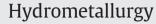
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Rheology of pyrite slurry and its dispersant for the biooxidation process

Lixin Sun^a, Xu Zhang^{a,*}, Wensong Tan^a, Minglong Zhu^a, Ruiqiang Liu^b, Chunqiang Li^b

^a State Key Laboratory of Bioreactor Engineering East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China ^b Shangdong MIC Biogold Limited, Yantai 261438, PR China

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ABSTRACT

Rheology of slurry significantly influenced the grindability, fine grinding performance and energy consumption of industrial minerals in wet grinding. The solid concentration, particle size, temperature and the dispersant, which affected the rheological characteristics of pyrite slurry and the biooxidation process were investigated in this study. This research aimed at the wet grinding process improved by the control of slurry rheology and getting a biocompatible dispersant.

The results revealed that the viscosity increased with the solid concentration, which was in agreement with the Chong model. There was a critical concentration (40 wt.%) that led to the flow behavior of slurry transformed from Newtonian fluids to shear-thinning non-Newtonian fluids which fitted to the Casson model. It was also found that the apparent viscosity of slurry increased with the decrease of the particle size and the temperature at high solid concentration.

Sodium Hexametaphosphate (SH) was selected experimentally as an effective dispersant for the mineral slurry. The appropriate concentration of SH was also determined at the range from 0.005 wt.% to 0.05 wt.%. The addition of dispersants could reduce the viscosity and yield stress, increase the zeta potential (ζ) of suspension pronouncedly. No negative effects on the growth rate of microorganisms and the pyrite biooxidation were observed. Therefore, dispersant separation and recovery process could be avoided.

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1. Introduction

Biooxidation of sulfidic-refractory gold minerals, such as pyrite or arsenopyrite, are primarily applied for the pretreatment of refractory sulfide gold concentrates. The pretreatment processing was necessary to decrease the refractory properties of the minerals and allow cyanide penetration (Ubaldini et al., 1997). Currently, the commercial process of the biooxidation had been successfully used in gold processing (Dew et al., 1997). Before the biooxidation process, the wet fine grinding technology was used to get fine powder (Corrans and Angove, 1991). It was well known that slurry rheology significantly influenced the grindability, fine grinding performance and energy consumption. He and Forssberg (2007) found the addition of dispersant or a lower solid concentration resulted in better grinding performance due to the maintenance of lower viscosities during grinding. The results of Yue and Klein (2004) confirmed that the yield stress was the dominant rheological parameter and strongly affected the power draw, particle breakage rate, net production of fines and the product size distribution. Other researchers in this field got similar results (Ding et al., 2007; He et al., 2006a; Kapur et al., 1996; Shi & Napier-Munn, 2002; Tangsathitkulchai, 2003).

Many researchers study the rheological characterization of mineral slurry, such as laterite slurry (Blakey and James, 2003; Klein & Hallbom, 2002), galena slurry (Prestidge, 1997), limestone slurry (He et al., 2006b), kaolin suspensions (Papo et al., 2002), and sulfide mineral slurry (Muster and Prestidge, 1995). The rheology of mineral suspension was highly complicated and there was no single parameter that could solely explain it. Physical and chemical properties of slurry, such as solid concentration, particle size, particle shape, pH value and slurry temperature, had a significant influence on the rheology of slurry (Ding and Pacek, 2008; He et al., 2004; He et al., 2006; Li et al., 2006; Tari et al., 1999).

Dispersants were usually used to control the rheology of slurry (Atesok et al., 2005; Baird & Walz, 2007; Klimpel, 1999). The use of a suitable dispersant could change the surface nature of particles in the slurry, which resulted in interparticle forces being entirely repulsive. According to the charge of particle surface, anionic, cationic, non-ionic or polymer dispersants were selected (Klimpel, 1999). For example, polyphosphate and naphthalene sulfonate formaldehyde condensate (NSF) were selected to reduce the yield stress of dewatered tailings and cemented paste backfill (Huynh et al., 2006); sodium laurate solution was determined an effective dispersing agent for the viscosity reduction of the red mud suspension (Clifton et al., 2007). But there were few reports about the dispersants used in pyrite suspension (Ding et al., 2007).

Thus, dispersants were usually used to improve efficiency of the wet grinding process by the reduction or elimination of the yield stress, excellent dispersion or decrease of viscosity. However,

^{*} Corresponding author. Tel.:+86 21 64252536; fax: +86 21 64252250. *E-mail address*: zhangxu@ecust.edu.cn (X. Zhang).

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dispersants, as inorganic or organic compounds, might inhibit the bioactivity of *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in the biooxidation process (Ren et al., 2009; Tuttle and Dugan, 1976). So that the dispersant added in the pyrite suspension need to be removed before the biooxidation of pyrite process in order to avoid the toxicity to bacteria. The operations of dispersant separation were usually complicated and costly. In order to improve the wet grinding processes, this research was carried out to study the rheology of pyrite slurry, find an appropriate dispersant to adjust the rheological characteristics of pyrite slurry, as well as with biocompatibility for the succeeding biooxidation process.

In this paper, the effects of solid concentration, particle size distribution, temperature and dispersants on the rheology characters of pyrite suspensions were investigated by rheology and zeta potential measurement. And then the effects of dispersant type and dosage on bacterial cell growth and biooxidizing activities in the biooxidation process were studied. The point of our paper was getting the basis data of the slurry rheology and a biocompatible dispersant, to support for the optimization of mineral grinding processes.

2. Materials and methods

2.1. Materials preparation

The low-grade refractory gold concentrate used in the experiments was kindly supplied by Tiancheng Co., Ltd., Shandong, P.R. China, and contained 24.9 g/t Au, 21.30% Fe, 20.09% S and 4.59% As. X-ray diffraction (XRD) analysis showed that the sample contained pyrite and quartz as the major components. The sample was sieved to obtain the particle size distribution in 130–150 μ m, 105–130 μ m, 74–105 μ m and below74 μ m.

The Sodium Hexametaphosphate (SH) produced by Ling Feng of the Shanghai Chemical Reagent Co., Ltd. (Shanghai, China), Tween-80 produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and Sodium lignosulfonate produced by Chengzheng Chemicals Co., Ltd. (Jiangsu, China), were used as dispersants. Pyrite (40 wt.%, 105– 130 µm) suspension with 0.01 wt.% various dispersants were prepared. Dispersant concentration was calculated by dividing dispersant weight by the weight of slurry.

2.2. Rheology measurements

An RS600 rotational rheometer (HAAKE, Germany) was used to measure the rheological property of the pyrite suspensions. About 15 ml of slurry sample was required for the measurement, with various solid concentrations and dispersant dosages. To avoid the undesirable influence from particle settling, the measurement of every sample started from highest shear rate 300 s^{-1} to 0 s^{-1} (Ding et al., 2007). The yield stress (τ_0) was determined by fitting the shear stress (τ) against shear rate (γ) flow curve date to the Casson model Casson (1959) shown in Eq. (1).

$$\tau^{\frac{1}{2}} = \tau_{0}^{\frac{1}{2}} (\eta_{\infty} \gamma)^{\frac{1}{2}}.$$
 (1)

2.3. Zeta potential measurements

The zeta potential measurements were carried out using Zetasizer 300HS Zeta Potential Analyzer (Malvern, American). Suspensions ($<74 \mu m$ pyrite) were made up in a 0.01 mol/L KNO₃ background electrolyte solution (Fullston et al., 1999). At the pH of 2, different dosages of dispersants were added to the mineral suspension.

2.4. Microorganism and culture medium

The stain of *A. ferrooxidans* was provided by Tiancheng Co. Ltd. The culture medium (iron-free 9K medium) was developed from the 9K

medium ((Silverman and Lundgren, 1959) The composition was as follows (g/L): (NH4)₂SO₄: 3.0; KCI: 0.1; K₂HPO4: 0.5; MgSO₄·7H₂O: 0.5; Ca (NO₃)₂: 0.01. The initial pH value of the medium was adjusted to 1.6 with sulfuric acid. All chemical reagents used were of analytical grade.

2.5. Biooxidation experiments and analyses

In the biooxidation experiment, 100 ml iron-free 9K medium with pyrite (10% w/v, $105-130 \mu\text{m}$) as energy source was added to 250 ml Erlenmeyer flasks. The cells were inoculated in the end of the logarithmic phase to have an initial population of environ at 1.0×10^7 cells/ml. All of the flasks were agitated in a rotary shaker incubator (160 rpm, 37 °C).

The pH and oxidation-reduction potential (ORP) of the samples were measured by a pH/Eh meter (Mettler model FE20). The amount of free cells in solution was measured by direct microscopic counting using a Pettrof–Hauser-type cell counter. Pyrite dissolution was followed by measuring the iron concentration in solution. The concentration of ferrous iron was determined by titration with potassium dichromate in the presence of *N*-phenylanthranilic acid as an indicator (Vogel, 1961). The ferric iron was determined by titration EDTA at pH 2 in the presence of Sulphosalicylic acid as an indicator (Davis and Jacobsen, 1960). Total iron concentration in the liquid phase was the summation of both above. The pyrite oxidation was calculated as Eq. (2).

The pyrite oxidation =
$$\left(\frac{Fe_{\rm f} - Fe_{\rm i}}{Fe_{\rm p}}\right) \times 100\%.$$
 (2)

Where Fe_f was the final iron mass in the liquid, Fe_i was the initial iron mass in the liquid and Fe_p was the iron mass in the pyrite before biooxidation.

3. Results and discussion

3.1. Effect of solid concentration on rheology of pyrite slurry

The flow curves were established with the apparent viscosity versus shear rate with a different solid concentration as shown in Fig. 1. The rheological characters of pyrite slurry were strongly influenced by the solid concentration. It was shown that there were two types of flow behaviors at low and high solid concentrations. At low concentration (below 40 wt.%), the viscosity was almost constant. The suspension behaved as Newtonian fluids. With the solid concentration increases, it would become progressively more strongly non-Newtonian fluids, signifying a remarkable shear-thinning characteristic over the entire shear rate range. These conclusions were similar to the results of Bhattacharya et al. (1998) and Prestidge (1997).

The flow behavior observed was typical with the suspension of micron-sized particles in which interparticle forces were predominant in controlling the suspension rheology. At low solid loading, the magnitude of interparticle forces would be small, due to the relatively large distance between mineral particles. So the viscosity of slurry and flow behavior were dependent on the suspension medium. As the distance between the particles became smaller when the solid concentration increased, the interparticle interactions became more significant. It could lead to the formation of particulate structures, which were subsequently broken down by shear stress, resulting in shear-thinning and yield stress characteristics (Logos & Nguyen, 1996).

The data of rheological characteristics analyzed by adopting the Casson model (Eq. (2)) of non-Newtonian fluid were shown in

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