Recovery of Cr(VI) from vanadium precipitated solution by precipitation with PbSO₄

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Abstract. The recovery of Cr(VI) from vanadium precipitated solution obtained by adding Ca(OH)₂ into chromium-containing vanadate solution and ball milling was investigated by precipitation with PbSO₄. It was found that Cr can be effectively precipitated from the solution by PbSO₄. The precipitate is mixture of PbSO₄ and PbCrO₄·PbO. The concentration of Cr remained in the solution decreases from 2.360 g/L to 0.002 g/L by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under pH 11.5 and stirring for 120 min at 30 ℃. After filtration, the precipitates were leached in H₂SO₄-Na₂SO₄ system solution to obtain Na₂Cr₂O₇ solution and the filtrate can be reused to leach the precipitate contain PbSO₄ and PbCrO₄·PbO.

1 Introduction

Vanadium and chromium are very important industrial elements and strategic metals which are widely used in the fields of metallurgy, chemical industry, material preparation and so on [1]. Due to the similar nature of vanadium and chromium, they are often in the form of symbiosis existing in minerals [2]. During the smelting process of vanadium bearing titano-magnetite, vanadium and chromium are mainly enriched in converter slag, which is usually called vanadium slag as well as the main material of V₂O₅ production [3].

After extraction of vanadium from the vanadium slag, wastewater containing Cr(VI) and a small amount of V(V) was generated. The Cr(VI) and V(V) in aqueous are harmful to lives, and sometimes can be fatal [4]. The wastewater is mostly treated by reduction with sodium pyrosulfite, followed by neutralization to form V-Cr-bearing reducing slag [5]. V-Cr-bearing reducing slag is dangerous solid waste, and several methods have been proposed to handling of it including direct leaching using NaOH+H₂O₂ [6] and NaOH leaching under electric field strengthening [7]. The treatment process of V-Cr-bearing reducing slag has recently made new progress, however it is still cumbersome and uneconomical [8]. On the basis of recovery of Cr from the hydrolized solution by copper salt precipitation, the modified process of V₂O₅ production with vanadium slag is proposed, see Fig.1. The present work focuses on the Cr precipitation from vanadium precipitated solution.

2 Experimental

Chromium-containing vanadate solution was provided by Pangang Group Vanadium & Titanium Resources Co., Ltd.. The V precipitated solution was obtained by adding Ca(OH)₂ and ball milling, and its composition is listed in Table 1. 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) [9]. The X-ray diffraction (XRD) patterns were recorded on a
Rigaku Miniflex diffractometer with Cu Kα X-ray radiation at 35 kV and 20 mA. The pH was determined with ORION-230A which was made in USA, the degree of accuracy is 0.01.

**Table 1.** Experiment results of Cr recovered from V precipitated solution with PbSO₄.

| Elements                     | V  | Cr  | Pb  |
|------------------------------|----|-----|-----|
| V precipitated solution, g/L  | 0.01 | 2.360 | --- |
| Cr precipitated solution, g/L | 0.007 | 0.002 | --- |
| Cr precipitated cake, %      | --- | 8.31 | 72.16 |

Fig. 2 is ion concentration ratio of chromium (VI) in solution under different pH. The chromium (VI) was mainly existed in form of Cr₂O₇²⁻ and HCrO₄⁻ at pH < 6, and then converted to CrO₄²⁻ as pH value increased. It indicated that the pH value of solution affected the species in the solution and also the Cr precipitation should be conducted at pH > 8.0. The pH of V precipitated solution was adjusted to different value with hydrochloric acid and sodium hydroxide, then adding PbSO₄ according to different molar ratio stirring for 30-240 min at 30-80 ℃. After filtration, Cr precipitated solution and precipitate were sampled and analyzed separately, and the results are listed in Table 1 as well.

![Fig. 2](image)

**Fig. 2.** Ion concentration ratio of chromium (VI) in solution under different pH.

**3 Results and discussion**

**3.1 Effect of initial pH value of solution**

The effect of initial pH on the precipitation of chromium was studied and the experimental results obtained by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under different pH and stirring for 120 min at 30 ℃. As seen in Fig. 3, Cr concentration decreases from 0.476 g/L to 0.003 g/L with the increase in pH from 8.0 to 11.5, and it is almost unchanged with the further increase in pH. However, Cr concentration sharply increases from 0.002 g/L to 0.645 g/L with the further increase in pH from 12.5 to 13.5. This indicates that formed lead chromate and lead hydroxide are dissolved into the solution at pH >13, and the chemical reactions can be expressed by equations (1) and (2). Therefore, the initial pH of 11.5 was chosen in the following experiments.

$$\text{Pb(OH)}_2 + 2\text{OH}^- = \text{PbO}_2\text{^2-} + 2\text{H}_2\text{O} \quad (1)$$

$$\text{PbCrO}_4 + 4\text{OH}^- = \text{PbO}_2\text{^2-} + 2\text{H}_2\text{O} + \text{CrO}_4\text{^2-} \quad (2)$$

![Fig. 3](image)

**Fig. 3.** Effect of initial pH on chromium precipitation.

Fig. 4 is XRD patterns of Cr precipitate obtained by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under pH 11.5 and stirring for 120 min at 30 ℃. As seen, the precipitate is mixture of PbSO₄ and PbCrO₄·PbO. The precipitation can be expressed as follow:

$$\text{PbSO}_4 + 2\text{OH}^- = \text{Pb(OH)}_2\downarrow + \text{SO}_4\text{^2-} \quad (3)$$

$$2\text{Pb(OH)}_2 + \text{CrO}_4\text{^2-} = \text{PbCrO}_4\cdot\text{Pb(OH)}_2\downarrow + 2\text{OH}^- \quad (4)$$

![Fig. 4](image)

**Fig. 4.** XRD patterns of Cr precipitate. (pH 11.5)

**3.2 Effect of PbSO₄ addition**
Fig. 5 is the experimental results obtained by adding PbSO₄ into vanadium precipitated solution according to different PbSO₄/Cr molar ratio under pH 11.5 and stirring for 120 min at 30 ℃. As seen, Cr concentration decreases sharply from 0.853 g/L to 0.005 g/L with the increase in PbSO₄/Cr molar ratio from 1.0 to 2.5. Further increase in the addition of PbSO₄ not only resulted in a hardly increase in precipitation efficiency of chromium, but also leads to the mass of precipitation. Hence the molar ratio of PbSO₄/Cr 3.0 was chosen in subsequent experiments.

![Fig. 5. Effect of PbSO₄ addition on chromium precipitation.](image)

**3.3 Effect of stirring time**

The effect of stirring time on the precipitation of chromium was studied and the experimental results obtained by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under pH 11.5 and stirring for different time at 30 ℃. It is observed from Fig. 6 that Cr concentration decreases from 0.680 g/L to 0.003 g/L with the increase in stirring time from 20 min to 100 min, and it is almost unchanged with the further increase in stirring time. Therefore, the stirring time should be ≥ 100 min.

![Fig. 6. Effect of stirring time on chromium precipitation.](image)

**3.4 Effect of temperature**

Fig. 7 is the experimental results obtained by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under pH 11.5 and stirring for 120 min at different temperature. It can be seen that the effect of reaction temperature on precipitation efficiency of chromium was insignificant, and the Cr concentration in the solution was all about 2 ppm. Therefore, the precipitation of chromium should be carried out at 30 ℃.

![Fig. 7. Effect of temperature on chromium precipitation.](image)

**4 Conclusion**

A process of vanadium precipitation with calcium salt followed by chromium precipitation with lead salt was adopted to extract vanadium and chromium from chromium-containing vanadate solution. From the study results, several conclusions are made as following:

1. The initial pH of V precipitated solution and PbSO₄ addition had big influence on the precipitation efficiency of chromium.

2. Chromium in vanadium precipitated solution can be effectively precipitated with PbSO₄ and the precipitate is the mixture of PbSO₄ and PbCrO₄·PbO. The concentration of Cr remained in solution decreases from 2.360 g/L to 0.002 g/L by adding PbSO₄ into vanadium precipitated solution according to PbSO₄/Cr molar ratio 3.0 under pH 11.5 and stirring for 120 min at 30 ℃.

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