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Original Research Paper

Enhancement of copper dissolution by mechanochemical activation of copper ores: Correlation between leaching experiments and DEM simulations

Masaya Minagawa [a], Shosei Hisatomi [a], Tatsuya Kato [a], Giuseppe Granata [b], Chiharu Tokoro [b,*]

[a] Graduate School of Creative Science and Engineering, Waseda University, Japan
[b] Faculty of Science and Engineering, Waseda University, Japan

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ABSTRACT

In this work we investigated the influence of planetary ball milling and vertical stirred ball milling on the leaching of a copper ore containing copper sulfate and covellite. We used a mixed experimental-simulation approach to correlate the kinetic parameters of leaching to the collision energy during grinding. The effect of milling was studied by scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS). Results showed that both high-intensity grinding techniques resulted into a dramatic decrease of particle size. Furthermore, under specific grinding conditions, the planetary ball milling determined also the partial amorphization of covellite. The collision energies corresponding to specific grinding conditions in terms of rotational speed and number of grinding media were assessed by DEM simulations and were related to the specific surface area after grinding. The specific surface area of grinded samples was found to be directly proportional to the collision energy in grinding. The leaching of the ore occurred through three subsequent steps: (i) dissolution of copper sulfate, (ii) dissolution of amorphousized covellite and (iii) dissolution of residual crystalline covellite. The results of kinetic fitting highlighted an increase of the rate constants for the leaching of amorphous and crystalline covellite by intensifying the milling conditions. By correlating the collision energies from DEM simulation with the leaching rate constants, we confirmed that the rate constants for the leaching of covellite increased due to an occurred mechanochemical reaction. The mechanochemical reaction that determined the partial amorphization of covellite occurred above 0.25 J/s · g. On the other hand, the rate constants for the leaching of the residual crystalline covellite constantly and progressively increased with the collision energy, thus highlighting an improvement of leaching due to an increase of surface area.

1. Introduction

Copper is one of the most important metals, having a wide range of applications, from the electronic industry to the medical field [1,2]. In the last decades, due to an imbalance between copper demand and copper supply, the production of copper has been gradually increasing [3]. At the same time, the concentration of copper in ores has been dramatically decreasing up to 0.2–2% [4] while the concentration of impurities like arsenic increased [5]. In this scenario, the copper industry needs to process also low-grade and refractory ores such as chalcopyrite and covellite. However, since low-grade copper ores containing sulfide minerals are not convenient to process by pyrometallurgy, hydrometallurgical processes have recently gained much importance for the copper industry.

Since the effectiveness of hydrometallurgical processes strongly depends on the amount of copper that can be leached out from the ore, having efficient leaching operations is crucial. The leaching of refractory sulfide ores such as chalcopyrite and covellite has been widely studied by using different leaching agents. Among them, hydrochloric [6] and sulfuric acids [7–10] were the most investigated.

Aiming to recover metal copper by elctrowinning, the sulfate media is more suitable than the chloride one [11]. However, the leaching in sulfate media is very slow or incomplete due to the formation of refractory compounds (elemental sulfur, polysulfide, etc.) on the mineral surface during leaching [12]. This problem, known as passivation, dramatically affects the dissolution of

* Corresponding author.
E-mail address: tokoro@waseda.jp (C. Tokoro).

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copper from sulfide minerals [13,14]. To overcome this issue, researchers have proposed different kinds of solutions like the use of strong oxidizing or reducing agents such as H_2O_2 and $Fe_2(SO_4)_3$ [15–17]. Alternatively, some researcher proposed the addition of compounds like pyrite [18], silver [19], and manganese oxide [20] to improve the leaching performances through the generation of galvanic interactions within the minerals.

As alternative to the addition of chemicals, the leaching performances could be improved by mechanochemical activation [21]. The method allows for an improvement of the leaching performances by means of high-intensity grinding techniques [22]. In the first place, the improvement is the result of a dramatic decrease of particle size, which in turn determines an increase of the specific surface area of the mineral and the consequent enhancement of the leaching physical kinetics [23]. Furthermore, the intense mechanical stress due to high-intensity grinding could induce the rupture of the crystal structure with a decrease of crystallinity [24–32]. These changes within the crystal structure of the minerals, also known as mechanochemical effect, can lead to more leachable minerals and to a higher dissolution of copper [33]. Last but not least, whereas the mineral surface underwent passivation during leaching, the high-intensity grinding could continuously refresh the solid surface, thereby increasing the exposure of unleached bulk mineral to the leaching agent.

Although recent researches proved the effectiveness of high-intensity grinding methods for the activation of refractory minerals, the mechanism of mechanochemical activation still needs to be elucidated. Moreover, a method to elucidate whether the activation occurs due to generation of new surface area or due to mechanochemical reaction still needs to be developed. In this study, we investigated the mechanochemical activation of a covellite-based copper ore by a mixed experimental-simulation approach. By means of discrete element method (DEM) simulations [34–36], grinding experiments and leaching experiments, we elucidated the mechanism responsible for the enhancement of leaching. Two different types of high-intensity milling methods were tested: planetary ball milling and vertical stirred ball milling. We first studied the influence of grinding conditions on particle size and crystal structure by scanning electron microscope (FE-SEM) and X-ray diffraction (XRD). Following this step, the leaching of the covellite-based copper ore was thoroughly investigated in sulfate media in order to (i) confirm the effectiveness of grinding and (ii) to find the kinetic parameters of leaching. Finally, with the goal to distinguish between leaching enhancement due to generation of new surface area and leaching enhancement due to mechanochemical reaction, we performed DEM simulations to relate the leaching rate constants to the collision energy in grinding.

2. Experimental

2.1. Materials

The copper ore used in this research was a raw ore from Chile while the sulfuric acid used for the leaching experiments was an analytical grade reagent by Kanto Kagaku (JAPAN).

2.2. Grinding experiments

The solid samples used in the high-intensity milling experiments were previously crushed roughly by a jaw crusher (Furukawa Industrial Machinery Systems Co., Ltd, JAPAN) and sieved in the range 75–3000 μm by wire sieves (Tokyo Screen Company Limited, JAPAN). After sieving, 30 g of samples were grinded for 1 h, either by a planetary ball mill (High G, Kurimoto ltd., JAPAN), or by a vertical stirred ball mill (Powder Lab, Nippon Coke & Engineering Co., Ltd, JAPAN), both equipped with 10 mm zirconia balls as grinding media. In the planetary ball mill, rotation to revolution speed ratio was set at 0.497 while the direction of rotation was inverse. All milling conditions are summarized in Table 1.

2.3. Analysis

The mineralogical composition of the copper ore was determined by mineral liberation analysis (MLA, QUANTA FEG450, FEI, United States) while the chemical composition was assessed through X-ray fluorescence (XRF, ZSX Primus2, Rigaku Corporation, JAPAN) and inductively-coupled plasma spectrometry (ICP-AES, SPS7800, Seiko Instruments Inc., JAPAN) after digestion in aqua regia. ICP-AES was also used in order to determine the concentration of dissolved copper in the leaching experiments. The phase composition of grinded samples was determined by XRD (Smart Lab, Rigaku Corporation, JAPAN) with Co Kα radiation (λ = 1.789 Å) operated at 40 kV and 40 mA emission condition. The Cu K-edge X-ray absorption data were obtained by X-ray adsorption fine structure (XAFS) analysis applying the BL5S1 beamline of the Aichi Synchrotron Radiation Center (Aichi Science and Technology Foundation, Japan). The particle size distribution of the ore samples before and after grinding was analysed by FE-SEM (S-4500S, Hitachi High-Technologies Corporation, JAPAN) and image analysis of SEM micrographs as described elsewhere [37].

2.4. Leaching experiments

In the leaching experiments, 5 g of finely grinded samples were suspended with 1 dm^3 of 0.06 M H_2SO_4 to be 5 g/dm^3 of ore concentration at room temperature and under magnetic stirring (200 min^{-1}). Sampling was performed after 1, 2, 4, 8, 24, 48, 72, and 96 h from the start of the experiments. Samples were filtered by 0.1 μm syringe filters (Acrodisc Syringe Filters, Pall Corporation), diluted and analysed to determine the dissolution of copper. Experiments were conducted in triplicates to express results as average values with error bars as standard deviations.

2.5. Simulation conditions

In this research, the three-dimensional motion of particles and media balls during milling was simulated by DEM. In this study, conventional DEM simulation was conducted with Voigt model as collision model without any breakage [38–40]. Table 2 shows a summary of the simulation conditions. The spring constant and friction coefficient were set as average values from literature [34,41,42].The restitution coefficient was determined through a rebound test with zirconia balls.

The intensity of collisions between the different elements in the mills (particles, media balls and wall of the mill), was calculated based on the masses and the relative velocities of the colliding elements, as in Eq. (1).

$$E_T = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2} v^2 \quad (1)$$

where m_1 and m_2 are the masses of the two colliding elements (i.e. particles, grinding balls, mill walls) while v represents the relative velocity. For particle-wall collisions, the mass of the element wall was considered as infinite.

The total collision energy per unit of time and unit of mass (J/s · g), calculated as the sum of the collision energies of each element in the system, was used for correlation with the leaching results in terms of rate constants.

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