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Recovery of chromium from residue of sulfuric acid leaching of chromite



Qing Zhao^{a,b,*}, Chengjun Liu^{a,b}, Baokuan Li^b, Ron Zevenhoven^c, Henrik Saxén^c, Maofa Jiang^{a,b}

^a Key Laboratory for Ecological Metallurgy of Multimetallic Ores (Ministry of Education), Northeastern University, Shenyang 110819, China

^b School of Metallurgy, Northeastern University, Shenyang 110819, China

^c Thermal and Flow Engineering Laboratory, Åbo Akademi University, Åbo/Turku 20500, Finland

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ABSTRACT

The sulfuric acid leaching process is widely considered to be a cleaner technology to prepare chromium salt from natural chromite as no Cr(VI)-bearing wastes are generated or discharged. However, some insoluble anhydrous chromium sulfate could precipitate causing a serious chromium resource loss and potential pollution problems. For the purpose of recovery of chromium from leaching residue, a Box–Behnken design (BBD) based ammonium leaching treatment is investigated and optimized. A second-order polynomial regression model that reveals the functional relationship between processing parameters and recovery time is established and verified by the analysis of variance (ANOVA). Predicted results show a good agreement with the experimental data. The main and interactive effects of the processing parameters on the recovery time are illustrated by three-dimensional (3D) response surfaces. It was found that increasing temperature (from 70 to 90 °C) and acidity (pH value from 0 to –0.5) of solution have positive effect on the leaching efficiency, and the plot of recovery time versus ammonium dosage shows a parabola-shape. On the basis of the findings in this study, an advanced sulfuric acid leaching process of chromite is proposed. Experimental results showed that hydrous and anhydrous chromium sulfate were completely recovered, and the average difference between the predicted and actual recovery times was less than 4%. All of the chromium resources can be utilized in the novel process, and no hazardous wastes or potential pollutants are discharged to the environment.

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1. Introduction

Cr(III) salts are important chemical feedstocks that serve as tanning agent, pigments, catalyst etc. in various applications. Alkaline roast processes including calcium-roasting and low- or non-calcium-roasting are principal technologies for preparing Cr(III) salts from natural chromite. In the strong oxidizing environment at high temperature, chromite decomposes due to the transformation from Cr(III) into Cr(VI) and chromium concentrates, and subsequently Cr(III) salt products are prepared after a reduction treatment for Cr(VI)-bearing substances (Yarkadaş and Yildiz, 2013). In these processes, significant

amounts of Cr(VI)-bearing chromite ore processing residue (COPR) are generated and discharged to the environment (Freese et al., 2014; Wang et al., 2017). It is known that Cr(VI) is a carcinogen and a dermatological and pulmonary sensitizer that is 500 times more toxic than Cr(III) (Kowalski, 1994; Chrysochoou et al., 2009), but the remediation and comprehensive utilization of COPR are still thorny problems (Sheng et al., 2006). Millions of tons of COPR have been deposited in residential and industrial areas causing grave pollution problems in many countries around the globe (Burke et al., 1991; Liou et al., 1992; Farmer et al., 1999; Darrie, 2001; Matern et al., 2016).

To avoid the formation of Cr(VI) from the source, a sulfuric acid leaching process was proposed and extensively studied (Zhao et al.,

* Corresponding author at: Mailbox 288, Northeastern University, Wenhua Road, Heping District, Shenyang, China.

E-mail address: zhaoq@smm.neu.edu.cn (Q. Zhao).

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2015, 2017; Zhang et al., 2016). Literature indicates that in this process, with a suitable oxidant, chromium can be extracted from chromite in trivalent state using a heated sulfuric acid solution (Geveci et al., 2002; Liu et al., 2011). A lot of effort is being made to improve this cleaner process for manufacturing Cr(III) salts, but the extraction yield of chromium (normally around 80%) is still unsatisfactory (Geveci et al., 2002; Zhang et al., 2016).

Biermann and Heinrichs (1960) suggested the main reason of the incomplete recovery of chromium to be the precipitation of a Cr(III)-rich multicomponent sulfates, which was reported to be grey-green in color and acid-insoluble. Vardar et al. (1994) found similar phases in the residue after sulfuric acid leaching treatment applied to UG-2 chromite, and speculated that the precipitation of the sulfates may be a function of processing conditions. Experimental results indicated that when the leaching tests were conducted using 75 wt.% sulfuric acid at 210 °C, sulfates in the residue add up to 80 wt.%. Geveci et al. (2002) detected $\text{Cr}_2(\text{SO}_4)_3$ in leaching residue using X-ray diffraction (XRD) analysis, and attributed the incomplete extraction of chromium to the sulfate precipitation.

These findings were verified by the authors of this paper. Scanning electron microscopy (SEM) images of the sulfates generated in the leaching process of South African chromite has been presented in our earlier reporting. Factors were proposed that could result in an ionic supersaturation in the solid-liquid reaction boundary layer, which would cause the precipitation of Cr-rich sulfates (Zhao et al., 2014). Furthermore, the precipitated sulfates were found to cover the unreacted chromite powder limiting the chromite dissolution. Therefore, the extraction yield of chromium has a significant negative correlation with the precipitation quantity (Jiang et al., 2014). It was noted that Cr(III) is not stable in the form of sulfate in the residue. It may be oxidized to the toxic Cr(VI), especially in alkaline oxidizing conditions (Eary and Davis, 2007), making the slag field an potential source of chromium contamination of nearby soils and waters (Elzinga and Ashley, 2010). Even if the chromium is not oxidized, the pollution risks still remain. Accumulation of Cr(III) in soils can inhibit various enzyme systems of living organisms, and the influence of Cr(III) on the surrounding environment could be more serious with the presence of organic ligands and/or under acidic conditions (Ghaedi et al., 2006; Anirudhan and Radhakrishnan, 2007). Despite this, the stabilization or recycling of the Cr-bearing residue generated in sulfuric acid leaching process of chromite has not been described in the open literature.

Our earlier studies showed that the generation of Cr-rich sulfates could be restricted or even avoided by optimizing leaching process parameters for South African chromite in the laboratory (Jiang et al., 2014). For industrial production or for other kinds of chromites, however, the risk of chromium loss and pollution cannot only rely on the process control. Therefore, specific treatments for chromium recovery and remediation of residue need to be implemented.

It has been confirmed that the precipitated sulfates contain both water-soluble hydrous chromium sulfate and water-insoluble anhydrous chromium sulfate. The former substance can be easily recovered by washing treatment, and the Cr(III) extraction from aqueous phase is well studied (Aravindhan et al., 2004; Fahim et al., 2006; Dettmer et al., 2010). However, little research addressed the recovery of anhydrous chromium sulfate from solid wastes. One concept for separating this phase from unreacted chromite powder is to transform it into water-soluble phases, by which chromium recovery and unreacted chromite enrichment could be both achieved. Wenzel et al. (2010) added ammonium sulfate in the sulfuric acid leaching process of high carbon ferrochromium alloy at 170 °C to inhibit the formation of anhydrous chromium sulfate. Experimental results indicated that in the presence of ammonium sulfate almost all chromium was extracted in a soluble form while no remarkable effect on the Fe(II)-bearing substance was found. Acid-soluble ammonium chromium sulfate was claimed to be generated. However, whether the goal that transforming the anhydrous chromium sulfate into ammonium chromium sulfate in sulfuric acid leaching process can be achieved remains unknown.

Response surface methodology (RSM) is a group of mathematical and statistical techniques for analyzing the relationships between controllable input parameters and one or more measured responses

with a limited set of experiments (Kwak, 2005; Ravikumar et al., 2007). Box-Behnken design (BBD) is widely adopted by scientists in various research fields to provide experimental data for response surface modeling (Ferreira et al., 2007; Kiran and Thanasekaran, 2012; Das et al., 2014; Jeganathan et al., 2014). With the aim of extracting anhydrate chromium sulfate, an ammonium treatment was carried out in this work, and the combined effects of pH value of solution (pH), processing temperature (T), and ammonium dosage (R) on the chromium recovery behavior (i.e. time needed and efficiency) were studied by BBD and quadratic programming.

2. Thermodynamic analysis

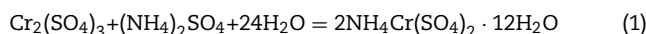
The formation of anhydrous chromium sulfate can be attributed to the dehydration effect of concentrated sulfuric acid at high temperature, which was proven by the evidence that more anhydrous chromium sulfate precipitated from aqueous solution when the temperature and/or concentration of sulfuric acid were high in the leaching process (Jiang et al., 2014; Zhao et al., 2014).

Due to the high solubility in acid solution it possesses, ammonium chromium sulfate has been suggested to be a promising reaction intermediate for recovering anhydrous chromium sulfate (Wenzel et al., 2010). An Eh-pH diagram of the Cr-N-S-H₂O at 160 °C as shown in Fig. 1 was calculated by the FactSage software (7.0, CRCT-ThermFact Inc., CAN; GTT-Technologies, GER). For negative ordinate ($E < 0$), the system is able to supply the electrons to the species found in the solution. By contrast, the system tends to remove electrons from the species if $E > 0$, which applies when oxidant is present. In the sulfuric acid leaching process for chromite, a strong oxidizing environment is maintained by the presence of oxidant and the employment of concentrated sulfuric acid. From Fig. 1 it can be confirmed that $\text{Cr}_2(\text{SO}_4)_3$ could precipitate from the solutions and be stable under leaching conditions (area delimited by the dotted box), while NH_4^+ can be oxidized into a N_2 if the solution is in a strongly oxidizing state. Therefore, different from the study reported by Wenzel et al. (2010), ammonium source materials cannot be directly added to the strong oxidizing acid solution that is used for decomposing chromite, thus the ammonium treatment for leaching residue after leaching process seems more reasonable.

3. Experimental

3.1. Materials

Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4 \geq 99.0$ wt.%) was employed as the ammonium source material for recovering anhydrous chromium sulfate, giving the ion reaction as follow:



For the purpose of exclusively investigating the reaction behavior of the two substances, a pure anhydrous chromium sulfate was prepared from hydrous chromium sulfate ($\text{Cr}_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \geq 98$ wt.%) by roasting in a muffle furnace at 350 °C for 4 h.

18.65 g of a typical leaching residue smaller than 10 μm obtained from a leaching test with a low leaching yield of chromium (37.5%) was also studied in this work. Processing details of the test and phases composition can be found in our earlier reporting (Jiang et al., 2014; Zhao et al., 2014). The residue was collected after filtration and analyzed

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