



## Original Research Paper

## Surface modification of basic copper carbonate by mechanochemical processing with sulfur and ammonium sulfate

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## ABSTRACT

Mechanochemical phenomena including mechanical activation and direct reaction have been widely observed particularly from dry grinding operation and various applications of the phenomena have been reported in many fields of chemistry. A new approach was introduced here to trigger partial reaction by co-grinding samples with small addition of water/liquid to achieve the purpose of surface modification with new phase formed. As one example, basic copper carbonate was wet ground with elemental sulfur and appropriate additives such as ammonium sulfate to transform the surface chemical composition from oxide to sulfide. Physicochemical characterizations of the prepared samples were conducted by a set of analytical methods, including X-ray diffraction analysis, Fourier Transform infrared spectroscopy, Raman spectroscopic analysis, SEM morphology analysis, Zeta potential and the dissolved copper concentration measurement. The beneficiation efficiency of the modified copper carbonate by a conventional froth flotation used usually for sulfide minerals was examined as a quantitative evaluation to optimize the experimental conditions for the modification operation. A metal yield over 80% was obtained easily after one step concentrating of the flotation operation, indicating that mechanochemically surface controlling concept may serve as a novel pathway to enrich and recycle carbonate-style nonferrous resources by applying the traditional mineral processing technology on the modified samples.

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## 1. Introduction

Mechanochemical operation has been widely used in various fields of chemistry, as an effective method to induce some changes or direct reactions to serve specific purpose for the next operation such as materials synthesis, metallurgical recovery, etc. [1–3]. On one hand, with an impact by mechanical force on a material, mechanical activation is usually reported to have occurred, covering the changes in particle morphology and specific surface area, formation of dislocations, point defects in the crystalline structure, polymorphic transformation, amorphization and crystallization [4–6]. On the other hand, direct reactions are also reported and the interest in this field tend to rise continuously, considering the increasing number of the related papers published annually [7–13]. We tried to summarize the experimental results and rationalize the observations to give a general rule for understanding the nature of the mechanochemical reaction [14,15]. As to the application of the mechanochemical operation, there is such a case

where the effect of mechanical activation may not be strong enough to meet the specific requirement and the result of a complete reaction by prolonged grinding with large amounts of additives may raise the operation cost too much to be applicable. In other word, there exists the need to control the effect of mechanical operation to answer the specific purpose at cost as low as possible. One idea is to change the surface compositions to answer the purpose and maintain the bulk property to reduce the cost. Treatment of basic copper carbonate, which serves as the model for oxidized copper mineral as well as metal composition in solid waste, is such an example.

A conventional froth flotation is generally used to concentrate sulfide minerals such as chalcopyrite. Unfortunately, it does not work well on copper carbonate due to the evident difference in surface property from the sulfide. Therefore, the concept of sulfidizing copper carbonate is applied by methods such as using soluble sulfide of Na<sub>2</sub>S in froth flotation operation [16–18], directly thermally converting metal oxides and carbonates into sulfides through hydrothermal or pyrometallurgical methods and even non-thermal mechanochemical process before beneficiation [19,20]. To develop a cost-effective and environment-friendly process to allow

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an efficient application of the traditional flotation operation on the copper carbonate without changing it into a pure copper sulfide, a new approach here is proposed to grind basic copper carbonate with elemental sulfur and appropriate additives such as ammonium sulfate to transform partial composition from oxide to sulfide.

The research was focused on controlling the degree of mechanochemical operation and studying the changes in chemical composition, morphology, chemical bonding of the modified particles. Correlation between the improvements in beneficial efficiency by flotation with the obtained changes was investigated and the results are reported. The concept proposed may not only serve as the basis for the development of a novel process to recover copper and other metals from oxidized minerals and solid wastes but also push the basic research in the field of mechanochemistry toward a wider application with reasonable cost consideration.

## 2. Experimental

All the used samples including basic copper carbonate, sulfur, ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), copper sulfate (CuSO<sub>4</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), potassium butyl xanthate and pine wine oil were provided by Sinopharm Chemical Reagent Co., Ltd, China and used as received. Basic copper carbonate was mixed with 20 wt% sulfur and certain activator at different weight ratios, as the starting compounds.

A planetary ball mill (QM-3SP4, Nanjing, China) was used to grind the mixtures. 6.25 g of the starting compounds and different proportions of deionized water were placed into a stainless steel pot (500 cm<sup>3</sup> inner volume) with 140 g stainless steel balls (7 balls with 17 mm in diameter), followed by grinding in air at 500 rpm for different periods of time. After grinding, the samples were recovered from the pot in a batch way and then dried in shade without heating. Parallel experiments were carried out throughout the whole experimental stages to obtain the accurate results.

The crystallographic compositions of the ground products were characterized by X-ray diffraction (XRD, RIGAKU, D/MAX-RB, Japan). Morphological changes of the samples before and after grinding were observed by a scanning electron microscope (SEM, JEOL Ltd, JSM-5610LV, Japan). The dissolution of Cu<sup>2+</sup> during milling process was measured by a coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer, Optima 4300DV, USA). The schematically functional groups of the surface before and after modification was detected by a FTIR analysis (FTIR, Thermo, Nicolet6700, USA). A Raman Spectrometer (Raman, RENISHAW, INVIA, UK) was used to analyze chemical bonding upon surfaces of ground samples. Zeta-potential measurement (Zetasizer Nano, Malvern, UK) was performed to investigate the changes in surface properties of various samples before and after grinding.

Flotation test was conducted for the ground particles through a conventional rougher flotation process by using a laboratory scale flotation cell (XFD-0.25 L) and the impeller speed was 1992 rpm. A 5-g sub-sample was fed to flotation cell and the pulp density was 10%. Potassium butyl xanthate was used as collector in a concentration of 2000 g/t and pine wine oil was used as a frother in concentration of 500 g/t. After the pulp was agitated for 5 min, the collector was added and conditioned for 5 min. Then the frother was added and conditioned for 2 min. The froth was removed by hand scraping every 10 s and the total scraping time was 3 min. After the test, the concentrates and tailings were dried and weighed. The flotation efficiency was evaluated on the basis of concentrate yield.

## 3. Results and discussion

XRD patterns of the samples ground with 20 wt% sulfur, 5 wt% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 6 ml water for different time at 500 rpm are shown

in Fig. 1. With grinding time less than 30 min, the original samples of sulfur and basic copper carbonate were remaining as the main phases with clear and strong peak intensity. With an increase in grinding time, the peaks of the original samples were becoming weaker and weaker, and nearly disappeared at 90 min grinding. The formation of CuS could be observed at 30 min grinding. It is understood that the increase in grinding time has resulted in the destruction of original particles and the combination reaction to form sulfide product. The co-existence of original samples and reaction product at 60 min grinding was comprehensively considered to be a suitable condition to serve the expected purpose. Prolonged grinding for 90 min was not reasonable for the disappearance of the original samples.

Fig. 2 shows the XRD patterns of the ground samples with different additives and 6 ml water for 60 min. The pattern of the sample ground with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was found to be different from that of the samples ground with other additives. Compared with the other three patterns, the formation of CuS phase was clearly observable and the peak intensity of the original samples was very low, in the case of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. It can be understood that the mechanochemical interaction between basic copper carbonate particles and sulfur was greatly improved in the presence of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. No obvious reaction occurred with the other additives for the grinding operation.

The changes in zeta potentials of ground particles with different additives were measured at pH value corresponding to initial condition and results are shown in Fig. 3. The zeta potentials of the copper carbonate particles ground with each salt additive before sulfur addition were of relatively high positive values. However, obvious decreases in the value of zeta potential after adding sulfur in the grinding operation were observed, implying that the existence of sulfur coating pushed the high potential of positive value to the negative side. The largest negative movement of particle surface potential was observed in the case of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, indicating the stable existence of sulfide layer upon particle surface after mechanochemical treatment under (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> promotion.

ICP analysis of Cu<sup>2+</sup> concentrations after wet milling with or without sulfur under different additives was conducted to assess the metal dissolution and immobilization rate as sulfide formation. As shown in Table 1, when observing the changes in Cu<sup>2+</sup> concentration with and without sulfur addition, it is interesting to note that clear decreases in Cu<sup>2+</sup> concentration were observed with all the three additives when sulfur was added, suggesting an obvious combination of Cu<sup>2+</sup> ions with sulfur to form an insoluble composition during the wet grinding operation. However, in both cases of NH<sub>4</sub>NO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>, whether with or without sulfur addition, the Cu<sup>2+</sup> concentrations remained very low, indicating that few copper

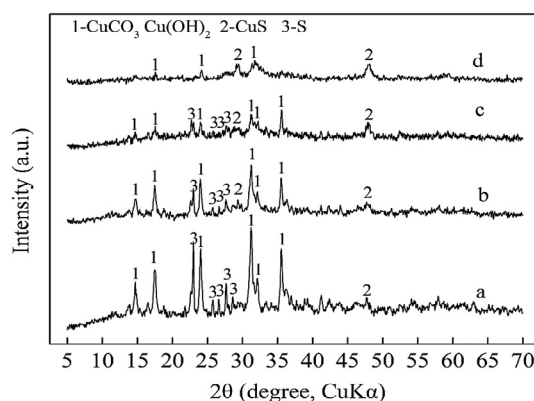


Fig. 1. XRD patterns of samples ground for different times (a-5 min, b-30 min, c-60 min, d-90 min).

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