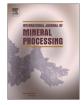
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Selective reverse flotation of apatite from dolomite in collophanite ore using saponified gutter oil fatty acid as a collector



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ABSTRACT

Reverse flotation is an effective method for separating apatite from gangue minerals (such as dolomite) in collophanite ore. However, collophanite ore flotation using traditional fatty acid collectors is uneconomical because of the relatively high cost of the raw materials. In this work, saponified gutter oil fatty acid (GOFA) was used as the collector, and its effect on collophanite ore flotation and the mechanism of adsorption were studied. The results showed that Ca^{2+} is the active site for reaction with GOFA and initiates apatite flotation. The dissolution of Ca^{2+} from dolomite was found to be thermodynamically more favorable than that from apatite, and the relative abundance of Ca^{2+} enhanced the reaction of dolomite with GOFA. XPS analysis revealed that the interaction between GOFA and magnesium on the dolomite surface strengthened chemisorption. As magnesium is a major constituent of dolomite, but not of apatite, GOFA was selectively chemisorbed onto the dolomite surface. Closed-circuit reverse flotation tests using GOFA as the collector resulted in an excellent concentrate with 28.46 wt% P₂O₅ and 0.65 wt% MgO, corresponding to a P₂O₅ recovery of 87.2%. GOFA was demonstrated to exhibit outstanding selectivity for dolomite in the reverse flotation of collophanite ore. The use of GOFA as an environment-friendly, cost-effective, and selective collector is expected to provide new insights into low-cost collophanite ore flotation.

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1. Introduction

Phosphate ore, which is exhaustible, non-renewable, non-recyclable, and irreplaceable, has been listed as a mineral resource that cannot meet the requirements of China's economic development post-2010. Moreover, beneficiation of phosphate ore involves several challenges owing to the abundance of low-grade ores relative to high-grade ores, difficulties in separation from sedimentary metamorphic phosphorite, and the large amount of refractory phosphate rock reserves (Blazy and Samama, 2001; Mohammadkhani et al., 2011; Zheng and Smith, 1997).

Sichuan province (China) is a region with large reserves of phosphate ore. However, nearly all these resources are of low P_2O_5 grade, with fine dissemination size and complex ore properties, especially collophanite ore from Qingping, Sichuan. Collophanite ore is a kind of colloidal apatite that is usually highly intergrown with gangue minerals, such as dolomite. The separation of apatite from dolomite is an important step in the flotation of collophanite ore. The complexities of separating apatite and dolomite in collophanite ore is mainly attributable

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to the fine dissemination size and complex ore properties, such as similar surface mineral compositions, which result in the floatation of dolomite (or apatite) when using collectors that float apatite (or dolomite) (Abdel-Khalek, 2000; Al-Fariss et al., 2013; Amankonah and Sumasundaran, 1985).

Reverse flotation is an effective method for obtaining apatite concentrates by floating dolomite from phosphate ore (Abouzeid, 2008; Sis and Chander, 2003a). The most widely used collectors for the flotation separation of apatite from dolomite are conventional fatty acids. Cao et al. (2015) and Guimaraes et al. (2005) examined the effects of different components of vegetable oil fatty acids on apatite flotation. Cao et al. (2015) demonstrated that the use of a mixed collector of linoleic acid and palmitic acid facilitates apatite flotation, with superior flotation efficiency achieved for an oleic acid to linoleic acid ratio of 1.5. Structural analyses of fatty acid collectors have indicated that the flotation properties depend primarily on the length of the alkyl carbon chain, number of unsaturated bonds, and relative positions of the bonds (Wang et al., 2006).

Traditional fatty acid collectors are commonly produced by saponification or obtained from the tailings of rapeseed oil, cotton oil, soybean oil, or other vegetable oils (Guimaraes et al., 2005). The relatively high costs of these materials (vegetable oils) result in higher production costs, rendering the flotation process uneconomical. To achieve

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selective separation, it is crucial to develop a cost-effective and selective collector (Ge et al., 2008; Hernáinz et al., 2004; Sis and Chander, 2003b).

Gutter oil, a kind of waste admixture (consisting of vegetable oils and animal fats), is a common byproduct of routine domestic and industrial activities. Waste gutter oil is usually disposed of directly into urban sewers or rivers, resulting in serious environmental pollution, especially in China. The recovery and reuse of waste gutter oil is a challenging task.

The reuse of inexpensive gutter oil as a collector material would reduce both collector cost and environmental pollution. Therefore, a new kind of collector, saponified gutter oil fatty acid (GOFA), was developed for selective separation of apatite from dolomite. To illustrate the effect of GOFA on the selective reverse flotation of apatite from dolomite in collophanite ore and elucidate the mechanism of adsorption, batch-flotation and closed-circuit tests, microflotation tests, and X-ray photoelectron spectroscopy (XPS) analyses were carried out systematically.

2. Materials and methods

2.1. Mineral samples

The collophanite ore sample used for batch flotation was obtained from Qingping Phosphate Ore Mine (Sichuan, China). As shown in the X-ray diffraction (XRD) pattern (Fig. 1), the major constituents of this ore sample are colloidal apatite, dolomite, kaolinite, quartz, and various types of svanbergite, pyrite, etc. Colorimetry, inductively coupled plasma mass spectrometry (ICP-MS), and gravimetric analyses (Table 1) showed that the ore sample contained 22.78 wt% P_2O_5 and 3.61 wt% MgO, corresponding to the middle-low grade collophanite ore category (Sengul et al., 2006).

High purity apatite and dolomite samples were used for Ca^{2+} dissolution tests, microflotation tests, and XPS analyses. The XRD patterns of these samples are shown in Figs. 2 and 3. The apatite sample mainly consisted of fluorapatite ($Ca_5(PO_4)_3F$) with very small amounts of calcium oxide and quartz. The dolomite sample contained some silica as an impurity. Based on chemical analyses, the P_2O_5 grades of the apatite and dolomite samples were 39.69 and 0.19 wt%, respectively, and the

Table 1

hemical composition of the collophanite ore sample (wt%).

Oxides	$P_{2}O_{5}$	MgO	CaO	Al_2O_3	Fe_2O_3	SiO ₂	K ₂ 0	Na ₂ O	F^{-}
Grade	22.78	3.61	35.75	4.18	1.96	15.90	0.61	0.12	2.07
Oxides	S	С	SrO	Ι-	REO ^a	Ignition loss		Acid insoluble	
Grade	1.36	2.57	0.44	0.012	0.038	10.21		18.71	

^a REO is the abbreviation of rare-earth oxide.

purity of each sample was above 90%. The samples were ground in a ceramic ball mill, and particle sizes of $-150 + 38 \,\mu m$ were used for Ca²⁺ dissolution and microflotation tests, whereas particles sizes of $-150 \,\mu m$ were used for XPS analyses.

2.2. Reagents

Gas chromatographic analysis using a GC102AF instrument (Shanghai Precision Scientific, China) demonstrated that the GOFA sample (technical-grade purity, Shufeng Company, China) consisted of 44.64% oleic acid, 28.09% linoleic acid, 18.20% palmitic acid, and small amounts of stearic acid and amines. The oleic acid/linoleic acid ratio of 1.59 is similar to that reported by Cao et al. (2015), indicating that this GOFA is suitable for selective separation of apatite from dolomite.

The new GOFA collector was obtained by saponification of the GOFA sample by treatment with sodium hydroxide (NaOH, analytical reagent, Kelong Company, China) at a mass ratio of 100:16. Analytical-grade sulfuric acid (H_2SO_4), hydrochloric acid (HCl), citric acid (H_3Cit), and calcium chloride (CaCl₂) were used as regulators. Tap water was used for ore grinding and flotation processes, whereas deionized water was used for Ca²⁺ dissolution, microflotation, and XPS measurements.

2.3. Ore grinding and flotation

A self-aerating flotation machine equipped with mechanical stirring (XFD_{0.75}, Jilin Prospecting Machinery, China) was used for the batch

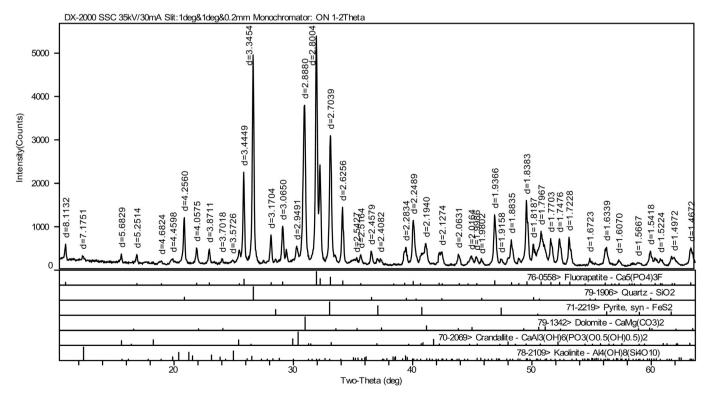


Fig. 1. XRD pattern of the collophanite ore sample.

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