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The effect of graphene oxide on the slime coatings of serpentine in the flotation of pentlandite

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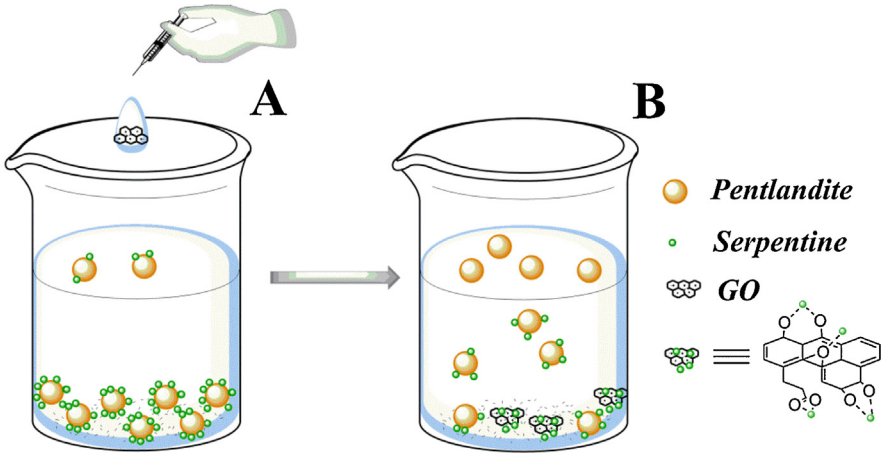
HIGHLIGHTS

- Synthesized graphene oxide improves the flotation recovery of pentlandite in pentlandite/serpentine flotation system.
- Graphene oxide acts as both a dispersant and a flocculant for serpentine in the flotation separation.
- Graphene oxide might be a potential depressant in froth flotation of sulfides.

GRAPHICAL ABSTRACT

Proposed model for the changes of pentlandite/serpentine system in deionized water (A) and in GO solution (B).



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ABSTRACT

This paper studied the effects of graphene oxide (GO) on the slime coatings of serpentine in the flotation of pentlandite. The flotation results showed that the flotation recovery of pentlandite was improved with the addition of GO, compared with carboxymethyl cellulose (CMC). The possible mechanisms of the improved flotation recovery were investigated by electrokinetic study, FTIR study, sedimentation tests and scanning electronic microscopy (SEM) analysis. The experimental results demonstrated that both of the two depressants dispersed the hydrophilic serpentine particles from the pentlandite surface. For GO, however, the flocculation of serpentine was a further reason responsible for the enhanced recovery of pentlandite.

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1. Introduction

Serpentine is a typical alteration product of pyroxenes or olivines during hydrothermal metamorphosis [1], which seriously interferes with the concentration of pentlandite in the froth flotation of copper–nickel sulfide ore. The mechanisms by which serpentine affects the flotation behavior of pentlandite include entrainment [2], physical entrapment [3] and hetero-aggregation (so-called "slime coatings") [4].

Depressants play an important role in efficient flotation separation of pentlandite from serpentine [5]. It is generally accepted that natural polysaccharides such as starch, dextrin, guar gum, cellulose and their derivatives are promising non–toxic organic depressants [6]. Among these polymers, carboxymethyl cellulose (CMC) is commonly used to disperse slime particles of MgO type minerals from sulfide surfaces [7,8].

Nanomaterials have been widely used in various fields and attracted increasing attention since the beginning of the 21st century. In 2013, Pelton and co-workers reported that hydrophobic polystyrene nanoparticles could be used as replacement collectors for pentlandite flotation to improve the processing of ultramafic ores [9]. To our knowledge, this was the first application of nanomaterials in froth flotation process. Inspired by the precedent, we believe that some other nanomaterials can also be used as flotation reagents.

Graphene oxide (GO), produced by the exfoliation of graphite, is emerging as a versatile material employed in synthetic transformation [10,11], surface functionalization [12], drug delivery [13], enzyme immobilization [14] and many other areas in the last decade. Based on our prior experience in the flotation separation of pentlandite from serpentine [15,16], we expected that GO could act as an novel selective depressant for serpentine because GO has the advantages such as high water dispersibility [17], good colloidal stability [18], excellent amphiphilic property [19] and containing multiple oxygen-containing functional groups (mostly hydroxyl, carboxyl and epoxy groups) [20]. Herein, we studied the effect of GO on the interaction of pentlandite with serpentine. Comparative studies using CMC were also performed to evaluate the superiority of GO.

2. Materials and methods

2.1. Materials

The pure mineral samples of serpentine and pentlandite for microflotation flotation tests and other experiments were obtained from Donghai, Jinchuan in China. X-ray powder diffraction (XRD) data confirmed that serpentine was 99% pure and pentlandite was 96.8% pure. Optical microscope images showed that both of the samples were almost free of impurities [15]. The serpentine sample was ground in an agate ball mill (with the average particle size of 4.4 μm), while pentlandite was crushed to the average particle size of below 75 μm. Pentlandite sample was further ground in an agate ball mill for zeta potential measurements.

The copper–nickel sulfide ore for batch flotation was obtained from the Jinchuan copper–nickel sulfide mine. The multi-elemental chemical analysis of the ore was conducted by Atomic Adsorption Spectroscopy (AAS), and the analysis results are shown in Table 1. The minerals contained 1.33% Ni, 1.3% Cu, 12.31% Fe, 16.42% Mg and 0.03% Co. Yang have confirmed that for Jinchuan copper–nickel sulfide ore, nickel and copper existed mainly in the form of pentlandite and chalcopyrite, respectively; while the predominant gangue minerals were magnesium silicate gangue (serpentine) [21]. For the batch flotation tests, the copper–nickel sulfide ore (800 g, crushed to ~2 mm before grinding) was ground to 80% passing 74 μm in a closed XMQ–240 × 90 mm steel ball mill at the pulp density of 50% by weight.

Sodium Butyl Xanthate (NaBX) was used as the collector and Methyl Isobutyl Carbinol (MIBC) acted as the frother. Potassium nitrate (KNO_3) was used to maintain the ionic strength and pH value was regulated by hydrochloric acid and potassium hydroxide. All the reagents described above were of analytical grade. KNO_3 solution (10^{-3} M) used in all experiments was prepared using deionized water. GO synthesized in Section 2.2 and commercial CMC (chemically pure) were utilized as depressants for serpentine. The depressant solution was prepared by adding depressants into KNO_3 solution, and then stirring under ultrasound for 2 h to ensure that the depressants are dispersed evenly in KNO_3 solution.

2.2. Synthesis of GO

GO was prepared according to the method described with a little modification [22]: (1) 5.0 g of graphite power was added into a mixture of 5.0 g of $NaNO_3$ and 120 mL of concentrated H_2SO_4 in a 500 mL flask. (2) After mechanical stirring for 30 min in an ice–salt–bath, 30 g of $KMnO_4$ was gradually added under vigorous mechanical stirring while the temperature was kept below 5 °C for 0.5 h. (3) After mechanical stirring at room temperature for 12 h, the mixture gradually became paste-like and the color turned light brownish. (4) After the addition of 300 mL water under mechanical stirring, the mixture was heated to 98 °C in a short time and kept at this temperature for 24 h, giving a yellow sample. (5) 120 mL of H_2O_2 (30 wt%) was added to the mixture, mechanical stirring continued for 24 h at room temperature. (6) After dialyzing repeatedly to remove the impurity in the sample, the GO was obtained by freeze drying.

The structures of pristine graphite and the product GO were confirmed by FTIR spectrum (Fig. 1). For graphite, the peaks at 3435, 1630 and 1029 cm^{-1} indicated the O–H stretching, the carbon skeletal vibration and the C–O stretching vibration, respectively, which were the characteristics of graphite [23]. After the oxidation of graphite to graphene oxide, oxygen-containing functional groups were observed from GO. The peaks at 1731, 1396 and 1069 cm^{-1} indicated the C=O stretching vibration, the O–H deformation vibration and the epoxy group stretching vibration, respectively, which proved the introduction of the carboxyl, extra hydroxyl and epoxy groups into the structure of GO via oxidation process [24,25].

The SEM photographs reflected the differences between graphite and GO (Fig. 2). Pristine graphite showed the smooth surfaces because the van der Vaals forces hold the layers together (Fig. 2(A)) [26], but the graphs of GO showed the changes of the surface morphology, distinguished from graphite. Fig. 2(B) showed that after oxidation, the tightly packed conjugated systems in the laminated structure of graphite layers were destroyed, and new thin wrinkled sheets were formed. This common surface morphology change of GO was due to the deformation of graphene because fully exfoliated GO aggregated and formed crumpled GO sheets [27,28].

2.3. Methods

2.3.1. Microflotation tests

Mineral flotation tests were carried out in an inflatable hanging slot flotation machine (XFGC $_{II}$), and the impeller rotation speed was set at 2000 r/min. The pentlandite suspension was prepared by adding 2.0 g of pentlandite to 50 mL of KNO_3 solutions. Serpentine (4 g/L) and depressant solutions were added at the beginning of the conditioning period when needed. The conditioning time was allotted as follows: 2 min for the depressants, 2 min for the collector and 2 min for the frother, respectively. Then flotation was