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Inhibition of spontaneous combustion of sulfide ores by thermopile sulfide oxidation

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ABSTRACT

Sulfide oxidation using thermophile can be employed to decrease the sulfur content in ore surface to reduce the risk of spontaneous combustion. In this study, the experimental results show that, under the influence of thermophile, the maximum degree of oxidation of 32.9% can be achieved in 28 days and the degree of oxidation is inversely proportional to the ore particle size. Further analyses indicate that, the oxidation weight gain rate of the sulfide ore in the first 5 days decreases from 2.55% to 0.64% while the spontaneous combustion point of the ore increases from 140.7 °C to 368.7 °C. As a result, the spontaneous combustion tendency level of the sulfide ore has been downgraded from level I to level III. This work demonstrates and quantifies the effectiveness of using thermophile oxidation to reduce the risk of spontaneous combustion in mining high-sulfur content ores.

1. Introduction

The fire caused by spontaneous combustion due to the oxidation of sulfide ore is one of the major disasters in mining high sulfur content ores (HSO), which affects about 30% of metalliferous mines in China (Qian, 2005). Traditional fire-fighting technologies mainly focus on removing the oxygen from the heap or decreasing the temperature by some heat dissipation procedures (Wu et al., 2004 and Li, 2003). However, the sulfur element contained in the ore, the real cause of the problem, is in general not given enough attention in the fire-fighting process, which makes it difficult to eradicate the problem completely.

Based on past studies of the mechanism of spontaneous combustions in HSO mines, the authors believe that the bio-oxidation technology using certain type of bacteria to remove the sulfide at the ore surface can be used as an effective measure to lower significantly the risk of ore spontaneous combustions (Luo et al., 2012). Published relevant applications, however, mainly focus on coal desulphurization and pyrite cinder desulphurization (Komnitsas and Pooley, 1991; Komnitsas et al., 1995; Aller et al., 2001; Zilberchmidt et al., 2004, Cardona and Márquez, 2009 and Adamus et al., 2011), aiming to improve either the coal quality or the re-usability of solid wastes. There has been little research on using the technology to deal directly with the problem of spontaneous combustions in HSO mining operations.

Previous laboratory tests show that normal mesophilic bacteria (*Thiobacillus ferrooxidans*), which can only work at ambient temperature of about 30 °C, is not very effective to remove sulfur at ore surfaces. It can only manage to achieve the degree of oxidation between 12.89% and 15.25% in a shake flask environment (Wang et al., 2012). Considering the high temperature condition in the heap of HSO due to the accumulation of heat generated by ore oxidation (D'Hugues et al., 2002), we focus our work in this research on investigating the effect of thermophiles on the desulphurization process. Experiments were carried out to study the desulphurization effect of thermopile on various parameters related to the spontaneous combustion tendency of HSO. The application of the thermophile treatment will increase the mining cost, however safety of the mining operation is the major concern here. The results are useful in helping derive an effective procedure to prevent HSO spontaneous combustion using the proposed bacteria oxidation technology. Detailed discussions about how to apply this technology for HSO mining operations are beyond the scope of this paper, but potential applications include spraying the solution that contains thermopiles over blasted stope, ROM (run of mine) stockpile and waste dump to inhibit the oxidation process so as to reduce the self-heating and the potential of spontaneous combustion. The results reported here can help derive an effective monitoring process based on bacterial concentration, sulfur content, PH value and *E* value after spraying the solution to ensure a safe mining operation.

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2. Experiment

2.1. Sample selection and preparation

2.1.1. Ore samples

The sulfide ore used in this experiment contains 45.87% of sulfur so it can be classified as HSO with high spontaneous combustion tendency level (Level I, see below). The ore particles have the size of −12 mm after crushing and were separated by sieving according to different size requirements set by the experimental program. Ore particles were sealed in plastic bags and stored in a dry place before the test.

2.1.2. Thermophile

The bacteria (thermophiles) used in this research were sourced from the hot spring of Tengchong, Yunnan Province (Zhang et al., 2010) . The temperature of the hot spring is 90 °C.

$(NH_4)_2SO_4$, K_2HPO_4, $MgSO_4{\cdot}7H_2O$, KCl, $Ca(NO_3)_2$ are the main ingredients used in this research as the culture medium for thermophiles. 0.01% yeast extract (YE/w V^{-1}) was added to the medium to ensure the activity of thermophiles (Janssen et al., 2009). Before cultivation, the medium was autoclaved to ensure there were no other bacteria in existence in the culture medium.

To fully maintain the quantity and the activity of the bacteria, a 150 mL sample containing the thermopiles was inoculated to the medium without dilution. A transgenic cultivation was conducted when a significant increase of bacteria was observed after 3 days. In transgenic cultivation, 20 mL bacteria solution was mixed with 180 mL medium in a 300 mL flask before the sterilized sulfur powder was added and then the pH was adjusted to 2.5. The flask was put in an incubator under the temperature of 70 °C and the agitation of 50 rpm for 7 days (Zhang et al., 2008 and Vilcáez et al., 2008). The strain was ready to be applied to the leaching column experiment after five generations.

2.1.3. Apparatus

Apparatus used in the cultivation of the high temperature bacteria includes a 620 laboratory pH meter, a Nikon 50i biological electron microscopy and a constant temperature oscillator. The model of the constant temperature oscillator is THZ-C, with the highest achievable temperature of 80 °C and the range of the oscillation frequency of 10–250 rpm. Double plexiglass columns were used in the column leaching experiments, with the internal diameter of 50 mm and the height of 500 mm. In order to maintain the bacterial activity, the temperature of the plexiglass columns was controlled using a water bath.

The weight gain rate by oxidation and the kindling point are the main parameters to be measured in the experiment. Related apparatus for these measurements includes a constant temperature humidity chamber, a crucible resistance furnace and a temperature logger. The model of the constant temperature humidity chamber is HS-100, which has the temperature control range of 10–100 °C, the humidity control range of 85–98% and the heating rate of 0.7–1.2 °C min^{-1}. The model of the crucible resistance furnace is SG2-5-10, which has the maximum achievable temperature of 1000 °C. The model of the temperature logger is AI-518, which has the measuring range of −50 to 1300 °C, the sampling rate of 8 times per second and the control period of 0.24–300 s.

2.2. Cultivation of thermophiles

2.2.1. Growth cycle monitoring

When thermophiles are inoculated in the original medium, the bacteria number can be obtained using spectrophotometer. The spectrophotometer measures optical density (OD) which is closely related to the bacteria number. The wavelength of the spectrophotometer used in this test is set to 340.0 nm as the absorbency peaks at that wavelength (0.396).

2.2.2. Strain identification

The strain identification was conducted by sequencing 16Sr DNA of the thermophiles. The thermopiles in exponential reproduction phase were sampled after centrifugation (1 min) with the rotation speed of 1000 rpm. The extracted genomic DNA was used as the template for the 16Sr DNA Polymerase Chain Reaction (PCR) amplification. The product was sent for sequencing and the result was then submitted to GenBank for correlation sequence comparison with the Basic Local Alignment Search Tool (BLAST).

2.3. Column bio-leaching

To simplify the experiment while maintaining its accuracy and to help derive some empirical relationships based on multivariate regression analysis (see Section 3.3), uniform experimental design (UD) was used in our research. UD is capable of providing a suitable design of an efficient experimental program for a multi-factor and multi-level experimental scheme (Fang et al., 2000). UD is used in our study because of its two major characteristics: (1) the occurrence of each level of each factor in the experiment is once only and (2) the number of experimental trials is the same as the level of factors that need to be explored. These characteristics help ensure that a better regression analysis can be conducted based on a smaller set of experiments.

Factors considered in our experiment include the pH value of the solution at initial stage, the solution injection rate and the ore particle size, which are the three most important factors in bio-oxidation. A three-factor and six-level uniform design scheme of six experiment groups was used, as shown in Table 1. Details of UD are given in Table 2. Based Tables 1 and 2, the test scheme is derived, as shown in Table 3. The bacterial concentration is kept at a constant of 10% for these tests.

The crushed ore samples were sieved and separated into six groups according to size. Each group of ore samples were weighed and packed into each leaching column. The solution containing the strain was formulated based on the required volume and pH value (1.0–3.5) and was then used to fill the column. The rate of solution injection into the columns was controlled between 80 and 400 L m^{-2} h^{-1}. The column is a closed system and the solution is circulated through the column and an external pipe. The flow injection is from the bottom of the column so the flow direction inside the column is upward.

During the 28-day experiment period, the leaching columns were sampled regularly at the interval of once every 4 days to measure SO_4^{2-} to derive the sulfur content. Degree of oxidation was then evaluated. Degree of oxidation is defined as the ratio between the sulfur leached in the solution and the initial sulfur amount in the ore, i.e.:

$$R = \frac{\alpha \cdot V}{Q \cdot C} \times 100\% \tag{1}$$

Table 1
Factors and their levels to be considered in the column leaching experiment.

Levels	pH value	Solution injection rate (L m^{-2} h^{-1})	Ore particle size (mm)
1	1.0	80	1–2
2	1.5	120	2–4
3	2.0	160	4–6
4	2.5	240	6–8
5	3.0	360	8–10
6	3.5	400	10–12