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A clean metallurgical process for separation and recovery of vanadium and chromium from V-Cr-bearing reducing slag

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ABSTRACT

In this work, a clean metallurgical process is used to separate and recover vanadium and chromium from V-Cr-bearing reducing slag. Comparing with the traditional process, the process not only reduces the use of sulfuric acid, but also saves the cost of wastewater purification. The process consists of four procedures: low temperature sulphating roasting, reduction leaching, selectively oxidizing and the oxides of vanadium and chromium preparing. Among these, the reduction leaching and selectively oxidizing are the key steps. Low temperature sulphating roasting is used to strengthen the decomposition of V-Cr-bearing reducing slag, Na_2SO_3 is used for the reduction of vanadium from V(V) to V(IV) or V(III), CrO_3 is used to selectively oxidize the vanadium in the leached solution, $(NH_4)_2SO_4$ is used to make the vanadium precipitated in the form of ammonium polyvanadate, and NaOH is used to precipitate Cr(III) from the V precipitated solution. It was found that the leaching efficiencies of Cr and V can reach 99.7% and 99.6% respectively by low temperature sulphating roasting and reduction leaching. The products of V_2O_5 with purity 99.1% and Cr_2O_3 with purity 98.9% were obtained by treating the ammonium polyvanadate and the precipitate of Cr(III), respectively.

1. Introduction

Vanadium (V) is an important nonferrous metal element which is widely applied in metallurgical, material and chemical industries (Mase et al., 2013; Liu et al., 2016a). Vanadium titano–magnetite ore is one kind of important vanadium resources (Li et al., 2016a; Qiu et al., 2013), about 88% of vanadium is extracted from it in China (Qiu et al., 2013). During the smelting process of vanadium titano–magnetite ore, vanadium is reduced into hot metal and then oxidized and enriched into solid slag which is commonly referred to as vanadium slag (Chen, 1992).

Due to the similar nature of vanadium and chromium, they are often existing in vanadium titano–magnetite ore in the form of symbiosis (Moskalyk and Alfantazi, 2003; Zhang et al., 2012), and both enriched in the vanadium slag. The process of vanadium extraction from vanadium slag produces the wastewater containing Cr(VI) and V(V) (Zhang et al., 2009). Generally, the wastewater is treated by reducing with elemental Fe or $FeSO_4$ followed by neutralization to form the precipitate containing Cr(III), V(IV) and/or V(III) (Yang et al., 2010a,b; Fan et al., 2013; Peng et al., 2015), which is usually called as V-Cr-bearing reducing slag (Wen and Yang, 1988; Yang et al., 2014). The contents of V and Cr in V-Cr-bearing reducing slag are 5–10% and 10–20%, respectively (Wang et al., 2017).

Although many methods can be used to extract V from vanadium slag, such as sodium roasting-water leaching (Chen et al., 2013), acid leaching (Liu et al., 2016b), alkali leaching (Wang et al., 2015) and ammonia leaching (Li et al., 2016b). It was found that these methods are all not suitable to recover V and Cr from V-Cr-bearing reducing slag (Yang et al., 2010a; Wen and Yang, 1988). Since V-Cr-containing reducing slag contains flocculating agents and silica colloids, not only the effective utilization rate of sulfuric acid is low (about 50%), but also the solid-liquid separation of the leaching residue is difficult (Yang et al., 2010a; Wang et al., 2017). When V-Cr-bearing reducing slag was leached in 50% NaOH solution, V can be selectively leached, but its leaching efficiency was < 75%. The use of $KClO_3$ can further improve the leaching efficiency of V in alkaline leaching process, but the treatment cost is too high (Yang et al., 2010b). After oxygen-enriched calcined, V can be effectively extracted from V-Cr-bearing reducing slag by alkaline leaching, while the Cr remained in the leached residue cannot be utilized (Jiang and Wu, 2015). The handling of V-Cr-bearing reducing slag has become a thorny problem in many plants in China.

In this work, a clean metallurgical process is presented to separate

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Table 1
Compositions of V-Cr-bearing reducing slag and its leached residue, %.

Elements	Cr	V	Na	Si	O	Ca	S	Other
V-Cr-bearing reducing slag	13.4	5.1	7.8	3.8	45.0	0.8	13.5	10.6
Leached residue	0.06	0.04	0.03	21.8	53.1	4.6	3.7	16.7

and recover vanadium and chromium from V-Cr-bearing reducing slag. By using the process, not only the leaching efficiencies of vanadium and chromium were greatly improved, but also the high purity products of V_2O_5 and Cr_2O_3 were obtained, respectively.

2. Experimental

2.1. Materials and analysis

The V-Cr-bearing reducing slag used in the study was obtained from Panzhihua city, Sichuan province, China. The slag is yellowish green and has the granularity $-150\,\mu m$ before using. The x-ray fluorescence (XRF) analytical result of the V-Cr-bearing reducing slag is listed in Table 1. Sulfuric acid (H_2SO_4), chromium trioxide (CrO_3), ammonium sulfate ($(NH_4)_2SO_4$), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were all purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Unless otherwise stated all above chemicals and reagents were of analytical grade and commercial available, and used without further purification. Distilled water was used in all experiments.

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 Kα X-ray radiation at 35 kV and 20 mA using a scan speed of $4^\circ min^{-1}$ in 2θ ranges from 10° to 80°. The pH was determined with ORION-230A which was made in USA, the degree of accuracy is 0.01.

2.2. Method

The recovery of vanadium and chromium from V-Cr-bearing reducing slag was performed according to the flow sheet as shown in Fig. 1, which includes the procedures of low temperature sulphating roasting, reduction leaching, selective oxidizing, and oxide preparation of vanadium as well as chromium.

The low temperature sulphating roasting was performed in a 200 ml ceramic cup. 10 ml of distilled water and calculated amounts of sulfuric acid (98%) were added into the cup, and then 25 g of V-Cr-bearing reducing slag was mixed under stirring. The cup was covered and put in a muffle furnace to roast at 140–250 °C for 2 h. After cooled to < 80 °C, the roasted material was crushed to $-120\,\mu m$, and leached in Na_2SO_3 solution (0.6–2.0%) with liquid-solid ratio (L/S) 1–6:1 ml/g at 20–90 °C for 1–3 h. The leached solution and the leached residue were obtained after filtration. The leached residue was dried, weighed and analyzed for V and Cr contents. The leaching efficiency *(LE)* of target metal was calculated as followed:

$$LE = \left(1 - \frac{X_b \bullet M_b}{X_a \bullet M_a}\right) \times 100\% \qquad (1)$$

where X_a and X_b represent the content of the metal in V-Cr-bearing reducing slag and leached residue respectively, M_a and M_b are the mass of V-Cr-bearing reducing slag and leached residue respectively.

The leached residue was filtrated with a sand core funnel, and then it was dried and weighed in the funnel. The difference between the leaching efficiency *(LE)* calculated based on head and leached residue and that calculated based on head and leached solution is < 2%.

The vanadium was separated and recovered from the leached solution by adding CrO_3 and $(NH_4)_2SO_4$ under the pH about 2.0 at 95 °C stirring for 2 h. The addition of CrO_3 was according to 1.5–3.0 times of the amount needed to oxidize the vanadium from V(IV) to V(V), and that of $(NH_4)_2SO_4$ was about 2 times of the amount needed to form the precipitate of ammonium polyvanadate. After contacting for the required time, the ammonium polyvanadate was obtained by filtration. Then high quality V_2O_5 was acquired by calcining the ammonium polyvanadate at 550 °C for 2.5 h.

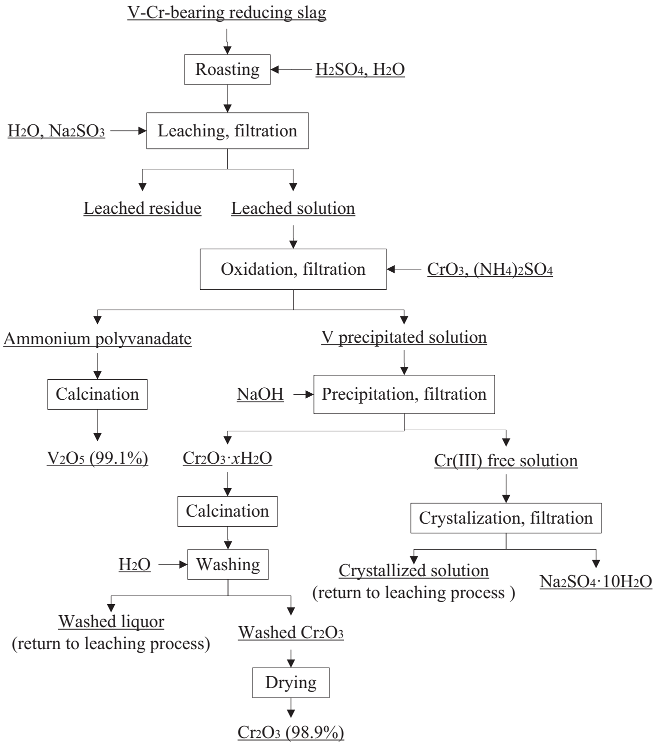

Fig. 1. Flowsheet of recovery vanadium and chromium from V-Cr-bearing reducing slag.

Before Cr(III) was precipitated, the V precipitated solution was purified to remove Fe and other impurities by adding Na_2CO_3 to adjust the pH to about 3.1 at 85 °C. Then the purified solution was neutralized with NaOH to make the Cr(III) precipitated in pH about 8.5 at 90 °C. After filtration, the precipitate was first calcined at 950 °C for 2.5 h, and then refined by grinding the calcined material to 150 μm and washing with distilled water to remove soluble impurities. At last, the product of Cr_2O_3 was obtained by drying the refined material at 110 °C for 2 h. The Cr(III) precipitated solution was cooled to 0–10 °C to make $Na_2SO_4{\cdot}10H_2O$ crystallized before it can be returned to the reduction leaching procedure.

3. Results and discussion

3.1. Low temperature sulphating roasting and water leaching

3.1.1. Effect of H_2SO_4 addition

The XRD patterns of the V-Cr-bearing reducing slag are shown in Fig. 2. As can be seen, there are four crystal mineral phases in the V-Cr-bearing reducing slag, they are lecorite ($NaNH_4SO_4(H_2O)_2$), thenardite (Na_2SO_4), grimaldite ($CrO(OH)$) and trisondium vanadium trissulfate ($Na_3V(SO_4)_3$). From Table 1 it can be roughly estimated that to completely extract vanadium and chromium from the V-Cr-bearing reducing slag, the theoretical addition of H_2SO_4 is about 40 wt% (mass ratio of sulfuric acid to V-Cr-bearing reducing slag):

$$2CrO(OH) + 3H_2SO_4 = Cr_2(SO_4)_3 + 4H_2O \qquad (2)$$

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