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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 1571−1577
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effect of biological pretreatment on flotation recovery of pyrolusite

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Received 19 June 2013; accepted 6 September 2013

Abstract: *Bacillus mucilaginosus* was used in pretreatment of pyrolusite to facilitate the flotation removal of quartz from pyrolusite minerals. Quartz was activated by *B. mucilaginosus*, whereas pyrolusite was unaffected at pH 7 with laurylamine as collector. Flotation recovery of pyrolusite with *B. mucilaginosus* pretreatment is 73.62%, slightly lower than that of the process without biopretreament, namely 74.70%. The grade of concentrate of recovered pyrolusite is 19.44%, 2.18% higher than that of the recovered pyrolusite without *B. mucilaginosus* pretreatment (17.26%). The results of FTIR and SEM showed that no bacteria were adsorbed on the surface of quartz or pyrolusite, indicating that the better selectivity and collectability of flotation resulted from bacterial byproducts. And interaction of bacterial byproducts such as extracellular bacterial polysaccharide, extracellular bacterial protein and acetic acid, on minerals were studied by FTIR and adsorption.

Key words: flotation; pyrolusite; quartz; laurylamine

1 Introduction

Pyrolusite is an important mineral consisting essentially of manganese dioxide (MnO_2). Quartz, as its primary associated mineral, is difficult to be separated from pyrolusite. Pyrolusite ore flotation practice is well described in the technical literature and typically involves flotation of manganese dioxide using octyl hydroxamate as collector [1]. Hydroxamate forms strong chelate bonds with manganese ions and consequently strongly chemisorbs on manganese-containing minerals. What's more, FUERSTENAU and SHIBATA [2] used electrokinetics to interpret the flotation and interfacial behavior of manganese dioxide. Part of the studies also involved the flotation of manganese dioxide with oleic acid or oleate soap, the most commonly used collector for the flotation of oxide minerals. There is almost no research using cationic reverse flotation for the removal of silicate gangues from pyrolusite ore.

Cationic reverse flotation of quartz is the most important technique for the concentration of ores for the silicate minerals [3]. The mechanism of amine−silicate interaction has been studied extensively by indirect methods and ex-situ measurements such as flotation recovery response, adsorption experiments, contact angle, zeta-potential and FTIR spectroscopy in the last several decades.

Biobeneficiation is a process that utilizes microorganisms as surface modifiers to enhance the separation of one mineral from another by flotation or flocculation [4−9]. Most biological activities, such as bioleaching and biobeneficiation, depend on attachment or adsorption of microorganisms to the mineral surfaces. Although the use of microorganisms in ore leaching is well established, the mechanism of biobeneficiation is not fully explained. The development of biotechnology is promising in solving some problems generated by mineral processing [10]. Separation of quartz from hematite/corundum mixture was successfully achieved with the aid of *E. coli* strain Sip [11]. As well known, some of microorganisms have a selective activating or depressing effect on mineral froth flotation [12]. The effect of using microorganisms can be realized by the adhesion of microorganism cells onto the mineral surface, the oxidation of the mineral surface by chemolithotrophic bacteria and attack of metabolic reagents produced by the microorganism cells.

Foundation item: Projects (21176026, 21176242) supported by the National Natural Science Foundation of China; Project (2012AA062401) supported by the Hi-tech Research and Development Program of China
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DOI: 10.1016/S1003-6326(14)63227-1

Bacillus mucilaginosus is a common soil bacterium, and usually used as a model bacterium in studying microbe-mineral interactions. Several reaction mechanisms of *B. mucilaginosus* weathering silicate minerals were proposed [13−15]. These studies regarded *B. mucilaginosus* weathering silicate minerals, variations in the concentrations of various ions composing the silicates, but variations in the concentrations could not reflect weathering rates. Actually the silicate minerals, were dissolved, further formed secondary silicate minerals [16]. Therefore, it is interesting to study the flotation of the silicate minerals weathered by *B. mucilaginosus*.

In this work, pyrolusite was pretreated by *B. mucilaginosus* and then cationic reverse flotation silicate gangues from pyrolusite was conducted with laurylamine as collector. The objective of the present investigation is to understand the underlying probability of laurylamine reverse flotation silicate minerals from pyrolusite and the role of *B. mucilaginosus* pretreatment.

2 Experimental

2.1 Materials preparation

The sample of pyrolusite was obtained from a mine in the southern part of China, and dry ground using a porcelain ball and then sieved through 74 μm standard specification sieve. The chemical analysis of ore samples indicated that the sample contained mainly: 59.08% SiO_2, 15.24% Mn, and 7.19% Fe. By combining the information obtained from XRD and ore microscopy, an approximate mineralogical composition of the ore sample was pyrolusite (15%−16%), quartz (58%−60%), hematite (10%−12%), and mica (3%−4%).

2.2 Bacterial strain, media and growth

A pure strain of *B. mucilaginosus*, which was stored at the Environmental Biological Science and Technology Research Center, Institute of Geochemistry, Chinese Academy of Sciences, was used in this study. *B. mucilaginosus* was cultured and maintained in the liquid medium with 5.0 g/L $C_{12}H_{22}O_{11}$ (sucrose), 2.0 g/L Na_2HPO_4, 0.5 g/L $MgSO_4{\cdot}7H_2O$, 0.005 g/L $FeCl_3$, 0.1 g/L $CaCO_3$, 0.5 g/L $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ (kaolin) and pH of 7.0−7.2. A 10% active cell culture was added to the medium and incubated in a rotary shaker at 100 r/min at 30 °C. The cells were harvested from the culture at the beginning of the stationary phase of their growth. After 48 h of incubation, the liquid suspensions containing the cells were used in pyrolusite biotreatment.

2.3 Biological pretreatment

50 g pyrolusite powder, 25 mL *B. mucilaginosus* suspension, and a desired amount of medium were added to a 500 mL flask. The total volume of the pulp was 250 mL and all tests were conducted at pH 7. Afterwards, the pulp was incubated at 30 °C on a rotary shaker at 150 r/min so that the microbe and mineral interaction occurred. Biological pretreatment time varied in different tests. In the control experiment, deionized water was added to the system instead of *B. mucilaginosus* suspension and the medium.

2.4 Flotation tests

The flotation tests were carried out in a 0.5 L laboratory flotation cell, using 50 g mineral sample. Laurylamine was used as the collector, while sodium hexametaphosphate was used as modifier. All the reagents used in this study were of analytical grade. The biotreatment samples were first transferred to flotation cell and diluted with deionized water to 0.5 L and then the modifier and collector were added and conditioned for 3 min and floated for 6 min at pH 7. The effects of biotreatment time and different dosages of collector and modifier on recovery rate were examined. Tests were also performed in the absence of biotreatment. Once the flotation product was obtained, the concentrates and tailings were washed, filtered, dried and finally weighed to obtain the percentage of flotation. The floatability was calculated as the grade and recovery of the concentrate.

The average values of the results of two paralleled tests were shown in this paper. Furthermore, to check the reliability of the results obtained, several pyrolusite recovery tests were carried out.

2.5 Fourier transformed infrared spectroscopy

The BRUKER ALPHA-T instrument was used for recording the infrared absorption spectra; a KBr matrix was used as background. The spectra of pyrolusite, before and after the *B. mucilaginosus* pretreatment, were evaluated. The *B. mucilaginosus* cell suspension and the minerals samples were filtered and dried at 75 °C. The dried powder was properly mixed in a KBr matrix. All the spectra were recorded between 4000 and 700 cm^{-1}.

2.6 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to check the surface images of the mineral particles before and after biological pretreatment. After washing and drying, the minerals of the adsorption tests were gold coated under vacuum in a BAL-TEC sputter coater. Secondary electron images were acquired in a Carl Zeiss-DSM 630 scanning electron microscope.

2.7 Adsorption experiment

Adsorption experiments were carried out on two samples (quartz and manganese dioxide). In each case, 5.0 g sample was added to 20 mL metabolic product