated solution to precipitate and enrich Cr. Finally, $NaHCO_3$ and water are separated and recovered by electrodialysis to realize the recycling of $NaHCO_3$ and water in the process. The present work focused on the separation and recovery of vanadium.

2 Experimental

2.1 Materials and analysis

The chromium-containing vanadate solution was provided by Pangang Group Vanadium & Titanium Resources Co., Ltd., which was obtained by leaching vanadium slag roasted with Na_2CO_3. The solution was used as the feed liquid in the experiments. The compositions of the solution and the vanadium slag are both listed in Table 1. All the reagents used in tests are of analytical grade. The compositions of experimental samples were determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP) with a PS−6 Plasma Spectrovac, Baird (USA). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K_α X-ray radiation at 35 kV and 20 mA. The pH was determined with ORION−230A which was made in USA, and the degree of accuracy was 0.01. The internal structure of the precipitate particles was observed with 4XC metallographic microscope (Shanghai Optical Instrument No. 5 Factory Co., Ltd.).

Table 1 Compositions of solution and vanadium slag in cyclic metallurgical process to separate and recover V

Solution or slag	Composition					pH
	V	Cr	Na	SiO_2	P	
Vanadium slag[1]	7.79	1.70	0.51	14.57	0.06	6.50 (Ti)
Feed liquid[2]	16.95	2.39	13.51	0.91	0.02	8.93
V-free solution[2]	0.01	2.36	13.43	0.01	0.01	10.51
Precipitated cake[1]	17.84	0.04	0.05	0.97	0.01	−
Leached solution[2]	35.45	0.058	16.32	0.055	0.008	9.67

1−Unit: g/L; 2−Unit: g/t

2.2 Experimental procedure

The separation and recovery of vanadium from feed liquid were performed according to the flow sheet shown in Fig. 1, which includes the procedure of vanadium selective precipitation, vanadium leaching and vanadium pentoxide preparation.

The procedure of vanadium selective precipitation is performed by adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio of 1.35−1.75 and ball milling for 20−70 min under different speeds at room temperature. After filtration, the V free solution is used to recover chromium.

The vanadium in the precipitate was leached with $NaHCO_3$ solution. Meanwhile, the calcium was changed into calcium carbonate. The leaching was carried out by adding $NaHCO_3$ into water according to $NaHCO_3$/V molar ratio of 1.96−2.74 with L/S ratio of 4:1 mL/g and leaching for 10−120 min at different temperatures. Then, the crystals of NH_4VO_3 were obtained by adding NH_4HCO_3 into the leaching solution according to NH_4HCO_3/V molar ratio of 1:1 under pH 8. After NH_4VO_3 crystal was separated, the solution was returned to leach V so as to avoid the discharge of ammonia−nitrogen wastewater. Finally, the product of V_2O_5 with purity 99.6% was obtained by calcining the NH_4VO_3 crystals at 560 °C for 2 h.

3 Results and discussion

3.1 Selective precipitation of vanadium

3.1.1 Vanadium precipitation method

It was known that calcium vanadate is insoluble, while calcium chromate is soluble and its solubility is >20 g/L at room temperature [20]. Therefore, $Ca(OH)_2$ can be used as the precipitator

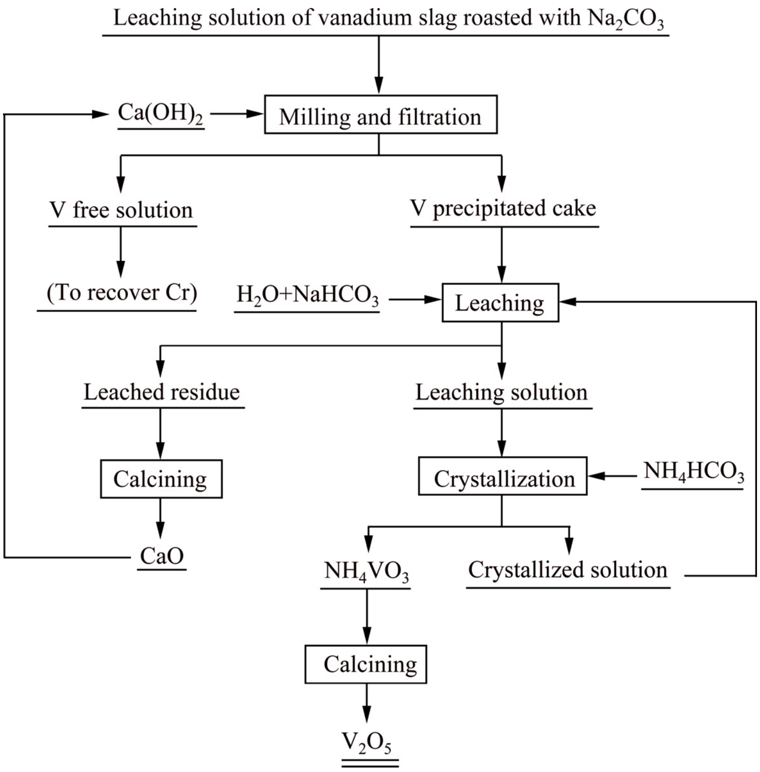

Fig. 1 Schematic flow-sheet of modified production process of V_2O_5 with vanadium slag

to selectively precipitate vanadium from chromium-containing vanadate solution. According to Ref. [8], the forms of calcium vanadate precipitates are different under different pH. The precipitate is $Ca(VO_3)_2$ under pH 5−8; when the pH is 9−10.6, the precipitate is $Ca_2V_2O_7$; if the pH is 10.6−12, the precipitate is $Ca_3(VO_4)_2$ [18]. It is found that by adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio of 1.5:1 and stirring for 1 h at room temperature, the precipitation efficiency of V is only 42.31%, the pH of precipitated solution is 9.3, the surface of the precipitate particles is $Ca(VO_3)_2$, and there is a lot of unreacted $Ca(OH)_2$ inside the particles; by stirring for 1 h at 80 °C, the precipitation efficiency of V is 88.24%, the pH is 9.7, the surface of the precipitate particles is mainly $Ca_2V_2O_7$, and unreacted $Ca(OH)_2$ inside the particles is reduced; by ball milling for 1 h at room temperature, the precipitation efficiency of V is 97.31%, the pH is 10.2, the precipitate particles are all aggregates of $Ca_3(VO_4)_2$, and unreacted $Ca(OH)_2$ in the particles is difficult to find. As we all know, $Ca(OH)_2$ is slightly soluble in water. When $Ca(OH)_2$ is added into feed liquid under stirring, the precipitates of calcium vanadate formed by the reaction immediately adhere to the surface of $Ca(OH)_2$. As the thickness of the calcium vanadate coating increases, the reaction rate decreases and eventually the reaction stops. However, under ball milling, the calcium vanadate attached to the surface of $Ca(OH)_2$ can be stripped off in time, and the reaction interface is constantly updated to ensure that the added $Ca(OH)_2$ can be fully utilized. Therefore, ball milling to precipitate vanadium was used in the subsequent experiments.

3.1.2 Effect of Cr concentration

Figure 2 shows the experimental results obtained by adding $Ca(OH)_2$ into feed liquid with different Cr concentrations according to Ca/V molar ratio of 2:1 and ball milling for 60 min under 120 r/min at room temperature. The concentration of Cr in feed liquid is adjusted by adding Na_2CrO_4. Figure 2 shows that Cr concentration has little effect on the precipitation efficiency of V. With the increase in Cr concentration from 1.5 to 15.5 g/L, the concentration of V in the precipitated solution hardly changes, which is maintained at ~0.05 g/L, that is, the precipitation efficiency of V is about 99.7%, and the content of Cr in the precipitates is <0.05%. This indicates that by adding $Ca(OH)_2$, V can be selectively precipitated from the leaching solutions of low-chromium or high-chromium vanadium slag.

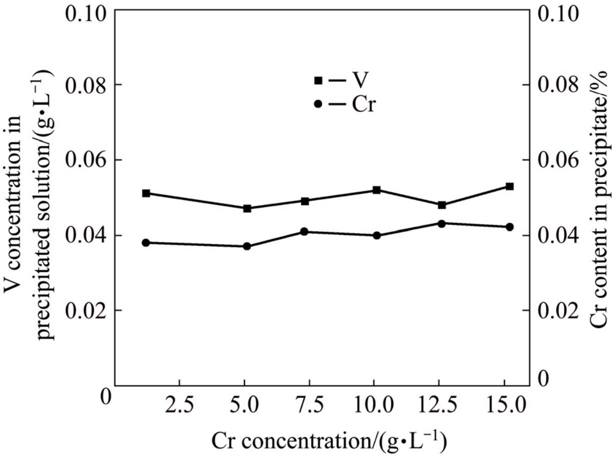

Fig. 2 Effect of Cr concentration on vanadium precipitation (Ca/V molar ratio of 2:1)

3.1.3 Effect of $Ca(OH)_2$ addition

Figure 3 shows the experimental results obtained by adding $Ca(OH)_2$ into feed liquid according to different Ca/V molar ratios and ball milling for 60 min under 120 r/min at room temperature. As can be seen, the precipitation efficiency of V increases from 84.23% to 99.59% with the increase in Ca/V molar ratio from 1.35:1 to 1.75:1, and then there is no significant change with the further increase in Ca/V molar ratio. However, the precipitation efficiency of Cr is always kept at ~1.5%, which is caused by mechanical entrainment. Therefore, the Ca/V molar ratio was maintained at 1.75:1 in the subsequent experiments.

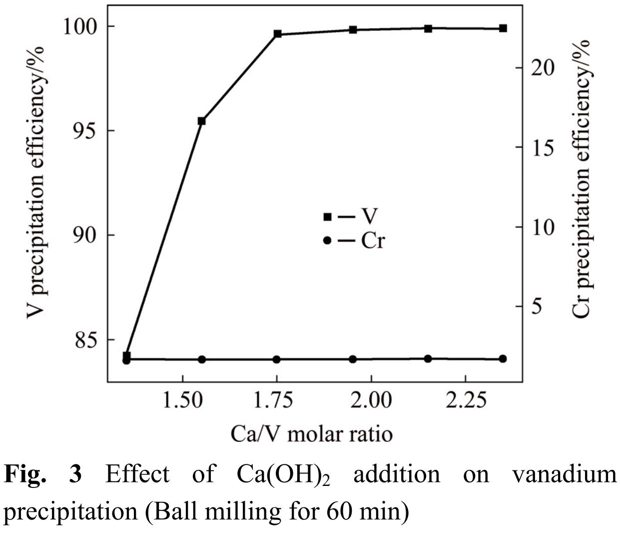

Fig. 3 Effect of $Ca(OH)_2$ addition on vanadium precipitation (Ball milling for 60 min)

Figure 4 shows the XRD pattern of the precipitate obtained by adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio 1.75:1 and ball milling for 60 min under 120 r/min at room temperature. The compositions of V free solution and precipitated cake are listed in Table 1. As seen, there are $Ca_3(VO_4)_2$, $Ca_2V_2O_7$, $CaSiO_3$, Ca_2SiO_4 and $Ca(OH)_2$ in the cake. This indicates that the form of V in the cake is mainly $Ca_3(VO_4)_2$, and the effective utilization rate of added $Ca(OH)_2$ reaches ~85.7%. Adding $Ca(OH)_2$ to precipitate V can cause the reaction of solid−solid transformation to occur in solution, so the added $Ca(OH)_2$ is difficult to be fully utilized, especially by stirring. During the experiment, it is found that with the increase in $Ca(OH)_2$ addition, the existing form of calcium vanadate is different. It turns from $Ca(VO_3)_2$, $Ca_2V_2O_7$ to $Ca_3(VO_4)_2$, and the transformation is faster under ball milling. The precipitation can be expressed by the following equations:

$$2VO_3^- + Ca^{2+} = Ca(VO_3)_2\downarrow \quad (1)$$

$$Ca(VO_3)_2 + Ca(OH)_2 = Ca_2V_2O_7\downarrow + H_2O \quad (2)$$

$$Ca_2V_2O_7 + Ca(OH)_2 = Ca_3(VO_4)_2\downarrow + H_2O \quad (3)$$

$$SiO_4^{4-} + 2Ca^{2+} = Ca_2SiO_4\downarrow \quad (4)$$

$$SiO_3^{2-} + Ca^{2+} = CaSiO_3\downarrow \quad (5)$$

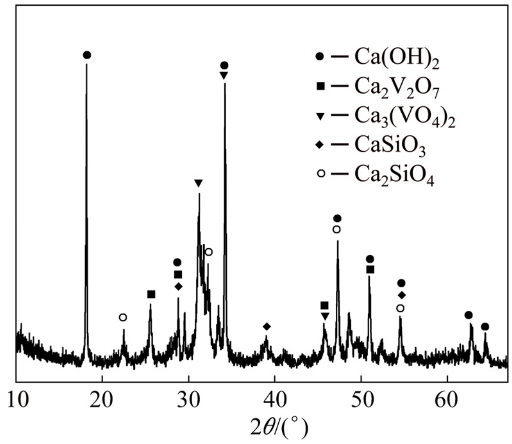

Fig. 4 XRD pattern of V precipitated cake

3.1.4 Effect of ball milling time

Figure 5 shows the experimental results obtained by adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio of 1.75:1 and ball milling for different time under 120 r/min at room temperature. It is shown that the initial speed of V precipitation in the solution is very fast, and then it becomes slow. As the reaction progresses, the probability of contact between $Ca(OH)_2$ and V in the solution becomes low. The precipitation efficiency of V reaches 77.43% after ball milling for 20 min, and then it increases from 77.43% to 99.15% with the increase in ball milling time from 20 to 40 min. Then, the precipitation efficiency of V remains almost the same with the further increase in ball milling time. Therefore, the ball milling time should be ≥40 min.

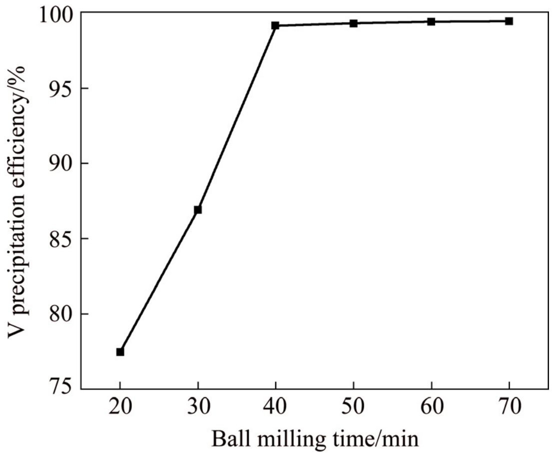

Fig. 5 Effect of ball milling time on vanadium precipitation (Rotating speed of 120 r/min)

3.1.5 Effect of rotating speed

Figure 6 shows the experimental results obtained by adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio of 1.75:1 and ball milling for 60 min under different speeds at room temperature. As seen, the precipitation efficiency of V increases from 86.13% to 99.25% with the increase in ball milling rotating speed from 40 to 100 r/min. Then, it increases slowly with the further increase in rotating speed. This indicates that the

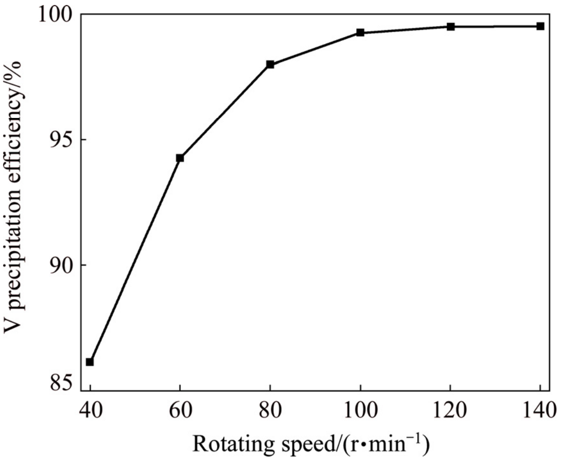

Fig. 6 Effect of ball milling rotating speed on vanadium precipitation (At room temperature)

calcium vanadate precipitates are easy to break, and maintaining ball milling rotating speed at 100−120 r/min can meet the process requirements.

3.2 Vanadium leaching

3.2.1 Vanadium leaching method

Figure 4 shows that the V existing in the precipitated cake is calcium vanadates, and the V can be leached with $NaHCO_3$ or Na_2CO_3. Exploration experiments show that the leaching performances of the precipitate obtained by different methods are different. By adding $Ca(OH)_2$ into feed liquid according to Ca/V molar ratio of 1.75:1 and stirring, and then adding $NaHCO_3$ into water according to $NaHCO_3$/V molar ratio of 3:1 to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for 1 h at 80 °C, the leaching efficiency of V is 95.12%, and the pH of leaching solution is 10.58; while by ball milling for 1 h at room temperature, the leaching efficiency of V is 99.61%, and the pH is 11.13. The content of V in the ball milling leached residue is 0.15%, while that in the stirring leached residue is 0.95%, which is consistent with the results (0.91% V) obtained by other authors [18]. The V in the stirring leached residue is mainly wrapped by calcium carbonate. However, when V precipitated cake is obtained by ball milling under other conditions, and then $NaHCO_3$ is added into water according to $NaHCO_3$/V molar ratio of 3:1 to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for 1 h at room temperature, the leaching efficiency of V is 99.27% and the pH is 9.65. This indicates that the mechanical activation by ball milling significantly increases the specific surface area, lattice distortion, and microscopic stress of the precipitate [21], and reduces unreacted $Ca(OH)_2$ encapsulated therein, thus improving the kinetic conditions of the precipitate leaching. In addition, there is no V wrapped by calcium carbonate in the residue obtained by using $NaHCO_3$ solution to leach the precipitate formed by ball milling. The leaching of V from the precipitate can be expressed by the following equations:

$$Ca_2V_2O_7+2NaHCO_3=2NaVO_3+2CaCO_3\downarrow+H_2O \quad (6)$$

$$Ca_3(VO_4)_2+3NaHCO_3= 2NaVO_3+3CaCO_3\downarrow+H_2O+NaOH \quad (7)$$

$$NaOH+NaHCO_3=Na_2CO_3+H_2O \quad (8)$$

$$Ca(OH)_2+2NaHCO_3=CaCO_3\downarrow+Na_2CO_3+2H_2O \quad (9)$$

$$Ca(OH)_2+Na_2CO_3=CaCO_3\downarrow+2NaOH \quad (10)$$

It can be seen that using $NaHCO_3$ solution to leach the precipitate formed by ball milling, the main reactions are Eqs. (6), (7) and (8), and the main components of the leaching solution are $NaVO_3$ and $NaHCO_3$ because the pH of the leaching solution is 9.65. However, when the precipitate obtained by stirring is leached with $NaHCO_3$ solution, in addition to the Reactions (6), (7) and (8), Reactions (9) and (10) also occur during the leaching, because the precipitate contains a large amount of unreacted $Ca(OH)_2$, which causes the main components of the leaching solution to became $NaVO_3$ and Na_2CO_3, and the pH of the leaching solution increases to 11.13. Because the precipitated cake is mechanically activated, it has good leaching performance. For easy operation, the stirring leaching is used in the subsequent experiments.

3.2.2 Effect of $NaHCO_3$ addition

Figure 7 shows the experimental results obtained by adding $NaHCO_3$ into water according to different $NaHCO_3$/V molar ratio to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for 60 min at 30 °C. As can be seen, the leaching efficiency of V increases from 84.13% to 99.38% with the increase in $NaHCO_3$/V molar ratio from 1.96:1 to 2.74:1. Then, it does not change with the further increase in $NaHCO_3$/V molar ratio. This indicates that the V in the precipitate can be completely leached as the addition of $NaHCO_3$ is close to twice the theoretical amount because the V in the cake mainly exists in the form of $Ca_3(VO_4)_2$. Therefore, the $NaHCO_3$/V molar ratio is maintained at 2.74:1 in the subsequent experiments.

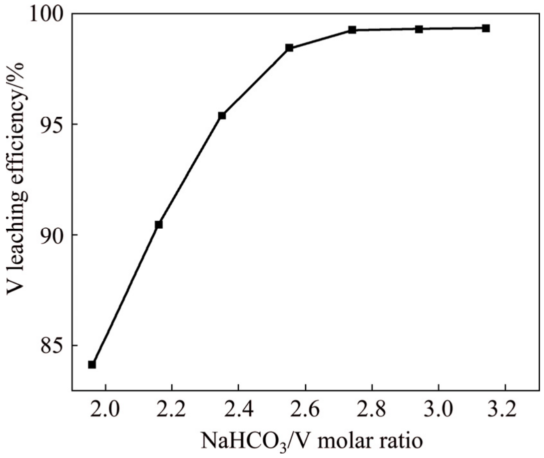

Fig. 7 Effect of $NaHCO_3$ addition on V leaching efficiency (Stirring for 60 min at 30 °C)

The composition of the leaching solution is listed in Table 1 as well. It can be seen that V can be completely leached with $NaHCO_3$ from the precipitate, while impurities Si and P are all remained in the leached residue. The pH of the solution is 9.67, which indicates that the main components of the leaching solution are $NaVO_3$ and $NaHCO_3$.

3.2.3 Effect of stirring time

Figure 8 shows the experimental results obtained by adding $NaHCO_3$ into water according to $NaHCO_3$/V molar ratio of 2.74:1 to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for different time at 30 °C. Figure 8 shows that the V in the precipitate can be easily leached. The leaching efficiency of V increases rapidly from 88.35% to 99.28% with the increase in stirring time from 10 to 60 min, and then it maintains almost the same with the further increase in stirring time. Therefore, the stirring time should be maintained for ≥60 min.

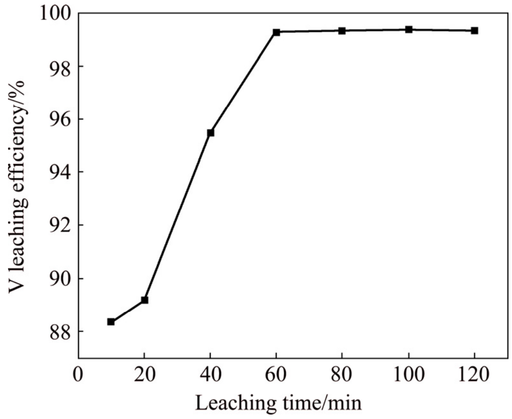

Fig. 8 Effect of stirring time on V leaching efficiency ($NaHCO_3$/V molar ratio of 2.74:1)

3.2.4 Effect of leaching temperature

Figure 9 shows the experimental results obtained by adding $NaHCO_3$ into water according to $NaHCO_3$/V molar ratio of 2.74:1 to leach V from the precipitate with L/S ratio of 4:1 mL/g and stirring for 60 min at different temperatures. It can be seen that after mechanical activation, the precipitate has good leaching performance. Even if after stirring for 1 h at room temperature, the leaching efficiency of V can reach >99.2%, and the effect of leaching temperature on leaching efficiency of V is insignificant. Therefore, the leaching of V should be carried out at room temperature.

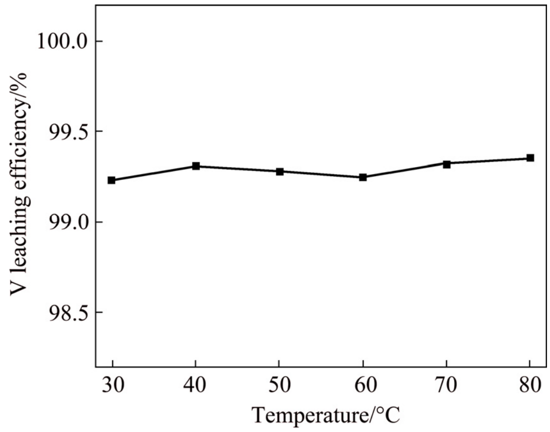

Fig. 9 Effect of temperature on V leaching efficiency (Stirring for 60 min)

3.3 Preparation of vanadium pentoxide

The solubility of NH_4VO_3 in water under different pH values is shown in Fig. 10, which is obtained by adding excess NH_4VO_3 into water under different pH values, stirring at 50 °C and keeping for 24 h at 25 °C. The concentration of V in the solution is determined after filtration. Figure 10 indicates that the crystallization of NH_4VO_3 in the leaching solution should be carried out under pH 7−8, and the leaching of V from the precipitate should be performed under pH>9 with the $NaHCO_3$ solution containing ammonia. In order to avoid the escape of ammonia, the pH of leaching solution is adjusted to be 8.0 with CO_2, and NH_4VO_3 is crystallized by adding NH_4HCO_3 into leaching solution according to NH_4HCO_3/$NaVO_3$ molar ratio of 1:1 and stirring for 8 h at room temperature. After NH_4VO_3 is crystallized, the solution is turned into the $NaHCO_3$ solution containing ammonia. The

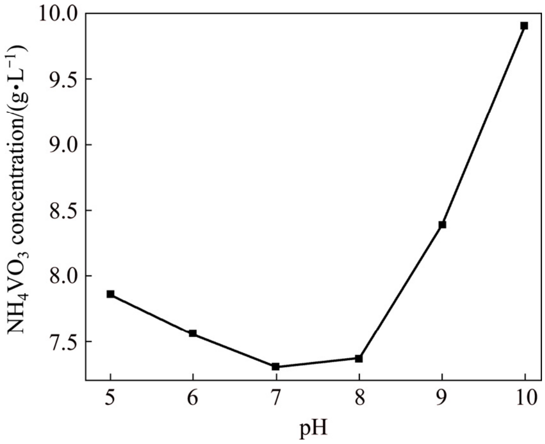

Fig. 10 Solubility of NH_4VO_3 in water under different pH values at 25 °C

crystallized solution can be returned to the leaching of the precipitate, and then the crystal of NH_4VO_3 can be obtained once again by adding an appropriate amount of NH_4HCO_3 into the leaching solution. V_2O_5 with purity of 99.6% is produced by calcining NH_4VO_3 crystals at 560 °C for 2 h. The production of V_2O_5 can be expressed by the following equations:

$$NaVO_3+NH_4HCO_3=NaHCO_3+NH_4VO_3\downarrow \tag{11}$$

$$2NH_4VO_3=V_2O_5+2NH_3\uparrow+H_2O\uparrow \tag{12}$$

3.4 Cyclic leaching experiment

In order to verify that the crystallized solution can be reused in the leaching of the precipitated, the cyclic leaching experiment was performed. The experimental results are given in Table 2. As can be seen, the leaching efficiency of V is ≥99.17% under the conditions: L/S ratio of 4:1 mL/g, pH 9.6−9.7 and stirring for 1 h at room temperature. This indicates that when the molar ratio of $NH_4HCO_3/NaVO_3$ is 1:1, the residual ammonium in the crystallized solution has no effect on the leaching of V from the precipitate, which is consistent with the experimental results shown in Fig. 10. However, it is found that when using the crystallized solution to leach the precipitate obtained by adding $Ca(OH)_2$ into the feed liquid and stirring, the leaching effect of vanadium is not ideal: by stirring for 1 h at room temperature, the leaching efficiency of V is 76.3%; by stirring for 1 h at 80 °C, the leaching efficiency of V is 94.8%, which is consistent with the results obtained by other authors [17,18]. When the leaching temperature rises to close to 80 °C, the escape of ammonia is already very serious. This fully reflects the advantages of using ball milling to precipitate calcium vanadate.

It is found that by ball milling, can not only the unreacted $Ca(OH)_2$ be significantly reduced in the precipitate, but also the particle size of the precipitate become finer and there is no calcium silicate shell on the particle surface, and these are all beneficial to the leaching of V. This is precisely because the precipitated cake formed by ball milling has good leaching performance. When the crystallized solution of NH_4VO_3 is returned for the leaching of the precipitated cake, the high leaching efficiency of V can be obtained by stirring leaching at room temperature. At the same time, because there are few unreacted $Ca(OH)_2$ in the precipitated cake, the pH of the leaching solution is always maintained below 10, and the lower pH at room temperature effectively suppresses the escape of ammonia.

Table 2 shows that the leached residue can be reused in the V precipitation after it is roasted at 900 °C. Although the content of the free CaO in the roasted product gradually decreases with the increase in the number of recycling, the effect on the activity of the V precipitation reaction is not obvious. Even if the SiO_2 in the leached residue is enriched to 15%, as the precipitant is added according to the molar ratio of the free CaO in the calcined product to the V in the solution (Ca/V) ≥1.75, by ball milling, the precipitation efficiency of V can be maintained ≥99.15%.

After ball milling, calcium silicates are dispersed in the calcium vanadate precipitates. Figure 11 shows the XRD pattern of the calcined product. As can be seen, CaO and $CaSiO_3$ exist as two separate phases in the calcined product, which is the key to lime recycling and its V precipitation activity does not decrease. Moreover, it is found that after the feed liquid is purified to remove Si, lime is added to precipitate V, and the content of Si in the resulting precipitate is very small, so the enrichment of Si can be avoided.

The above experimental results show that compared with the conventional process of V_2O_5 production with vanadium slag, although the procedures of using calcium to precipitate V and using $NaHCO_3$ to leach V are used in the modified process (see Fig. 1), the purification of the leaching solution, the production of V−Cr-bearing reducing

Table 2 Experimental results of cyclic leaching of precipitated cake with NH_4VO_3 crystallized solution

Reuse times	V concentration in crystallized solution/($g\cdot L^{-1}$)	V concentration in leaching solution/($g\cdot L^{-1}$)	V leaching efficiency/%	V content in leached residue/%	SiO_2 content in leached residue/%
1	10.15	35.45	99.35	0.11	1.67
2	10.21	44.97	99.17	0.15	3.12
3	10.18	45.28	99.21	0.13	4.71

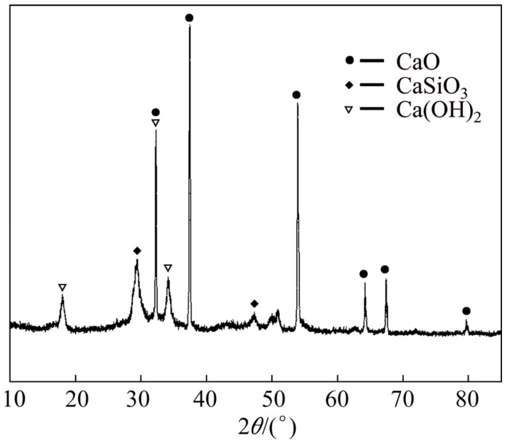

Fig. 11 XRD pattern of roasted product (Leached residue containing 12.75% SiO_2)

slag, and the treatment of the reduced and precipitation solution are reduced. In the modified process, by adding calcium to precipitate V, not only V and Cr can be completely separated, but also no V−Cr-bearing reducing slag is produced, and the crystallized solution of NH_4VO_3 is used to leach V from the precipitate without the discharging of ammonia nitrogen wastewater. Therefore, on the whole, the advantages of the modified process are very obvious.

4 Conclusions

(1) Vanadium can be effectively separated and recovered from chromium-containing vanadate solution by the cyclic metallurgical process including selective precipitation of vanadium, vanadium leaching and preparation of vanadium pentoxide.

(2) By adding $Ca(OH)_2$ into the chromium-containing vanadate solution and ball milling, can not only V be selectively precipitated, but also the effective utilization of $Ca(OH)_2$ be increased, and the leaching kinetics of the precipitate is significantly improved.

(3) Due to the precipitate of calcium vanadates formed by ball milling has good leaching performance, the V in it can be effectively leached with the crystallized solution of NH_4VO_3 at room temperature, so the escape of ammonia is greatly reduced. The water and $NaHCO_3$ used in the process are both recycled. Therefore, there is no ammonia nitrogen wastewater discharged in V_2O_5 production.

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钒渣提钒和铬循环冶金工艺：(I)含铬钒酸盐溶液分离回收钒

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摘　要：研究含铬钒酸盐溶液分离回收钒的循环冶金工艺，工艺过程包括溶液中钒的选择性沉淀、沉淀物中钒的浸出及五氧化二钒的制备。在含铬钒酸盐溶液中加入 $Ca(OH)_2$ 进行球磨，不仅可以使其中的钒选择性沉淀析出，而且沉淀物的浸出动力学性能得到显著改善。在含铬钒酸盐溶液中按 Ca/V 摩尔比 1.75:1 加入 $Ca(OH)_2$，室温球磨 60 min，钒的沉淀率达 99.59%，而铬的沉淀率只有 0.04%。过滤得到的沉钒渣按液固比 4:1 mL/g 加水，并按 $NaHCO_3$/V 摩尔比 2.74:1 加入 $NaHCO_3$，室温搅拌 60 min，过滤得浸出液，钒的浸出率为 99.35%。所得浸出液先通入 CO_2 调 pH 至 8.0，再按 $NH_4HCO_3/NaVO_3$ 摩尔比 1:1 加入 NH_4HCO_3，室温搅拌 8 h 结晶析出 NH_4VO_3，过滤后，含氨的结晶液重新用于钒酸钙沉淀的浸出，温室搅拌 1 h 后钒的浸出率>99%，最后，将所得 NH_4VO_3 晶体在 560 °C 煅烧 2 h 得到纯度为 99.6%的 V_2O_5。

关键词：含铬钒酸盐溶液；钙盐沉钒；碳酸氢钠浸出；铵盐沉钒；循环冶金工艺

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