



# Effect of citric acid and flotation performance of combined depressant on collophanite ore

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## ABSTRACT

Sulfuric acid ( $H_2SO_4$ ) is widely used as a depressant in the flotation of phosphorus minerals, usually in large dosages. This study used microflotation, flotation of the actual ore, X-ray photoelectron spectroscopy (XPS) analyses, reaction thermodynamic analyses and adsorption experiments, to examine the effect of citric acid ( $H_3Cit$ ) and a combined depressant ( $H_2SO_4/H_3Cit$ ) on collophanite ore flotation.  $H_2SO_4$  and  $H_3Cit$  both exhibit selective depressive effects on apatite when they are used individually as depressants. When combined, the added  $H_3Cit$  greatly reduced  $H_2SO_4$  dosages above 30% and produced better flotation results. Closed-circuit reverse flotation results for tests on the actual ore also confirmed this. Mechanism analyses demonstrated that  $H_3Cit$  adsorbs onto apatite surface via a chemical chelating reaction with  $Ca^{2+}$ .  $H_3Cit$  is selectively and largely adsorbed onto apatite, thus selectively depressing it. Compared with  $SO_4^{2-}$ , the reactions of  $Cit^{3-}$  and  $Ca^{2+}$  are thermodynamically favored at pH 5.5–13.0. Therefore  $H_3Cit$  manifested a stronger inhibitive effect than  $H_2SO_4$  and significantly reduced the required  $H_2SO_4$  dosage. A rough economic evaluation suggests that the combined depressant exhibits economic advantages and shows potential for industrial application.

## 1. Introduction

Phosphate ore is an exhaustible, non-renewable, non-recyclable and irreplaceable mineral resource. In general, phosphate ore enriched to a  $P_2O_5$  grade of approximately 28 wt.% meets the needs of the downstream phosphorus chemical industry (Abouzeid et al., 2009). Since most phosphate ore in China is of low grade, it is crucial and indispensable to increase the phosphorus content by mineral separation.

Collophanite, which is a most important phosphate ore, is a colloidal apatite usually occurring as intergrowths with gangue minerals such as dolomite, and is usually recovered by flotation. The difficulty of separating dolomite from apatite in collophanite ore is mainly due to their similar physical and chemical properties and the mineral compositions of both mineral surfaces. Both Ca and Mg are often the active sites, making flotation an arduous process (Abdel-Khalek, 2000; Amankonah and Sumasundaran, 1985).

Owing to its extensive sources and low unit cost,  $H_2SO_4$  is usually used as depressant in collophanite ore flotation. Xie et al. (2010) investigated the effect of  $H_2SO_4$  on collophanite ore flotation and argued that  $H_2SO_4$  decomposes ore particles and separates carbonates from phosphate ores, and also helps to separate the calcium and

magnesium carbonates from the ore. However, some limitations of  $H_2SO_4$  include the need for large doses (20 kg/t or more) for collophanite ore flotation, and the production of large amounts of sediment (Luo et al., 2016; Mohammadkhani et al., 2011).

$H_3Cit$  is an organic acid whose unit cost is much higher than that of the  $H_2SO_4$  used in industrial flotation. In mineral flotation,  $H_3Cit$  is often used as a modifier; for example, Yu et al. (2012) suggested that when it is used as a modifier in tungsten ore flotation,  $H_3Cit$  forms selective complexes with  $Ca^{2+}$  on the surface of scheelite and other calcium-bearing minerals, resulting in fewer active sites and the inhibition of mineral flotation. Xia et al. (2015), in a study of the role of  $H_3Cit$  for separating rare earth elements from silicates by flotation, reported that  $H_3Cit$  partially formed water-soluble metal–ligand complexes, resulting in the removal of Al ions from the mineral surface. In a study of organic regulator effects on the flotation of kyanite minerals, Zhang et al. (2015) suggested that  $H_3Cit$  has a weak inhibitive effect on quartz, but helps to activate kyanite.

However, the effect of  $H_3Cit$  in collophanite ore flotation and the associated mechanism have not been systematically demonstrated. Rao et al. (2015) studied the modified fatty acid products of  $H_3Cit$  reactions with different types of fatty acids and their use in mineral flotation. The results of phosphate ore flotation using a modified fatty acid as

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collector suggested that a higher-grade concentrate and better flotation recovery was obtained; however, their studies did not examine the effect of H<sub>3</sub>Cit as a depressant in phosphate ore flotation.

The few reports on the use of H<sub>3</sub>Cit as a depressant in collophanite flotation have referred to its high cost compared to the cost of H<sub>2</sub>SO<sub>4</sub> and thus the poor economic benefit of using only H<sub>3</sub>Cit as a depressant. The major aim of the present study was to examine the effect and mechanism of using H<sub>3</sub>Cit in a combined depressant for collophanite ore reverse flotation. Studies included microflotation, flotation of the collophanite ore, XPS analyses, adsorption experiments and reaction thermodynamic analyses. On this basis, the feasibility in economic benefits of a combined depressant was roughly evaluated.

## 2. Materials and methods

### 2.1. Mineral samples

The samples used in the microflotation and mechanism analyses were very pure apatite and dolomite. The apatite sample mainly comprised fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) and very small amounts of calcium oxide (CaO) and quartz (SiO<sub>2</sub>). The dolomite sample contained a very small amount of silica, as confirmed by X-ray diffraction (XRD) analysis. The P<sub>2</sub>O<sub>5</sub> grades in the apatite and dolomite samples were 39.69 wt.% and 0.19 wt.%, respectively; the purity of both samples exceeded 90%. The samples were separately ground in a ceramic ball mill and sieved. Particle sizes of  $-150 + 38 \mu\text{m}$  were used in the microflotation, adsorption and XPS experiments.

The specific surface areas of the apatite and dolomite used in the adsorption experiments were determined by the Brunauer, Emmett and Teller (BET) test (3H-2000BET-A, Beishide Instrument Company, Beijing, China). The average of three measurements under the same conditions (experimental error < 3%) are given in Table 1.

A sample of middle- to low-grade collophanite ore containing 22.77 wt.% P<sub>2</sub>O<sub>5</sub> and 3.61 wt.% MgO (Sengul et al., 2006) was obtained from the Qingping Phosphate Ore Mine (Sichuan Province, China) for the bench scale flotation test. The XRD analysis (Fig. 1) showed that the main minerals in the sample were collophanite, dolomite, kaolinite, quartz, various types of svanbergite, and pyrite. The chemical compositions are listed in Table 2.

### 2.2. Reagents

Various vegetable oil fatty acids, alone or in mixtures, have often been used as collectors in collophanite ore flotation, especially in industrial-scale ore processing operations. Cao et al. (2015) and Guimaraes et al. (2005) have studied the influence and effect of the different components in phosphate ore flotation. Cao et al. (2015) reported that certain proportions of linoleic acid and palmitic acid contribute to the flotation of phosphate ore, and that the result improves when the oleic:linoleic acid ratio is 1.50. In the present study, gas chromatographic analysis (GC102AF, Shanghai Precision Scientific Instrument Corp.) showed that the fatty acids extracted from “gutter oil” comprise 44.64% oleic acid, 28.09% linoleic acid, 18.20% palmitic acid, and a small amount of stearic acid and amine, with a ratio of oleic:linoleic acid of 1.59, [44.64–28.09 = 1.59] which is similar to the findings of Cao et al. (2015). In this study, gutter oil fatty acid (GOFA) sodium was used as the collector in flotation tests on the actual ore.

The conventional collector sodium oleate (NaOL) was used in

**Table 1**  
Specific surface areas of apatite and dolomite.

Particle size ( $\mu\text{m}$ )	Apatite ( $\text{m}^2/\text{g}$ )	Dolomite ( $\text{m}^2/\text{g}$ )
$-74 + 38$	1.358	1.961

microflotation. H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>Cit were used as regulators in all the flotation tests. Of the reagents, technically pure (TP) GOFA was obtained from the Shufeng company, China; all other analytical reagents (AR) were obtained from the Kelong company, China. Deionized water was used in the microflotation and adsorption experiments and in surface analyses. Tap water was used in the collophanite ore flotation tests.

### 2.3. Microflotation

The microflotation tests were performed using an XFG-II flotation machine (Jilin Prospecting Machinery Factory, China). Stir speed was fixed at 1800 rpm. The mineral suspensions were prepared by adding 5.0 g of individual mineral to 80 mL solution in the single mineral flotation tests, and 5.0 g mixed mineral (2.5 g apatite and 2.5 g dolomite; P<sub>2</sub>O<sub>5</sub> grade approximately 19.94 wt.%) to 80 mL solution in the artificial mixed mineral flotation tests. Firstly, H<sub>2</sub>SO<sub>4</sub> was added and stirred for 3 min if needed; then H<sub>3</sub>Cit was added and stirred for another 3 min if needed; NaOL was added, and stirred for another 3 min; finally, the flotation was carried out for 3 min. After completing flotation, the concentrate and tailing were filtered and dried separately. The flotation grades of the two products were assessed by chemical analysis. The listed results are the average values of three experiments under the same conditions (experimental error  $\pm 2\%$ ). All flotation tests were carried out at a temperature of  $25 \pm 1^\circ\text{C}$ .

### 2.4. Collophanite flotation

A self-aerating mechanical agitation flotation machine (XFD0.75, Jilin Prospecting Machinery Factory, China) was used for flotation tests on the actual collophanite ore, in which 0.25 kg of the ore was ground to 92 wt.% of  $-74 \mu\text{m}$  particle size (grinding concentration 62.5 wt.%) using a mining rod mill (XMB-70, Wuhan Prospecting Machinery Factory, China). The pulp was removed to the flotation cell and stirred for 1 min, H<sub>2</sub>SO<sub>4</sub> was added and stirred for 2 min, H<sub>3</sub>Cit was added and stirred for 2 min if needed and GOFA was added and stirred for another 2 min. All reagents were added and pulp conditioning was carried out without aeration. The conditioning tests were carried out in the roughing stage. All the presented results are averages of duplicate flotation experiments (experimental error  $\pm 3\%$ ). The closed-circuit flow sheet and corresponding conditions are shown in Fig. 2. Flotation temperature was  $25 \pm 1^\circ\text{C}$ . The concentrates and tailings were filtered, dried, weighed and subjected to chemical analysis after flotation was completed.

### 2.5. Surface analysis

XPS (XSAM-800, Kratos, Manchester, UK) was used to analyze the surface properties. The samples were prepared as for microflotation. H<sub>3</sub>Cit was added to one of the two apatite (or dolomite) samples and the slurry was stirred for 3 min. Then the samples were filtered and rinsed thoroughly with deionized water to remove any weakly adsorbed reagent. The filtered products were dried naturally for XPS analyses. The test chamber pressure was kept below  $10^{-9}$  mbar during spectral acquisition. The presented results (e.g., atomic concentration) are all the average of three duplicate measurements (measurement error < 5%). Binding energies were calibrated using a characteristic C1s carbon peak (C1s = 284.7 eV).

### 2.6. Adsorption experiments

The adsorbance of H<sub>3</sub>Cit was obtained by total organic carbon (TOC) measurement using a TNM-L analyzer (Shimadzu Corporation, Japan). After adding 5.0 g of apatite (or dolomite) to 80 mL of deionized water, the suspension was agitated for 5 min, then different dosages of H<sub>3</sub>Cit were added. The solution was stirred for a further

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