



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 Na₂S 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 ((NH₄)₂SO₄), copper sulfate (CuSO₄), ammonium nitrate (NH₄NO₃), sodium sulfate (Na₂SO₄), 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 cm³ 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 Cu²⁺ 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% (NH₄)₂SO₄ 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 (NH₄)₂SO₄ 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 (NH₄)₂SO₄. It can be understood that the mechanochemical interaction between basic copper carbonate particles and sulfur was greatly improved in the presence of (NH₄)₂SO₄. 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 (NH₄)₂SO₄, indicating the stable existence of sulfide layer upon particle surface after mechanochemical treatment under (NH₄)₂SO₄ promotion.

ICP analysis of Cu²⁺ 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 Cu²⁺ concentration with and without sulfur addition, it is interesting to note that clear decreases in Cu²⁺ concentration were observed with all the three additives when sulfur was added, suggesting an obvious combination of Cu²⁺ ions with sulfur to form an insoluble composition during the wet grinding operation. However, in both cases of NH₄NO₃ and Na₂SO₄, whether with or without sulfur addition, the Cu²⁺ concentrations remained very low, indicating that few copper

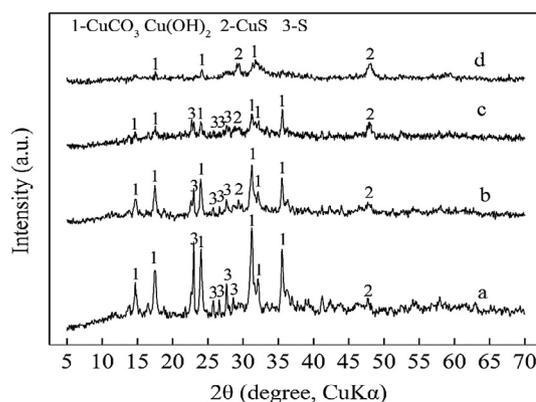


Fig. 1. XRD patterns of samples ground for different times (a-5 min, b-30 min, c-60 min, d-90 min).

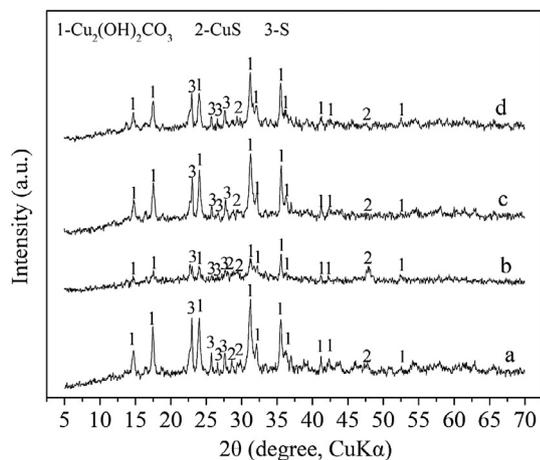


Fig. 2. XRD patterns of basic copper carbonate ground with S and different additives (a-none, b-(NH₄)₂SO₄, c-NH₄NO₃, d-Na₂SO₄).

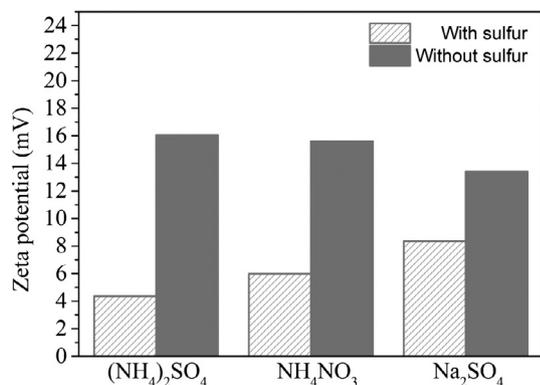


Fig. 3. Zeta potentials of particles ground with various activators.

Table 1
Cu²⁺ concentration (mg/L) of ground samples with different activators.

	(NH ₄) ₂ SO ₄	NH ₄ NO ₃	Na ₂ SO ₄
Without sulfur	233.9	4.2	15.4
With sulfur	36.6	1.5	11.0

ions were dissolved out from the copper carbonate crystal. Such low concentrations of Cu²⁺ ions matched with the unobservable formation of CuS sulfide by XRD analysis

When (NH₄)₂SO₄ was used, different from the above two cases, the Cu²⁺ concentration ground without sulfur was as high as 233.9 mg/L, indicating the much easier dissolution of copper from the bulk sample with (NH₄)₂SO₄ than that with NH₄NO₃ or Na₂SO₄. The Cu²⁺ concentration was found to sharply decrease to 36.6 mg/L when sulfur was added, confirming that the copper dissociated from inner crystal by the activation of (NH₄)₂SO₄ had reacted with sulfur to form a sulfide layer on the mineral surface.

The changes in Cu²⁺ ion concentration with the water volume used in wet grinding are shown in Table 2. It was noticed that, without sulfur addition, as the water volume increased, a large increase in Cu²⁺ ion concentration over 200 mg/L was obtained, confirming the easier dissolution of Cu²⁺ from the copper carbonate sample during the grinding operation with more water addition. It was more interesting to note that, in the presence of sulfur, Cu²⁺ concentrations were decreased to a relatively low level less than 60 mg/L, without large change in water volume, which suggested the occurrence of a reaction between the dissolved cop-

Table 2
Cu²⁺ concentration (mg/L) of ground samples with different water volumes.

	2 ml	4 ml	6 ml
Without sulfur	58.5	186.2	233.9
With sulfur	38.2	58.1	36.6

per and the added sulfur to consume the copper from the aqueous solution during the wet grinding.

More Cu was dissolved from particles and immobilized by sulfur as the water dosage increased. Ball milling operation is a chemical reaction induction process based on mechanical force and sensitive to solid-liquid ratio. Too much water might weaken the contact efficiency among particles and negatively affect the reaction activity. The balance of water volume between better metal dissolution and higher reaction activity is the key to wet milling operation.

As to investigate the schematically functional groups of the surface before and after modification, the FTIR analysis was carried out and expressed in Fig. 4. The broad adsorption between 3500 cm⁻¹ and 3000 cm⁻¹ represents the stretching/bending vibration of -OH belonging to the surface moisture or Cu(OH)₂ phase. Other bands represent to monodentate CO₃ observed at 1498 cm⁻¹, 1096 cm⁻¹, 1046 cm⁻¹ and 820 cm⁻¹. The bidentate CO₃ was observed at 873 cm⁻¹, 777 cm⁻¹ and 748 cm⁻¹ [21]. Compared with the raw material, the ground sample expresses almost the same schematically functional groups appearance indicating the accordance in chemical component before and after mechanochemical modification, indicating that the basic copper carbonate remains unchanged in general except for the surface modified. Nevertheless, an obviously peak situated at 617 cm⁻¹ in the ground sample is the characteristic Cu-S stretching bond of host lattice [22], implying the formation of a small amount of CuS. This phenomenon is agreeable to the XRD data.

In addition to XRD analysis, Raman analysis was conducted to characterize the ground copper carbonate with 5 wt% (NH₄)₂SO₄ and 6 ml water, with raw sample as reference. The results are shown in Fig. 5. The ground samples were dried in a vacuum dryer under ambient temperature. As shown in Fig. 5, besides the typical peak attributed to copper carbonate in the range of 250–300 cm⁻¹, new peaks were also observed from the ground particles, compared with raw materials. The peak positioned at 200–225 cm⁻¹ assigned to the S-S bond-bending mode of A_g symmetric and the

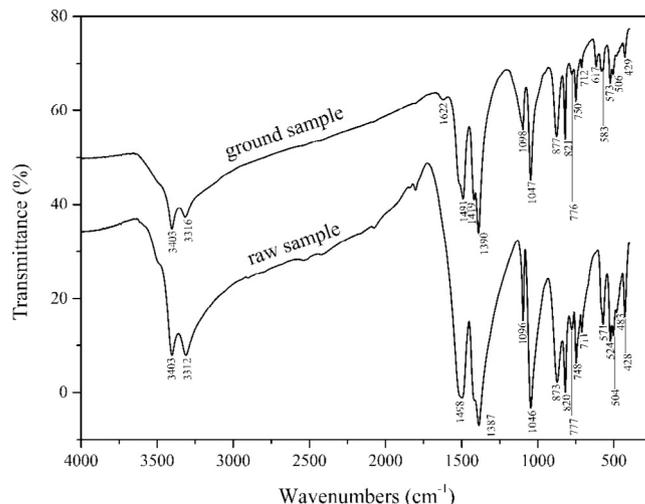


Fig. 4. FTIR spectra of feed sample of basic copper carbonate and the product sample from sulfidation with (NH₄)₂SO₄.

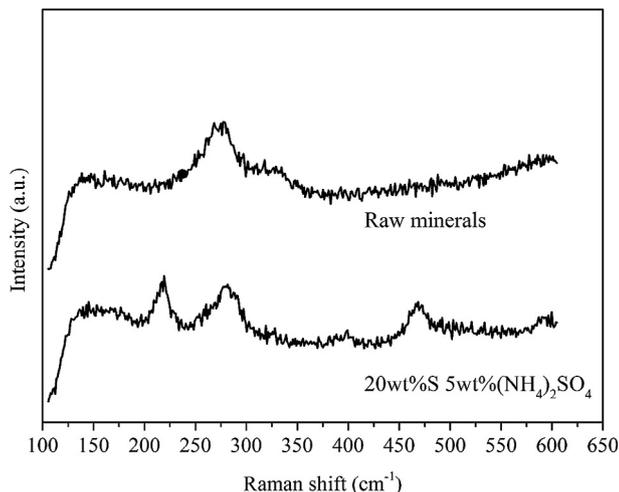


Fig. 5. Raman spectra of the ground sample with $(\text{NH}_4)_2\text{SO}_4$.

peak positioned at $450\text{--}500\text{ cm}^{-1}$ assigned to Cu–S bond-stretching mode of A_g symmetric [23–25]. The results from Raman analysis were consistent with those from the XRD analysis shown in Fig. 2, together confirming the formation of copper sulfide layer adhering on particles surface.

The surface morphology of mechanochemically sulfidized basic copper carbonate was investigated by SEM analysis shown in Fig. 6. After grinding with sulfur and $(\text{NH}_4)_2\text{SO}_4$, the micrograph of copper particles indicated a progressive increase in the roughness and porosity. Since the surface porosity of reactants plays an important role in solid state processing, the porous surface modified by the

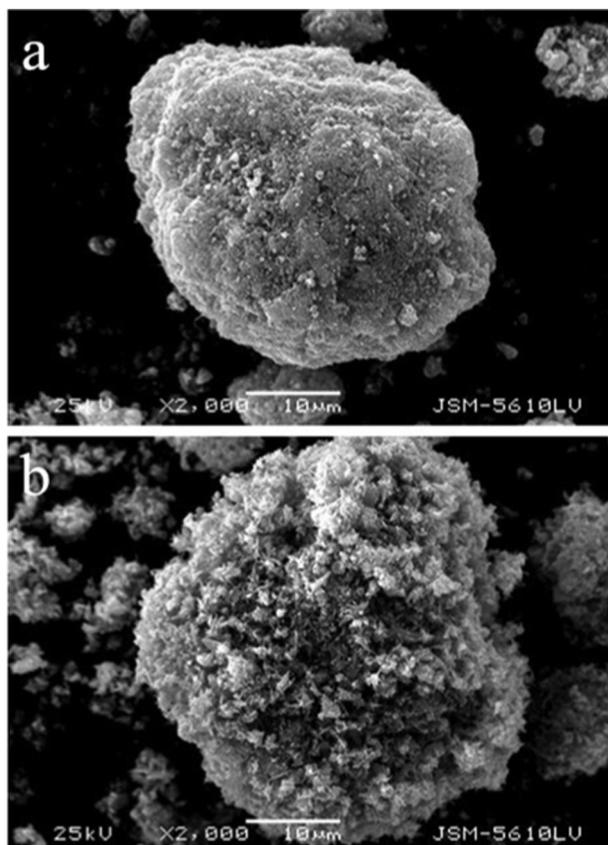


Fig. 6. SEM images of the feed sample of basic copper carbonate (a) and the product sample from sulfidation with $(\text{NH}_4)_2\text{SO}_4$ (b).

formation of sulfide layer was believed to make for the adsorption and permeation of various regulators during subsequent beneficiation process, resulting in the physical improvement on metal recycling.

As a kind of traditional method of particle separation and beneficiation by applying differences in surface properties, froth flotation has been widely used to recover metal resources [25]. This method was used to evaluate the prepared samples.

To understand the effect of $(\text{NH}_4)_2\text{SO}_4$ addition on flotation efficiency, comparison experiments with several additives with the same 5% addition rate were conducted with other parameters fixed as follows: 20 wt% sulfur dosage, 6 ml water and 60 min grinding. The results are shown in Fig. 7. The sample treated with sulfur only without other salt additions exhibited no obvious improvement of floatability. With the additions of ammonium nitrate and sodium sulfate, the floatability of the treated sample was improved slightly, but the recovery rates were still quite low below 30%. Evident improvements in flotation were obtained with the additions of ammonium sulfate. It could be understood that, together with the added sulfur, copper ions played an important role in converting the surface properties of carbonate into a composition beneficial to the flotation operation. In other words, copper dissolution occurred during the wet grinding with the addition of ammonium sulfate.

Fig. 8 shows the changes in flotation recovery as metal yield with both grinding time and water volume used. It is clearly observed that the recovery increased with the increase in grinding time and water volume. According to the XRD results shown in Fig. 1, the chemical bonding between copper and sulfur on particle

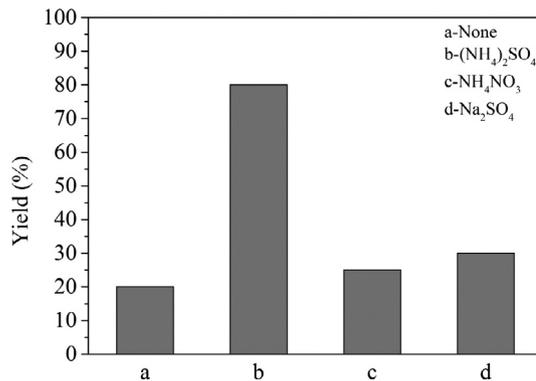


Fig. 7. Effects of additive use on the flotation efficiency.

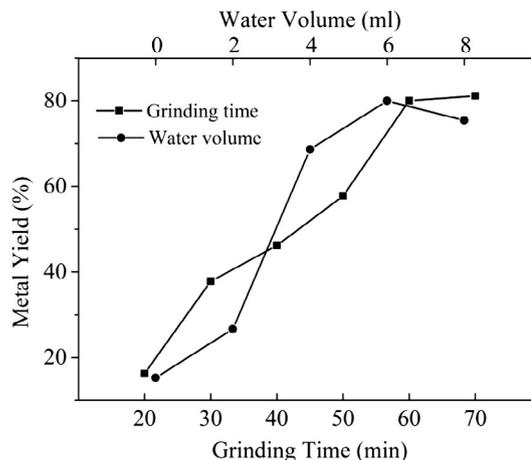


Fig. 8. Metal yield with grinding time and water volume.

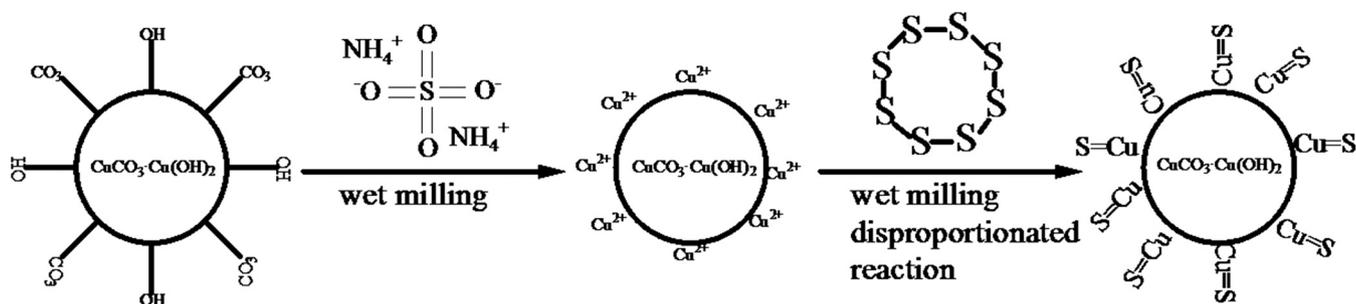


Fig. 9. Chemical reaction scheme for the mechanochemical modification of basic copper carbonate with sulfur and ammonium sulfate.

surfaces and formation of metal sulfide layer are the main contribution to the improved metal yield due to the feasibility of the obtained sample to flotation operation. As detected from Table 2, the increase in copper dissolution and subsequent formation of CuS from the water volume in wet milling were believed to be the main reasons for the improvement in metal yield. Although not shown here, further increase in flotation efficiency was easy to achieve by regulating the conditions used in flotation operation.

Under grinding with $(\text{NH}_4)_2\text{SO}_4$, copper dissolved from the bulk in the form of free bivalent ions, confirmed by ICP analysis, then combined with sulfate anions. After the addition of sulfur, most free Cu^{2+} reacted with sulfur to form a precipitate, which could be proved by the results of ICP analysis. The interaction between basic copper carbonate and sulfur were limited to the surface layers, of which the properties were quite similar to copper sulfide, leading to the performance improvement even by traditional flotation. The mechanism of sulfidizing operation involves both oxidation and reduction of sulfur. Such a disproportionated reaction has already been reported in our previous research [26]. Under such a mechanical grinding condition, the generated CuSO_4 was soluble in water, therefore not detected in the XRD pattern of the solid samples. The reaction scheme employed in present study is illustrated in Fig. 9.

Instead of complex solution chemistry regulation and other severe operating conditions to obtain a pure sulfide for flotation concentration, a novel surface modification proposed here demonstrated evident advantages for possible application in value metal recovery by traditional mineral processing as flotation. The surface characteristics controlling technology may serve as a novel concept for particles separation to treat both natural resource and solid wastes.

4. Conclusions

Grinding $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 \cdot \text{S} \cdot (\text{NH}_4)_2\text{SO}_4$ mixture with some water was conducted to form CuS sulfide product together with the original copper carbonate, confirming that it is possible to control the degree of mechanochemical reaction to give the sample suitable for specific purpose, as beneficiation by flotation in this case. The proposed concept will help to widen the understanding on mechanochemistry and expand the applications of mechanochemical operation in specific field.

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