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Comprehensive utilization of spent magnesia-chrome refractories with gravity separation followed by flotation

Kai Xue, Junwei Han, Fen Jiao*, Wei Liu, Wenqing Qin, Lianbing Cai, Tan Xu

School of Minerals Processing and Bioengineering, Central South University, 410083 Changsha, Hunan, China

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ABSTRACT

This study investigated the comprehensive utilization of spent magnesia-chrome refractories through gravity separation followed by flotation. The characteristics of refractories, the effects of various process parameters on the recovery of valuable metals and the adsorption mechanism of xanthate on silver were examined comprehensively. The results revealed that the metals penetrated into the refractories from cracks and holes. The penetrated metal particles were composed of different metal elements, several of which were dissolved in refractories. The optimum parameters were derived as follows: 60% particles passing a grinding fineness of 0.074 mm for gravity separation and regrinding tailing to 80% particles passing 0.074 mm for flotation, pH 8, 500 g/t of combined collector and 200 g/t of emulsified kerosene. Under these conditions, 99% Ag, 82% Pb and 81% Bi were recovered by a closed-circuit test. The obtained concentrates can be smelt as feeding, whereas the tailings with low impurities can be used as raw material for new refractories. The electrochemical and Fourier transform infrared measurements indicated that double xanthate and silver butyl xanthate were generated on the silver surface, which could improve the floatability of metals.

1. Introduction

For 50 years, the spinel structure has been used for refractory applications in metallurgical and other high-temperature industries. In particular, the chromite-based spinel is extensively used in various industries, such as secondary metallurgy, non-ferrous furnaces and cement making because of its high-temperature stability, low thermal expansion and outstanding erosion–corrosion performance at high temperatures (Gotod and Lee, 2005; Alper, 1970; Tabbert, 1992; Vezza et al., 1997; Gregurek et al., 2015). In general, magnesia-chrome refractories are produced from a mixture of magnesia and an immense assortment of chrome ores. Unfortunately, chrome ores are being massively depleted worldwide. Moreover, the heavy metal chromium (Cr) can transfer into soil and water and consequently affect the survival and development of humans (Zhao et al., 2006; Jiang and Wang, 2004; Qintie et al., 2013). The human body can easily absorb and be invaded by Cr (VI) through the digestive system, the respiratory system, the skin and mucous membranes (Han et al., 2012; Dhal et al., 2013). Thus, regulations that consider spent magnesia-chrome refractories as potentially hazardous waste have been enforced, making their disposal more difficult and expensive.

The introduction of material revolution and chrome-free materials in refractory linings have considerably reduced the application of Cr_2O_3-containing refractories. Although numerous studies have been conducted on chrome-free refractory materials, none of them can be widely applied in the industry because of their cost and fire performance (Schlesinger et al., 1998; Peng and Yang, 2016). In addition, none of the tested chrome-free alternatives could match the performance of magnesia-chrome reference refractories (Schlesinger et al., 1997; Crites and Schlesinger, 1999). Thus, magnesia-chrome refractories are still used in a large scale because of its outstanding erosion–corrosion performance. Refractory linings must be replaced every several months because of chemical, thermal and mechanical stresses (Rigaud, 2011; Malfliet et al., 2014). Many specialists suppose that 70% of refractory wear result from chemical corrosion (Wojsa et al., 2013; Scheunis et al., 2014). Chemical corrosion is not limited to the bath-lining interface influenced by capillary forces, as it can also occurs deep inside the pores of refractory bricks (Lee and Zhang, 1999; Zhang et al., 2000; Mukai et al., 2002; Matsui et al., 2002). Most refractory users find landfilling spent refractories as a more economical strategy than recycling the material because of the lack of economic and legislative driving forces in past decades (Vance et al., 2003). This approach leads to not only the wastes of resources but also serious environmental threats.

Considering the decrease in chrome ores and the increase in processing cost, researchers have gradually explored the recovery of spent

* Corresponding author.
E-mail address: jfen0601@126.com (F. Jiao).

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refractories. Given that the output of steel substantially exceeds that of non-ferrous metal, researchers have primarily focused on refractory materials produced by iron and steel enterprises (Lule González et al., 2006; Hanagiri and Matsui, 2012). Kim E. et al. performed selective Cr recovery from stainless steel slag by using NaOCl (Kim et al., 2016); however, this method is unsuitable for recycling magnesium-chrome refractories. The typical recycling scheme involves sorting, crushing, screening, separating and reusing raw materials (Fang et al., 1999). In addition, spent refractories are also recycled for construction uses, magnesia-based castables and metal production. Significant achievements have been attained in this field, but these technologies have yet to be widely applied in the industry because of the lack of an economic driving force (Han et al., 2016).

Both gravity separation and flotation are economical technologies that are extensively applied for the recovery of metals in the mineral processing field. In this study, a combined process of gravity separation and flotation was proposed for the reutilization of spent magnesia-chrome refractories. This process can effectively recycle the metals contained in spent refractories, whereas refractories with minor or trace metal impurities can be used as raw materials for renewable refractories. This technology does not use activators, inhibitors and other adjusting agents, such that the wastewater generated in the industrial production can be returned to production after being settled. Thus, the entire process does not generate wastewater. In addition, this technology offers many advantages, such as low cost and simple operation. To assess the feasibility of the proposed technology, a detailed mineralogical analysis of the spent refractory was conducted, and then a series of gravity separation tests and flotation experiments was performed. In addition, the adsorption mechanism of butyl xanthate on a silver surface was examined by electrochemical and infrared spectrum measurements to provide a theoretical guidance of the recycling of silver from refractories through flotation.

2. Experimental

2.1. Samples

The spent magnesia-chrome refractory bricks used in the study were obtained from a silver refining furnace lining provided by a silver smelting plant in Hunan, China. A bulk sample of 100 kg crushed to −3 mm was prepared for the experiment by using standard techniques, followed by sampling through coning and quartering. The chemical composition was analysed by X-ray fluorescence (XRF; Rigaku, model ZSX Primus II) spectroscopy. The results revealed that the spent refractory bricks contained valuable metals, including 1.72% Ag, 5.10% Pb and 3.99% Bi (Table 1). The morphological characteristics of the spent bricks were detected by optical microscopy (Leica DMRXP) and scanning electron microscopy (SEM, JEOL, JSM-6490LV) coupled with energy dispersive spectroscopy (EDS, JEOLJSM-6490LV).

The fine silver plate (3 mm thickness) used for the electrochemical and infrared spectra experiments was acquired from a silver smelter. XRF testing indicated that the purity of the silver plate was above 99%. After lathe machining and fine polishing, a sliver plate was cut into circular electrodes with a radius of 14 mm. The fine silver plate was sawed into sawdust and then grinded to 5 μm by using an agate mortar with the aid of sodium carbonate for infrared spectra experiment.

Other chemicals used in the flotation experiments include: dilute sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) as pH regulators; emulsified kerosene (EK) as an auxiliary collector; sodium isobutyl xanthate (SIBX), butylamine dithiophosphate (BAD), ammonium diethyl dithiocarbamate (ADD) and mixed advanced xanthate (MA) as collector candidates; and terpilenol oil as a frother. Sulfuric acid and sodium hydroxide were of analytical grade and the rest were of industrial grade.

2.2. Gravity separation and flotation process

The equipment used in the gravity separation tests were frequency conversion slime tables (RK/LY-1100 × 500). For each test, the materials were wet ground in a laboratory ball mill and then separated by the slime tables. The process parameters were as follows: processing capacity, 20 kg/h; pulp density, 20 wt%; lateral gradient, 0.65°; horizontal flush water, 400 L/h; stroke, 16 mm; and stroke frequency, 450 min^{-1}. The concentrates and tailings obtained after the slime table process were filtered, dried, weighed and analysed for metal contents.

The flotation experiments were conducted in a 1.5 L laboratory cell made of Plexiglass. Prior to each test, 500 g of the samples was ground with a wet ball mill, transferred to the cell and conditioned for 1 min at an agitation speed of 1992 rpm. If necessary, the sample was added with a scheduled amount of H_2SO_4 and conditioned for 2 min. Then, a scheduled amount of emulsified kerosene was added to the pulp, under vigorous stirring vigorously for 8 min at an agitation speed of 2596 rpm. After this process, a collector was added, and the sample was conditioning for 4 min. Then, 50 g/t of terpilenol was added before the froth was scraped. The concentrate was collected for 4 min. Finally, the froth and sink samples were collected, filtered, dried, weighed and analysed by XRF. The flotation recovery was calculated based on the solid weight distributions between the concentrate and the tailing.

2.3. Electrochemical and infrared spectra experiments

The electrochemical tests were performed using the Princeton Model 283 Potentiostat EG & G of the Princeton Electrochemical Measurement System. The round electrode surface was ultrasonically cleaned. The electrolytic cell was a three-electrode system, consisting of two wired graphite rods as the counter electrode and Ag/AgCl as the reference electrode. The potential values of this article were corrected to the standard hydrogen electrode potential. For each measurement, the electrode would be progressively polished with different types of sandpaper. Cyclic voltammetry tests were performed at the sweep rate of 20 mV/s.

The infrared spectrum measurements were conducted using a Nicolet NEXUS 670 Fourier Transform Infrared Spectrometer in the measurement range of 4000–400 cm^{-1}. For each measurement, 2 g of the sample (all particles were below 5 μm) was placed in a flotation tank, and 40 mL of distilled water was added to the tank. Then, the desired operating conditions were attained by adjusting the pH and adding reagents. After stirring for 30 min in the flotation machine, the samples were rinsed thrice with distilled water. The solid samples were dried in a vacuum oven at room temperature. The prepared samples were mixed with an amount of KBr, compressed and placed on the sample rack for testing.

Table 1
XRF analysis of spent magnesia-chrome refractories/%.

Elements	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr
Content	26.80	5.47	23.90	1.68	2.24	0.067	0.051	2.80	0.052	1.30	0.10	0.053	7.71
Elements	Co	Ni	Cu	Bi	As	Se	Rb	Sr	Ag	Pb	Sb	Te	Fe
Content	0.014	0.043	0.51	3.99	0.55	0.015	0.061	0.001	1.72	5.10	1.59	0.099	5.35