



# Cyclic metallurgical process for extracting V and Cr from vanadium slag: Part II. Separation and recovery of Cr from vanadium precipitated solution

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**Abstract:** Cyclic metallurgical process for separation and recovery of Cr from vanadium precipitated solution by precipitation with  $\text{PbCO}_3$  and leaching with  $\text{Na}_2\text{CO}_3$  was investigated. The concentration of Cr residue in the solution decreases from 2.360 to 0.001 g/L by adding  $\text{PbCO}_3$  into vanadium precipitated solution according to Pb/Cr molar ratio of 2.5, adjusting the pH to 3.0 and stirring for 180 min at 30 °C. Then, the precipitates were leached with hot  $\text{Na}_2\text{CO}_3$  solution to obtain leaching solution containing  $\text{Na}_2\text{CrO}_4$  and leaching residue containing  $\text{PbCO}_3$ . The leaching efficiency of Cr reaches 96.43% by adding the precipitates into 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution with the mass ratio of liquid to solid (L/S) of 10:1 mL/g and stirring for 60 min under pH 9.5 at 70 °C. After filtration, leaching residue is reused in Cr precipitation and leaching solution is used to circularly leach the Cr precipitates until  $\text{Na}_2\text{CrO}_4$  approaches the saturation. Finally, the product of  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  is obtained by evaporation and crystallization of leaching solution.

**Key words:** vanadium precipitated solution; lead salt precipitating chromium; sodium carbonate leaching chromium; cyclic metallurgical process

## 1 Introduction

Vanadium and chromium are important industrial elements and strategic metals, which are widely applied in metallurgical, material and chemical industries [1,2]. Due to the similar nature, they are often in the form of symbiosis existing in vanadium titanomagnetite ore [3,4]. After reduction smelting in blast furnace and selective oxidation in converter, vanadium and chromium in vanadium titanomagnetite are separated in the form of slag, which is usually referred to as vanadium slag in China [5–7]. Owing to the high value as well as high content of vanadium, vanadium slag is used as the raw material for the extraction of vanadium [8].

The conventional process of  $\text{V}_2\text{O}_5$  production

with leaching solution of vanadium slag roasted with  $\text{Na}_2\text{CO}_3$  is produced by adding  $(\text{NH}_4)_2\text{SO}_4$  into the purified leaching solution to obtain the precipitate of ammonium polyvanadate under pH 1.8–2.1 at 85–95 °C, and then calcine the precipitate at about 550 °C for 2–3 h [9]. In the process of vanadium extraction, wastewater containing Cr(VI) and a small amount of V(V) was produced. The Cr(VI) and V(V) in aqueous are harmful to lives, and sometimes can be fatal [10,11], and therefore they are strictly controlled to discharge. The wastewater is mostly treated by reduction with sodium pyrosulfite, followed by neutralization to form V–Cr-bearing reducing slag, which leads to a waste of chromium resources [12,13]. After filtration, the solution containing trace amounts of V and Cr is evaporated to form the mixture of  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  [14].

The mixture of  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  and V–Cr-bearing reducing slag are all dangerous solid waste, and the handling of them has become a thorny problem in many plants in China.

To separate and recover vanadium and chromium from the V–Cr-bearing reducing slag, several methods including solvent extraction [15], ion exchange [16], chemical and electrochemical precipitation, membrane filtration and sorption [17] have been proposed, for example, direct leaching using  $\text{NaOH}+\text{H}_2\text{O}_2$  [18],  $\text{NaOH}$  leaching under electric field strengthening [19] and roasting followed by  $\text{NaOH}$  leaching [20]. The leaching of vanadium in these methods is high in all cases, but chromium cannot be extracted.

Although the treatment process of V–Cr-bearing reducing slag has recently made new progress, it is still cumbersome and uneconomical. Therefore, the conventional process of  $\text{V}_2\text{O}_5$  production with vanadium slag needs to be modified. The motivation of this study is to avoid the generation of V–Cr-bearing reducing slag and the mixture of  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , and to achieve the cyclic metallurgical process [21]. 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 [22]. Cr(VI) can be recovered by  $\text{PbSO}_4$  efficiently [23], but  $\text{SO}_4^{2-}$  was introduced. In this work,  $\text{PbCO}_3$  was selected as precipitation agent to precipitate Cr(VI) from vanadium precipitated solution, which can avoid the introduction of  $\text{SO}_4^{2-}$ . In addition, the Cr leaching procedure is based on the difference of the solubility constant between  $\text{PbCrO}_4$  ( $2.8 \times 10^{-13}$ ) and  $\text{PbCO}_3$  ( $3.3 \times 10^{-14}$ ) [24]. Finally, the cyclic utilization of lead salt and leach solution in the process is realized. The present work is focused on the separation and recovery of chromium from vanadium precipitated solution.

## 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  $\text{Na}_2\text{CO}_3$ . Vanadium precipitated solution obtained by adding  $\text{Ca}(\text{OH})_2$  and ball milling was the raw material for this study, and its composition is listed in Table 1. Hydrochloric acid, sodium carbonate, sodium bicarbonate, sodium hydroxide and lead carbonate were used in the experiments, which are all 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  $\text{Cu K}_\alpha$  X-ray radiation at 35 kV and 20 mA. The pH was determined with ORION-230A made in USA, and the degree of accuracy is 0.01.

### 2.2 Experimental procedure

The separation and recovery of Cr from vanadium precipitated solution were performed according to the flow sheet shown in Fig. 1, which included the procedures of Cr precipitation and leaching.

The pH of vanadium precipitated solution was adjusted to different values with hydrochloric acid, and then different dosages of  $\text{PbCO}_3$  were added after stirring for 30–240 min at 30–80 °C. The chromium precipitated solution and the precipitate were sampled and analyzed separately, and the results are listed in Table 1 as well. When the concentration of chloride ions in chromium precipitated solution is enriched to a certain extent, antimony oxides can be used to remove chlorine. Sodium carbonate salt used in sodium roasting was

**Table 1** Experiment results of separation and recovery of Cr from vanadium precipitated solution

Solution or precipitate	Content/( $\text{g}\cdot\text{L}^{-1}$ )						pH
	V	Cr	Si	P	Na	Pb	
V precipitated solution	0.01	2.36	<0.001	0.01	13.43	–	11.91
Cr precipitated solution	0.01	<0.001	<0.001	0.01	8.46	–	8.43
Cr precipitate/%	–	9.01	<0.001	<0.01	0.12	72.16	–

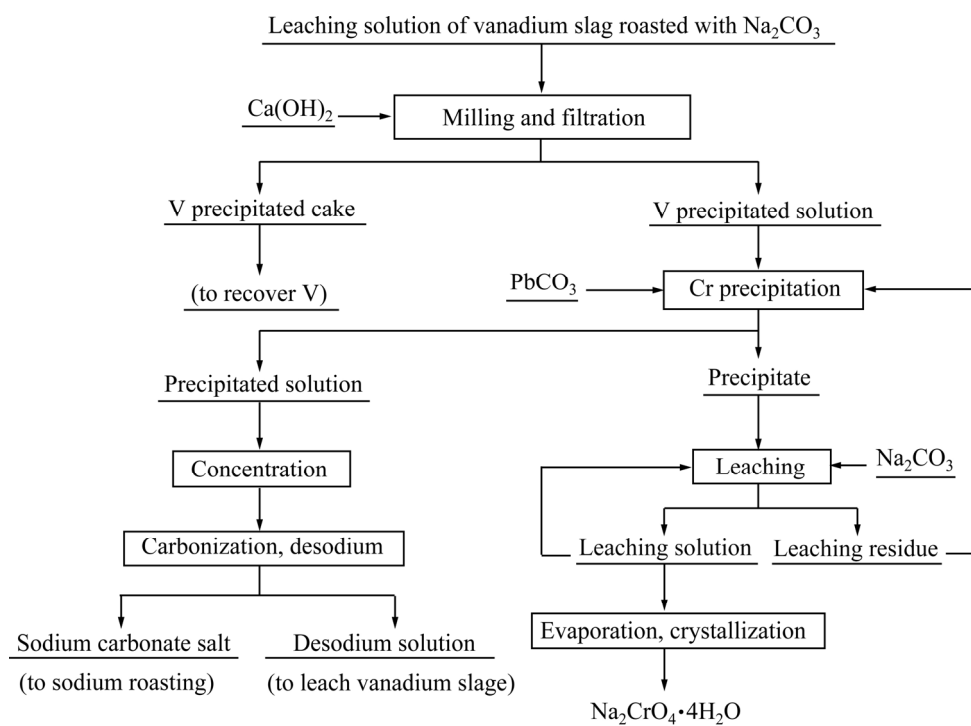


Fig. 1 Schematic flow-sheet of modified production process of  $V_2O_5$  with vanadium slag

recovered from the chromium precipitated solution by concentration, carbonization and disodium, and the solution after sodium removal was returned to the leaching of vanadium slag.

The chromium leaching was carried out by adding the precipitates into 0.5 mol/L  $Na_2CO_3$  solution with L/S ratio of 10:1 mL/g and stirring for 10–70 min under pH 9.5 at 30–80 °C. After filtration, leaching solution containing  $Na_2CrO_4$  and leaching residue containing  $PbCO_3$  were obtained. The concentration of Cr in the solution before and after leaching was analyzed to determine its leaching efficiency. The leaching residue was returned to Cr precipitation, while leaching solution after adding proper amount of  $Na_2CO_3$  was used to circularly leach Cr precipitates until  $Na_2CrO_4$  had near saturation. Finally, the product of  $Na_2CrO_4 \cdot 4H_2O$  with purity 99.3% was formed in the solution by evaporation and crystallization.

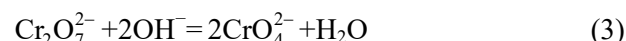
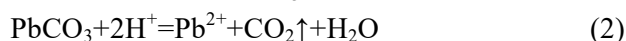
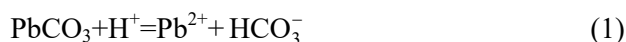
### 3 Results and discussion

#### 3.1 Chromium precipitation

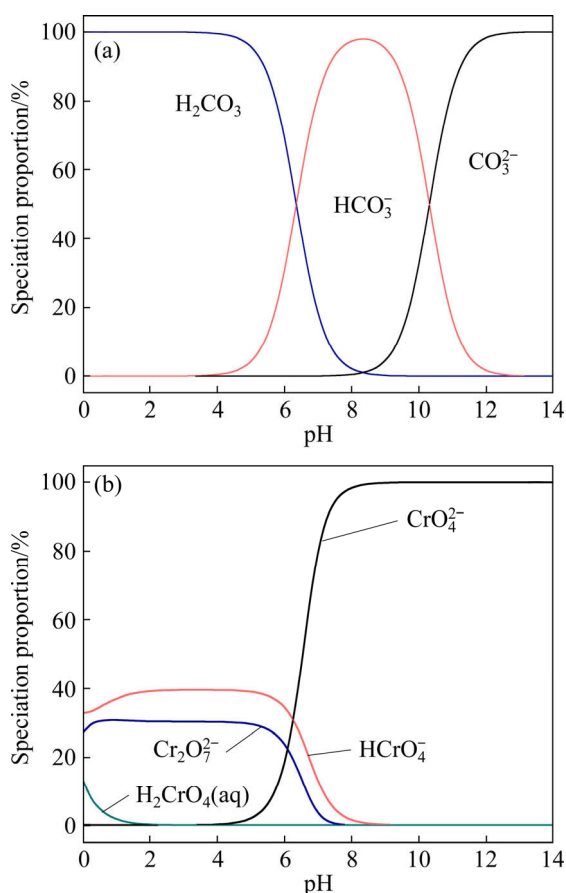
##### 3.1.1 Mechanism of precipitation

In order to avoid the introduction of  $SO_4^{2-}$ ,  $PbCO_3$  was selected as precipitation agent to precipitate Cr from vanadium precipitated solution.

To determine the content of  $CO_3^{2-}$  and  $CrO_4^{2-}$  in the aqueous solution, speciation proportion–pH curves with the concentrations of 0.10 mol/L and 0.05 mol/L, respectively, were calculated using Visual MINTEQ software. From Figs. 2(a, b), it can be found that  $HCO_3^-$  accounted for 97.94% when pH was 8.25, and chromium(VI) mainly existed in form of  $CrO_4^{2-}$  when  $pH > 8.0$ . It was indicated that the pH value of solution affected the species in the solution and the equilibrium pH value of Cr precipitation should be maintained at about 8.0–8.5 so as to form precipitate of  $PbCrO_4$ . The precipitation can be expressed by the following equations:



It can be seen that by adding  $PbCO_3$  into vanadium precipitated solution under pH 1.0–2.0, the main reactions are Eqs. (1) and (2), and  $[HCO_3^-]$  and pH increase with the increase in stirring time. The existing form of Cr(VI) turns from  $Cr_2O_7^{2-}$  to  $CrO_4^{2-}$ ; meanwhile,  $Pb^{2+}$  combines with  $CrO_4^{2-}$  to generate precipitate of  $PbCrO_4$ .



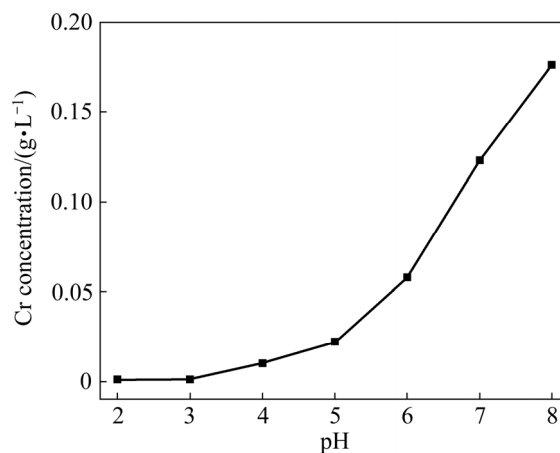
**Fig. 2** Speciation proportion–pH curves: (a)  $\text{CO}_3^{2-}$  ( $c=0.10$  mol/L); (b)  $\text{CrO}_4^{2-}$  ( $c=0.05$  mol/L)

### 3.1.2 Effect of initial pH value of solution

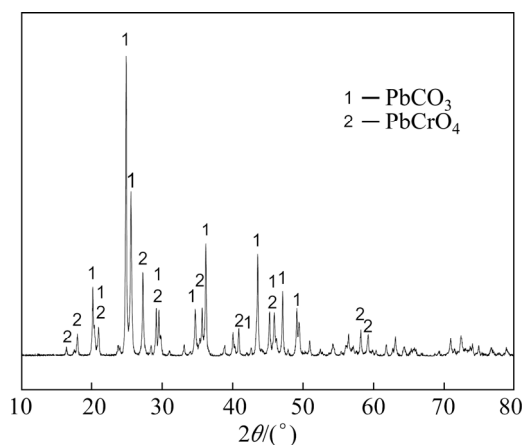
Figure 3 shows the experimental results obtained by adding  $\text{PbCO}_3$  into vanadium precipitated solution according to Pb/Cr molar ratio of 2.5, adjusting the pH to different values and stirring for 180 min at 30 °C. As can be seen, Cr concentration in the solution increases from 0.001 to 0.022 g/L with the increase in pH from 2.0 to 5.0, and then it sharply increases from 0.058 to 0.176 g/L with the further increase in pH from 6.0 to 8.0. It is found that bubbles are formed in chromium precipitated solution under pH 2.0, which indicates that carbon dioxide is generated from the solution when pH is below 2.0. Therefore, the pH is maintained at about 3.0 in the following experiments.

Figure 4 shows XRD patterns of Cr precipitate obtained by adding  $\text{PbCO}_3$  into vanadium precipitated solution according to Pb/Cr molar ratio of 2.5, adjusting the pH to 3.0 and stirring for 180 min at 30 °C, followed by filtering and drying. As seen, there are  $\text{PbCO}_3$  and  $\text{PbCrO}_4$  in the

precipitate. In addition, the pH of the chromium precipitated solution increases from 3.0 to 8.4, which is consistent with the result that the optimal equilibrium pH value of Cr precipitation should be maintained at about 8.0–8.5.



**Fig. 3** Effect of initial pH value of solution on chromium precipitation (Pb/Cr molar ratio of 2.5; stirring for 180 min at 30 °C)

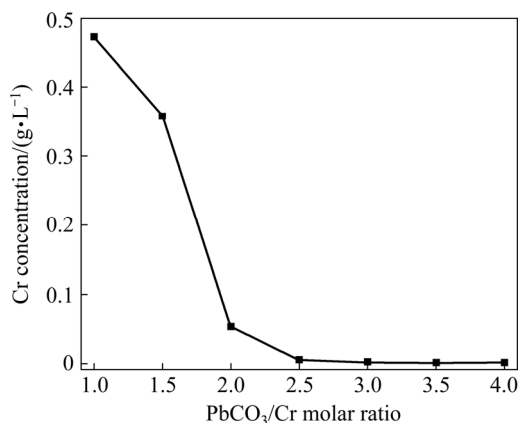


**Fig. 4** XRD pattern of Cr precipitate formed at pH 3.0 (Pb/Cr molar ratio of 2.5; stirring for 180 min at 30 °C)

### 3.1.3 Effect of dosage of $\text{PbCO}_3$

Figure 5 shows the experimental results obtained by adding  $\text{PbCO}_3$  into vanadium precipitated solution according to different Pb/Cr molar ratios, adjusting the pH to 3.0 and stirring for 180 min at 30 °C. As seen, Cr concentration in the solution decreases sharply from 0.473 to 0.005 g/L with the increase in Pb/Cr molar ratio from 1.0 to 2.5, and then there is no obvious change with further increase in Pb/Cr molar ratio. Further increase in the addition of  $\text{PbCO}_3$  not only results in a small increase in the precipitation of chromium, but also leads to more difficulty to filtrate the

mixture consisting of the precipitated solution and the precipitated residue. In order to reduce the mass of precipitation and also achieve high precipitation efficiency, the molar ratio of Pb/Cr is maintained at 2.5 in subsequent experiments.



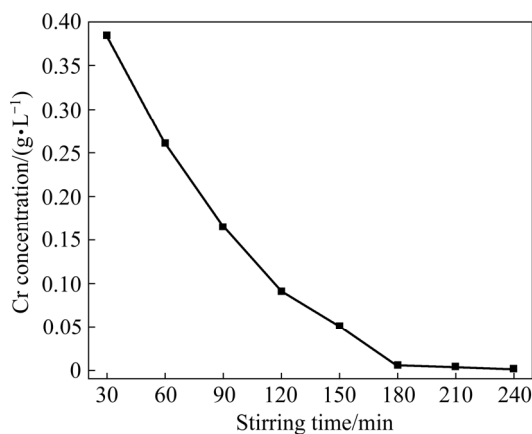
**Fig. 5** Effect of PbCO<sub>3</sub> addition on chromium precipitation (pH 3.0; stirring for 180 min at 30 °C)

#### 3.1.4 Effect of stirring time

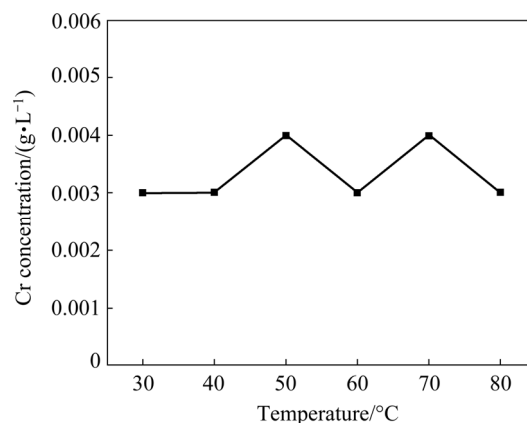
Figure 6 shows the experimental results obtained by adding PbCO<sub>3</sub> into the vanadium precipitated solution according to Pb/Cr molar ratio of 2.5, adjusting the pH to 3.0 and stirring for different time at 30 °C. It is shown that Cr concentration in the solution decreases from 0.386 to 0.006 g/L with the increase in stirring time from 30 to 180 min, and it is almost unchanged with the further increase in stirring time. Therefore, the stirring time should be longer than 180 min.

#### 3.1.5 Effect of temperature

Figure 7 shows the experimental results obtained by adding PbCO<sub>3</sub> into the vanadium precipitated solution according to Pb/Cr molar ratio



**Fig. 6** Effect of stirring time on chromium precipitation (pH 3.0; Pb/Cr molar ratio of 2.5; 30 °C)



**Fig. 7** Effect of temperature on chromium precipitation (pH 3.0; Pb/Cr molar ratio of 2.5; stirring time of 180 min)

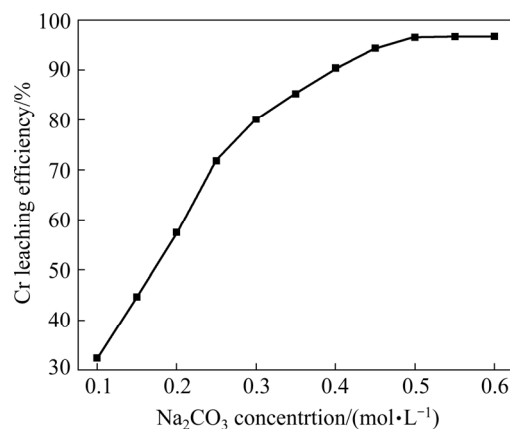
of 2.5, adjusting the pH to 3.0 and stirring for 180 min at different temperatures. It is shown that Cr concentration in the solution is almost unchanged with the increase in temperature. This indicates that the reaction temperature has little influence on the precipitation efficiency of chromium. Therefore, the precipitation of chromium should be carried out at 30 °C.

### 3.2 Chromium recovery

Chromium and lead in the precipitate were separated by leaching with Na<sub>2</sub>CO<sub>3</sub> solution. The leaching solution was used circularly in Cr leaching to produce Na<sub>2</sub>CrO<sub>4</sub> and the leaching residue was reused in Cr precipitation.

#### 3.2.1 Effect of Na<sub>2</sub>CO<sub>3</sub> concentration

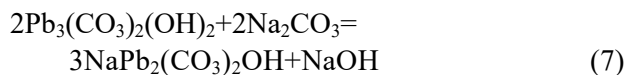
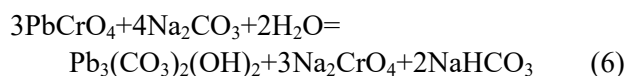
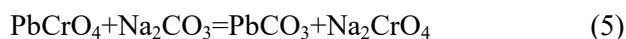
Figure 8 shows the experimental results obtained by adding Cr precipitate into different concentrations of Na<sub>2</sub>CO<sub>3</sub> solution to leach Cr with



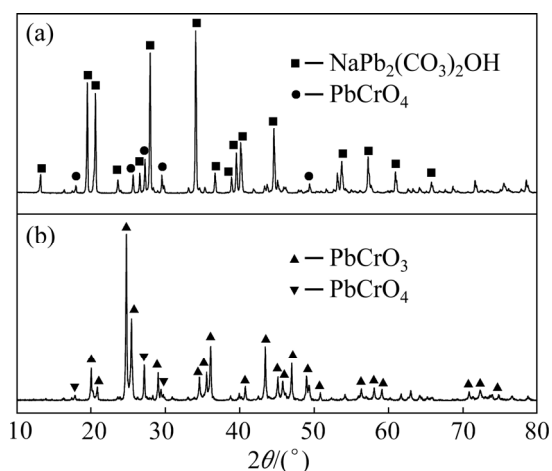
**Fig. 8** Effect of Na<sub>2</sub>CO<sub>3</sub> concentration on Cr leaching efficiency (L/S ratio of 10:1 mL/g; stirring for 60 min at 70 °C)

L/S ratio of 10:1 mL/g and stirring for 60 min at 70 °C. As can be seen, the leaching efficiency of Cr increases from 32.45% to 96.43% with the increase in concentration of  $\text{Na}_2\text{CO}_3$  from 0.1 to 0.5 mol/L. Further increase in the concentration of  $\text{Na}_2\text{CO}_3$  results hardly in the increase in the leaching efficiency of Cr. Therefore, the  $\text{Na}_2\text{CO}_3$  concentration is maintained at 0.5 mol/L in the subsequent experiments.

Figure 9(a) shows XRD patterns of the leaching residue obtained by adding Cr precipitate into 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution with L/S ratio of 10:1 mL/g and stirring for 60 min at 70 °C, followed by filtering and drying. There are  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$  and  $\text{PbCrO}_4$  in the leaching residue. Due to the high concentration of  $\text{Na}_2\text{CO}_3$  and high initial pH, the formed  $\text{PbCO}_3$  is combined with  $\text{Na}_2\text{CO}_3$  to form  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$  [25], which is not beneficial for leaching residue reusing in chromium precipitation. The leaching can be expressed by the following reactions:



In order to avoid the formation of  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ , the pH of  $\text{Na}_2\text{CO}_3$  solution was adjusted to 9.5 with 0.5 mol/L  $\text{NaHCO}_3$  solution. Figure 9(b) shows XRD patterns of the leaching residue obtained by adding Cr precipitate into the

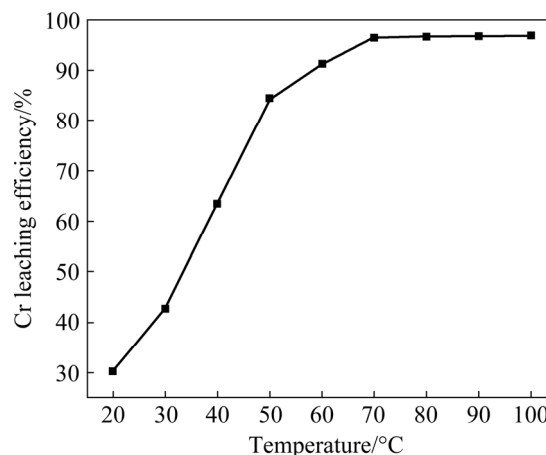


**Fig. 9** XRD patterns of leaching residue formed in 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution: (a) pH=11.9; (b) pH=9.5 (L/S ratio of 10:1 mL/g; stirring for 60 min at 70 °C)

0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution with L/S ratio of 10:1 mL/g and stirring for 60 min under pH 9.5 at 70 °C, followed by filtering and drying. As seen, there are  $\text{PbCO}_3$  and  $\text{PbCrO}_4$  in the leaching residue. Hence, the pH of  $\text{Na}_2\text{CO}_3$  solution was adjusted to 9.5 in the subsequent experiments.

### 3.2.2 Effect of temperature

Figure 10 shows the experimental results obtained by adding Cr precipitate into 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution to leach Cr with L/S ratio of 10:1 mL/g and stirring for 60 min under pH of 9.5 at different temperatures. As seen, the leaching efficiency of Cr increases rapidly from 30.29% to 96.43% with the increase in temperature from 20 to 70 °C, and then it does not change with the further increase in temperature. Therefore, the leaching of the precipitates should be carried out at 70 °C.



**Fig. 10** Effect of temperature on Cr leaching efficiency ( $\text{Na}_2\text{CO}_3$  concentration of 0.5 mol/L; L/S ratio of 10:1 mL/g; pH 9.5; stirring for 60 min)

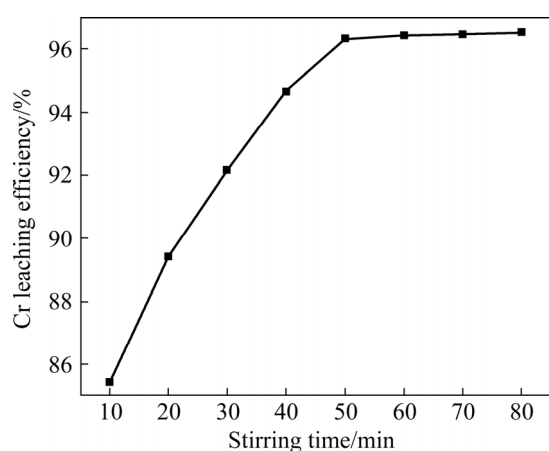
### 3.2.3 Effect of stirring time

Figure 11 shows the experimental results obtained by adding Cr precipitate into 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution to leach Cr with L/S ratio of 10:1 mL/g and stirring for different time under pH 9.5 at 70 °C. As seen, the leaching efficiency of Cr increases rapidly from 85.43% to 96.32% with the increase in stirring time from 10 to 50 min, and then it increases slowly with the further increase in stirring time. After stirring for 60 min, the leaching efficiency of Cr is 96.43%. Therefore, stirring for 1.0 h is enough.

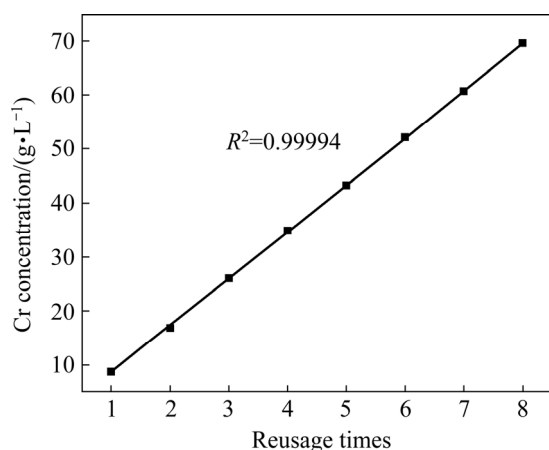
### 3.2.4 Circulation experiment

Figure 12 shows the experimental results of the reuse of chromium leached solution, which is performed by adding  $\text{Na}_2\text{CO}_3$  into the solution

to maintain  $\text{CO}_3^{2-}$  enough. The chromium precipitates were added into chromium leached solution with L/S ratio of 10:1 mL/g and stirring for 60 min under pH 9.5 at 70 °C. It is shown that Cr concentration is proportional to the times of leaching solution reuse. After reuse for 8 times, Cr concentration in the solution is enriched to 69.19 g/L. This indicates that before  $\text{Na}_2\text{CrO}_4$  reaches the saturation, Cr concentration in the solution has small effect on the leaching of Cr from the precipitate, and the solution can be reused as long as the  $\text{CO}_3^{2-}$  is enough.



**Fig. 11** Effect of stirring time on Cr leaching efficiency ( $\text{Na}_2\text{CO}_3$  concentration of 0.5 mol/L; L/S ratio of 10:1 mL/g; pH 9.5; 70 °C)



**Fig. 12** Experimental results of reusage of leaching solution (L/S ratio of 10:1 mL/g; pH 9.5; stirring for 60 min at 70 °C)

Chromium leached solution was used to circularly leach chromium precipitate until  $\text{Na}_2\text{CrO}_4$  approached the saturation. Finally, the product of  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  with purity of 99.3% was obtained by evaporation and crystallization of the saturated

$\text{Na}_2\text{CrO}_4$  solution. This not only significantly reduces the reagent consumption of Cr separation and recovery cost of  $\text{V}_2\text{O}_5$  production with vanadium slag, but also effectively avoids the formation of V–Cr-bearing reducing slag and the mixture of  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , which greatly reduces the environmental pressure.

## 4 Conclusions

(1) Cr in vanadium precipitated solution can be completely enriched in the form of  $\text{PbCrO}_4$ . The concentration of Cr remained in the solution decreases from 2.36 to 0.001 g/L by adding  $\text{PbCO}_3$  into vanadium precipitated solution according to Pb/Cr molar ratio of 2.5, adjusting the pH to 3.0 and stirring for 180 min at 30 °C.

(2) Cr in the precipitate of  $\text{PbCrO}_4$  can be effectively leached with hot  $\text{Na}_2\text{CO}_3$  solution. The leaching efficiency of Cr reaches 96.43% by adding the precipitates into 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution with L/S ratio of 10:1 mL/g and stirring for 180 min under pH 9.5 at 70 °C. The leach solution can be used to circularly leach the chromium precipitates until  $\text{Na}_2\text{CrO}_4$  approaches the saturation.

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## 钒渣提钒和铬循环冶金工艺: (II)沉钒后液分离回收铬

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**摘 要:** 研究通过用  $\text{PbCO}_3$  沉淀并用  $\text{Na}_2\text{CO}_3$  溶液浸出从钒沉淀溶液中分离和回收铬的循环冶金工艺。沉钒后液 pH 调至 3.0 后, 按 Pb/Cr 摩尔比 2.5 加入  $\text{PbCO}_3$ , 在 30 °C 搅拌 180 min, 铬浓度从 2.360 g/L 降到 0.001 g/L。过滤后, 沉铬富集渣用热  $\text{Na}_2\text{CO}_3$  溶液浸出得到含有  $\text{Na}_2\text{CrO}_4$  的浸出液和含有  $\text{PbCO}_3$  的浸出渣。沉铬富集渣按液固比 10:1 mL/g 加入到 0.5 mol/L 的  $\text{Na}_2\text{CO}_3$  溶液中, 调 pH 到 9.5, 在 70 °C 搅拌 60 min, 铬的浸出率为 96.43%。过滤后, 浸出渣返回沉铬, 浸出液循环浸出铬直至  $\text{Na}_2\text{CrO}_4$  接近饱和。最后, 浸出液蒸发结晶后获得  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  产物。

**关键词:** 沉钒后液; 铅盐沉铬; 碳酸钠浸出铬; 循环冶金工艺

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