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Synergistic effect between ultrasound and fierce mechanical activation towards mineral extraction: A case study of ZnO ore

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ABSTRACT

Though the positive role of ultrasound has been confirmed in the mineral extraction, its potential towards fiercely mechanically-activated mineral was not yet mentioned. In this study, as a novel mechanical activation style, bead milling (BM) was presented and ZnO ore was selected to determine its effectiveness. Results showed that median particle size of ZnO ore could be pulverized to as low as 1/164 of its original value (from ~29.2 μm to ~178 nm), indicating much higher activation potential of BM than that of conventional ball milling. Besides, structure destruction, even phase transformation with the direct participation of airborne CO_2 occurred. All these processes rendered the superior activation capacity of BM. In view of the extraction promotion, the combination of ultrasound and BM exerted more pronounced effect than those of individual ones, indicating the synergistic effect between extra energy input (by ultrasound) and inner energy storage (by fierce BM). The classic shrinking core model with the product layer diffusion as the rate-controlling step was found to well model the extraction kinetics. The modeling disclosed high capability of ultrasound and BM combination in decreasing the activation energy (E_a) (from 54.6 kJ/mol to 26.4 kJ/mol), while ultrasound, BM could only decrease the E_a to 44.9 kJ/mol, 41.5 kJ/mol, respectively. The dual roles of ultrasound were specially highlighted: (i) participation in the extraction process via direct energy input, (ii) regulation of the aggregation that the activated ore suspension was confronted with.

1. Introduction

As a very effective and non-polluting strategy of activation, ultrasound has been confirmed in various chemical-physical activities of the process industry in the past decades [1–3]. Ultrasound could accelerate the chemical reaction rate and promote the conversion efficiency via complicated cavitation processes involving shockwave and microjet formations [4]. All these processes have been found to be effective in reducing liquid film thickness, enhancing mass transfer and reducing bubble coalescence, which would be beneficial for the interfacial reaction [5]. Due to these underlying advantages, ultrasound was also revealed to present its effectiveness in the mineral extraction promotion [6,7]. For example, Ma et al., found that ultrasound could enhance potassium extraction from K-feldspar and they ascribed the ultrasound role to its capability in decreasing the apparent activation energy [8]. Similar conclusion was reached by Zhang et al., in which they found that ultrasound radiation significantly improved the leaching rates of Sb and Pb in lead-rich and antimony-rich oxidizing slag and the reaction time was sharply shorted [9]. However, though the positive role was noticed, relatively mild function was concluded for ultrasound promotion [8–10].

Considering that the prerequisite for mineral extraction was the breaking-up of the inherent lattices, mechanical activation emerged to be another feasible choice for mineral extraction promotion. Due to high feasibility and effectiveness, ball milling has been frequently adopted to mechanically activate the mineral particles [11,12]. Enhanced extractions of minerals that endured ball milling were frequently noted, which was closely correlated with its optimal capacity in particle pulverization and structure destruction [12–14]. However, ball milling could only pulverize the bulk particles (usually tens of microns) into those at the scale of several microns [11,13]. Recently, a novel bead milling process (BM) was presented and BM was reported to be able to pulverize micro-sized particles into near-nano scale ones [15,16], which indicated its much higher activation potential. However, its efficiency on mineral activation and subsequent extraction promotion remained unclear, which was within the scope of this investigation. Our previous work revealed the synergistic effect between ball milling and ultrasound towards mineral extraction [17]. Higher

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performance of ultrasound and BM combination in the mineral extraction was thereby reasonably forecasted. In fact, ultrasound was recommended to take indispensable role, as preliminary investigation showed that the MB activated mineral suspension would be confronted with severe aggregation, which would be adverse for the interfacial extraction.

In this investigation, natural ZnO ore was selected to (i) fully determine the potential of BM in solid activation, (ii) quantify the effectiveness of BM, ultrasound, and their combination in ore extraction promotion. Activation potential of BM was determined by comparing the physic-chemical properties of raw and activated ZnO ores, including particle size distribution, surface element speciation, solid phase composition. Note that mechanico-chemical reaction during BM process could induce phase transformation [18,19], which was also extensively revealed and discussed. The advantage of ultrasound and BM combination in ZnO ore extraction promotion was determined by comparing the extraction kinetics under various conditions. A classical shrinking core model was adopted to fit the experimental data, so as to obtain the activation energy for raw and activated ZnO ore extractions with/without the aid of ultrasound. These works would give deep sight into the mechanism of ultrasound and BM regulation.

2. Materials and methods

2.1. Reagents

All reagents (Sinopharm Chemical Reagent) were analytical grade and used without further purification. Natural ZnO ore was selected as the target mineral for BM and subsequent extraction investigation. Raw ZnO ore was mainly comprised of zinc oxide (ZnO), zinc ferrite ($ZnFe_2O_4$) and Zn-Al composite oxide ($Zn_6Al_2O_9$). The main chemical compositions of raw and bead millied ZnO ores were shown in Table 1. As can be seen, BM leaded to slight raise of TZn percentage, which was probably ascribed to the dissolution of other soluble substances during MA process. XRD patterns of the both ZnO ores would be presented later. Combining the XRD result with chemical composition analysis, it could be concluded that crystalline zinc phase of raw ZnO ore was almost entirely zinc oxide (ZnO, $ZnFe_2O_4$ and $Zn_6Al_2O_9$), without the presence of zinc sulphide (ZnS).

2.2. Bead milling and extraction procedures

The pulverization of raw ZnO ore particles was conducted using the BM process shown in Fig. S1. Briefly, the overall BM was composed of rough-milling and fine-milling processes. For rough- and fine-milling processes, all the other parameters were identical, except that 1.0 mm, 0.1 mm ZrO_2 ceramic beads, respectively, were adopted. Identical milling parameters included the flow rate, milling loading (30% solid/liquid ratio at a total volume of 1.0 L) and rotational speed, which would obtain constant energy transfer to the ore particles. Particularly, by connecting the output line back to the feed line, recirculation of the solid/liquid mixture was achieved, so as to fully activate the ore particles. In each pass scenario that ore particles gone through feed line to output line, the true milling took approximately 30 s. However, considering that various parameters kept identical and constant throughout the investigation, total milling time, instead of true milling time, was reasonably adopted. Typically, 3.0 h was selected for rough-milling, and 2.0 h for fine-milling. The solid–liquid mixture that endured BM was sampled, freeze-dried and ready for characterization and extraction.

Table 1
Main chemical compositions of raw and mechanically activated zinc oxide ores (mass fraction, %).

Sample ID	Component				
	TZn	TFe	TAl	CaO	MgO
raw ZnO	71.81	8.72	9.19	7.92	2.36
activated ZnO	78.83	7.34	9.04	2.66	2.13

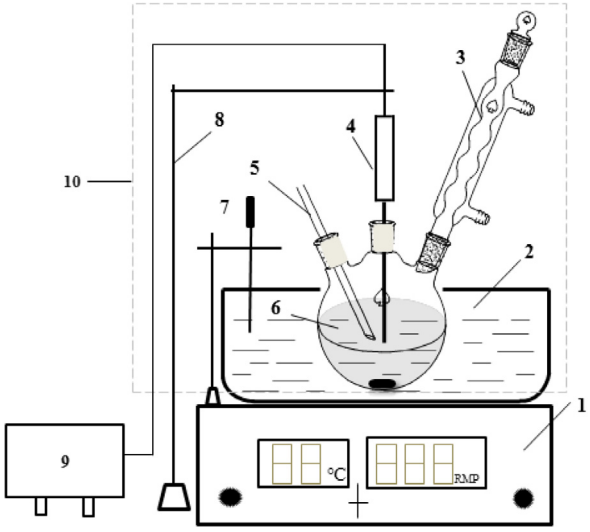

Fig. 1. Scheme experimental set-up for ZnO ore extraction. (1) magnetic stirrer, (2) thermostat water bath, (3) condenser, (4) ultrasonic probe, (5) sample point, (6) three-neck glass flask, (7) temperature probe, (8) iron support stand, (9) ultrasonic generator, (10) thermostat batch reactor.

A schematic illustration of the experimental set-up for ore extraction was shown in Fig. 1. All the extraction experiments were performed in a round-bottomed split flask with a three necked top, equipped with a magnetic stirrer, thermometer, and water-cooled condenser. To introduce ultrasound, a KBS-250 ultrasonic instrument was used. The round-bottomed split flask was immersed in a thermostatically controlled water batch. In each experiment, 400 mL sulfuric acid solution was added for pre-heating. After the desired temperature was reached, 10.0 g/L solid sample was added and stirred at 600 rmp. The operating frequency of the ultrasonic generator was kept to be 20 kHz and the output power was adjusted from the total power of 250 W.

2.3. Analytical methods and characterization

Physical-chemical properties of raw and activated ZnO ores were extensively characterized and compared. XRD patterns of the samples were collected on a D8 Advance Powder X-ray Diffractometer (Bruker, Germany) using a Cu Kα (λ = 1.5406 Å) radation source (40 kV, 40 mA). Morphologies of raw and activated ZnO ores were obtained by a field emission Scanning Electron Microscope (SEM) (Hitachi S-4800, Japan). Various element species on the surface of raw and activated ZnO ores were analyzed by X-ray Photoelectron Spectroscopy (XPS) using a PHI-5000 Versaprobe spectrometer equipped with a rotating Al anode generating Al Kα X-ray radiation at 1486.6 eV. Particle size distributions of raw and activated ZnO ores were measured by Mastersizer 3000 Laser Diffraction Particle Size Analyzer (Malvern, UK). The extracted zinc concentration was determined by ICP-AES (Agilent 720ES, USA).

3. Results and discussion

3.1. Activation potential of bead milling

3.1.1. High pulverization capability of bead milling

Fig. 2A presented the particle size distributions of raw and activated ZnO ore particles. Results showed that raw ZnO ore was composed of the particles with the median size (Dv(50)) distributed at ~29.2 μm,