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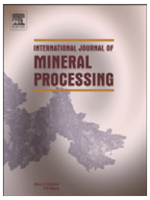

A new metallurgical process for the clean utilization of chromite ore

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ABSTRACT

A new metallurgical process for extracting chromium from chromite ore is proposed to overcome the severe chromium (VI) pollution in chromate production industry. When the 60 wt.% KOH solution was used to decompose chromite ore, the chromium and iron ions in chromite ore were oxidized into soluble K_2CrO_4 crystal and insoluble KFe_3O_5 particle, respectively. The chromium levels in the new residue meet the emission standard of chromium-containing waste due to the KFe_3O_5 crystal's compact appearance, hence the pollution problem of chromite ore process residue is thoroughly resolved. The effect of the main variables on this clean metallurgical process was systematically investigated. Under the condition of leaching temperature 200 °C, oxygen partial pressure 2.0 MPa, and particle size 0.045–0.063 mm, the chromium extraction reached up to 99.4% after 5 h reaction. There is no product layer existing during the leaching process, and the reaction rate is controlled by the surface reaction. The resistances of oxygen transport during the leaching process were calculated step by step, and the surface chemical reaction was the main resistance factor that was consistent with the kinetics study.

1. Introduction

Chromium compounds are widely used in many industries, and their demands on a global scale increase steadily year by year (SiWei, 1988; Yi and Zhu, 2003; Zhaoye, 2006). However, since millions of tons of toxic chromium-containing residue yielded from chromate production industry was piled up without detoxification every year, the environment problem caused by the residues has become the major resistance for the developing of chromate production industry (Freeman et al., 1992; MIIT, 2012).

Generally, chromite ore is the exclusive primary source of chromium for the chemical industries, and the alkali roasting process has always been the commercial extraction technology for chromate production. The development of alkali roasting process has undergone three steps: the high lime roasting, the low lime roasting and the lime-free roasting. Thereinto, lime-free technology, which can prevent $CaCrO_4$ generation and remarkably reduce the discharged residue yield, is the most advanced chromite ore roasting technology (Weber et al., 1993). Unfortunately, the maximum utilization ratio of chromium in this process is less than 85%, while the energy efficiency is only about 20%. Especially, since there is no economic and applicable technology to treat the toxic roasting residue, large amount of residue was buried worldwide in the past, and now the landfill sites of the residues have been a major source of chromium (VI) contamination (Antony et al., 2001; Bruen, 1974; Kowalski and Mazanek, 1998; Tathavadkar et al., 2003).

The liquid-phase oxidization method is an alternative to the roasting method for the chromate salts production. In this method, chromite ore is oxidized into soluble chromate salt in alkali-hydroxide solution by oxygen or other oxidizing agents. Since the mass transfer in the liquid phase is significantly improved, a higher chromium conversion can be achieved at a milder reaction condition. Additionally, the yield of residue is remarkably reduced for no filling is added. Therefore, the liquid-phase oxidization method has attracted much research attention, and many new technologies have been developed and investigated.

In recent years, an advanced liquid-phase oxidization technology, in which chromite ore is oxidized with highly concentrated KOH sub-molten salt media under ambient pressure, has been proposed by Zhang and her coworkers (Sun et al., 2009; Xu et al., 2005; Zhang et al., 2005; Zheng et al., 2006). Because of the advantageous characteristics of the KOH sub-molten salt media such as high mean ion activity coefficient, high boiling point and excellent performance in flow and transfer, the extraction of chromium from chromite ore becomes more efficient (Zhang et al., 2008). In this new technology, chromite ore was dissolved in 80 wt.% KOH sub-molten salt solution at 320 °C, and the chromium extraction surpassed 99% after 8 h reaction. Moreover, the amount of discharged residue was further decreased to 0.5 ton per ton of chromate salts which was about 60% of the residue amount from the developed lime-free roasting method. Therefore, this method not only achieved higher resource utilization efficiency but also reduced residue emission. Based on this green technology, a 10 kt/a scale

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demonstration plant has been built in He'nan province, PR China (Xu et al., 2006; Zheng et al., 2006).

However, the chromium (VI) levels of the residue from the green chromate production technology is about 0.1% by weight that much exceeds the emission permissible level of the chromium-containing waste (Xu et al., 2006). Despite great effort has been put into the innocuous disposition of this residue, no practical technology was achieved and large amounts of residue have to be stockpiled around the plant (Sun Zhi and Yi, 2005; Tao Qi et al., 1999). In order to solve this bottleneck problem, a new clean pressure leaching method is developed from the above green chromate production technology. By manipulating the concentration of KOH sub-molten salt solution, the iron in chromite ore was converted into compact KFe_3O_5 crystal other than the amorphous iron oxide residue. Following the detection standard of the chromium (VI) toxicity, the leach residue of this new technology is pollution-free that holds out a well prospect to eliminate the pollution of chromite ore processing residue. The kinetics of this clean metallurgical process was investigated, and the effects of the oxygen partial pressure and flow rate, the particle size and the reaction temperature on the chromium extraction were determined. In additional, the action of oxygen in the mineral dissolution process was discussed in the paper, and the resistances of oxygen transmission during the leaching process was first investigated.

2. Materials and experiments

2.1. Minerals

The chromite ore samples exploited from Philippines were obtained from Bluestar Yima Chrome Chemical Materials Co. Ltd., PR China. The chemical analysis of a typical sample by ICP-OES was given in Table 1. Prior to the experiments, the sample was crushed and dry-sieved to four particle-size fractions (0.045–0.063, 0.063–0.075, 0.075–0.090, 0.090–0.150 mm), and then dried overnight at 80 °C. The Cr_2O_3 and Fe_2O_3 contents of each size fraction were list in Table 2. All experiments were performed with the 0.045–0.063 mm fraction except otherwise stated. The potassium hydroxide employed in this work was of analytical grade and made by Beijing Chemical Plant. Commercial pure oxygen manufactured by the millennium Beijing gas sales center and ultrapure water (Millipore) were used in all experiments.

As shown in Fig. 1, the mineralogical analysis result of the Philippine chromite ore indicates that the sample mainly consists of (Fe, Mg)(Cr, $Fe)_2O_4$ (JCPDS Card #220349). The morphology of chromite ore was investigated by scanning electron microscopy (SEM). Several important features can be recognized: (1) the solid particles have a compact surface (Fig. 2). (2) the main elements including Cr, Fe and Al are uniformly distributed in the chromite ore (Fig. 3), suggesting that chromite ore has homogeneous structure.

2.2. Experimental apparatus and procedure

The diagram of the experiment set-up is shown in Fig. 4. All experiments were performed in a 1.0 L stainless steel autoclave of cylindrical shape. The autoclave was equipped with a temperature control unit, an electric heating furnace, a magnetic driven agitator with standard Rushton turbine propeller, and an internally mounted cooling coil. The temperature control unit consists of a thermocouple and a regulator of the heating furnace. The reaction temperature of the reactor is measured by the thermocouple and feeds back to the regulator of the heating furnace for adjusting the heating power. The reaction temperature can be maintained constant with a precision of ±1 °C. A gas pipe is fixed inside the bottom of the autoclave and oxygen is introduced through the pipe. The oxygen flow rate is set at the desired value by the flow control instrument during the leaching process. The intake pressure of oxygen is regulated with the pressure relief valve, and the back pressure valve is applied to retain the oxygen pressure.

Table 1
The chemical composition of Philippine chromite ore (%, wt).

Component[a]	Cr_2O_3	FeO	MgO	Al_2O_3	SiO_2	MnO
Wt (%)	47.35	30.49	5.31	8.80	2.06	0.58

[a] The difference between total chemical compositions and 100% is due to the loss of ignition.

Table 2
Cr_2O_3 and FeO content in different size of Philippine chromite ore.

Size fraction (mm)	0.045–0.063	0.063–0.076	0.076–0.097	0.097–0.150
Cr_2O_3 (%)	46.68	47.20	48.27	45.67
FeO (%)	29.44	32.09	33.00	32.21
Cr/Fe	1.39	1.29	1.29	1.25

All the experiments were carried out batch-wise by using 75 g chromite ore particles, 353 g potassium hydroxide (mass ratio of alkali-to-ore is 4:1), 150 mL ultra-pure water (the KOH mass fraction of the solution is about 60%). When the ultra-pure water was heated up to 40 °C, potassium hydroxide was added and dissolved. Subsequently, chromite ore particles were added. The autoclave was sealed and the slurry was stirred at 200 rpm to improve mixing. The reacting system was further heated to the preset temperature, and then oxygen was introduced. The oxygen pressure rose to the desired value quickly and then was regulated by the pressure regulation valve. Subsequently, the agitation speeded up and oxygen discharged from the reactor at the preset flow rate, and timing of the reaction time initiated. At selected time intervals, about 10 g pulp was withdrawn quickly and then separated by vacuum filtration to obtain residues for analysis.

In order to obtain the chromium extraction, the residues were filtered, washed with hot ultra-water, and then dried at 80 °C overnight. All experimental data were the average values of two or three parallel experiments. The chromium extraction of chromite ore was calculated using the following equation developed by Zhi Sun (Sun et al., 2009):

$$\text{Extraction of chromium} = \left(1-[\mathrm{Cr}]_r/[\mathrm{Cr}]_0\right) \times 100\% \qquad (1)$$

where $[Cr]_r$ and $[Cr]_0$ are the concentration of chromium in the residues and that in the chromite ore, respectively.

2.3. Analysis instruments

The chemical compositions of chromite ore and the residues were determined by ICP-OES (PE Optima 5300DV, PerkinElmer). The mineralogical phases of chromite ore and residues were determined with X-ray diffraction (XRD, Phillips PW223/30). The SEM-EDS results of

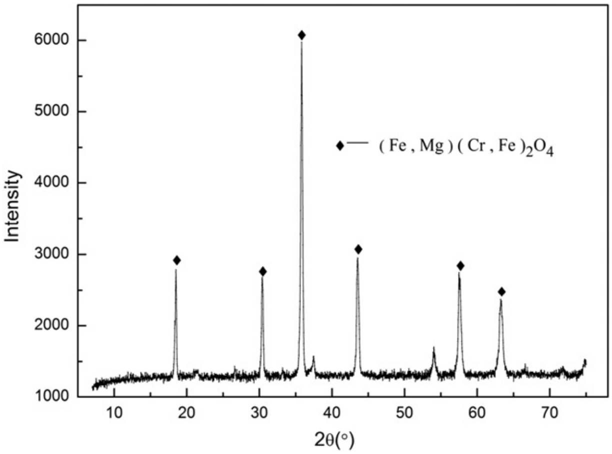

Fig. 1. XRD patterns of Philippine chromite ore.