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Short communication

Mechanochemical processing of celestine

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Abstract

Room temperature milling of celestine mineral and dry sodium hydroxide powder mixture was conducted in a planetary ball mill. Strontium sulfate, which is a main component in the celestine sample reacts spontaneously with sodium hydroxide powder during milling, forming strontium hydroxide. As a result of carbonation in a final product of milling, strontium hydroxide is transformed into strontium carbonate. The milling operation enables to accelerate the reaction rate. The strontium carbonate in the product can be concentrated up to over 90% by washing sodium sulfate out with water. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Grinding; Mechanochemical processing; Celestine; Strontium carbonate

1. Introduction

Strontium carbonate ($SrCO_3$) is one of the most important strontium compounds that have been used in a variety of technological and industrial applications; in particular, in the production of cathode ray tubes for TV imaging applications, magnetic ferrites or advanced ceramic materials [1]. Although $SrCO_3$ occurs naturally as mineral strontianite, the majority of it that is available has been produced chemically from celestine [2,3]. This mineral is composed mainly of strontium sulfate ($SrSO_4$) with the orthorhombic crystal structure [4,5]. At present, there are two processes to manufacture $SrCO_3$ from celestine. In the first process, agitating celestine powder in sodium carbonate (Na_2CO_3) solution at a temperature of around 368 K produces $SrCO_3$ and sodium sulfate (Na_2SO_4) [6]. The second process is the reductive roasting process, in which the sulfate mineral is calcined with coal to form water-soluble strontium sulfide. The sulfide is dissolved in a solution and the sulfide in the solution is subsequently carbonated by injecting CO_2 gas or soda ash, forming $SrCO_3$ as a precipitate [1,2].

In this paper, we discuss a new process for producing strontium carbonate from celestine without heat treatment, and instead using mechanochemical treatment with dry NaOH powder.

2. Experimental details

2.1. Samples

The celestine sample supplied from Sakai Chemicals Co. Ltd., Japan consisted of 96.0 wt.% $SrSO_4$, 0.7 wt.% $BaSO_4$, 2.5 wt.% $CaCO_3$ and 0.1 wt.% SiO_2. The starting sample was fine powder of particle size less than 44 μm (325 mesh). Dry NaOH powder was mixed with the celestine powder in a molar ratio of 1:2, which is equivalent to a stoichiometric ratio of the reaction, according to the formula

$$SrSO_4(s)+2NaOH(s)\rightarrow Sr(OH)_2(s)+Na_2SO_4(s) \quad (1)$$

2.2. Milling and leaching

In Fig. 1, the experimental procedure for milling the celestine and NaOH mixture and subsequently leaching the

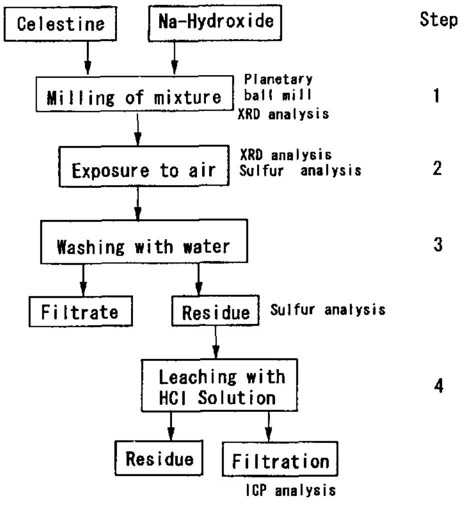

Fig. 1. Schematic diagram of the experimental procedure.

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exposed mixture is schematically presented. Milling of the mixture was conducted in air using a planetary ball mill (Fritsch Pulverisset-7) at a rotational speed of approximately 700 rev min^{-1}. 3.5 g of the mixture was introduced into an agate vial of inner volume 45 cm^3 with seven agate balls 10 mm in diameter. The powder mixture was milled for different periods of time. An unmilled mixture was prepared as a reference, by mixing in acetone for 30 min in a draft chamber as the evaporation of acetone finished. In the next step, the reference and milled samples were exposed to air for different times up to 1 week.

A leaching test of the exposed product was performed as follows. 1.0 g of the powder was dispersed in 25 ml of distilled water and agitated for 10 min. The solid particles in the suspension were separated from the Na_2SO_4 by filtration and washed out with 75 ml of distilled water. The residue on a filter was dried at 353 K in an oven. The dried residue was mixed with a 1 N HCl solution to leach $SrCO_3$.

2.3. Characterization

To identify the constituent components in the samples, X-ray diffraction (XRD) analysis of the reference and milled mixtures was performed using a Rigaku Giegerflex diffractometer using Cu Kα radiation with a pyrolytic graphite monochromator. The amounts of sulfur in the exposed mixtures and in the residues before and after washing with water were determined using a high temperature sulfur analysis method [7]. The concentration of Sr in the filtrates after leaching with HCl solution was determined using an inductively coupled plasma (ICP) analysis method.

3. Results and discussions

3.1. Mechanochemical activation

Fig. 2 shows the XRD patterns of the mixture milled for different times. The peak intensity of $SrSO_4$ decreases within 15 min of milling. In addition, very weak new peaks of $Sr(OH)_2$ are detected in the pattern, suggesting that substitution reaction (1) takes place. It then follows that the Gibbs free energy change of this reaction system indicates a negative value of -44 kJ mol^{-1}. The intensity of the $Sr(OH)_2$ peaks was found to increase as the milling progresses up to 30 min. However, another end product, i.e. Na_2SO_4, of the substitution reaction is not detected in the powder milled for 30 min. After 60 min of milling, the intensity of the $Sr(OH)_2$ peaks decreases, and the peaks of $Sr(OH)_2$ hydrate appear, as a result of the absorption of moisture during the milling and during the XRD measurements. Furthermore, Na_2SO_4 is found to be formed in the milled mixture. The difference in the formation period of the two end products may be attributed to the reaction mechanism. Specifically, the SO_4 tetrahedron structure in $SrSO_4$ is different from that in Na_2SO_4 [3]. Therefore, a certain milling time is required for the structure in $SrSO_4$ to change to that of Na_2SO_4 during the mechanochemical treatment. Small $SrSO_4$ peaks are still observed in the XRD patterns of the mixtures milled for more than 60 min. No clear explanation can be given for this result, so further investigations are needed.

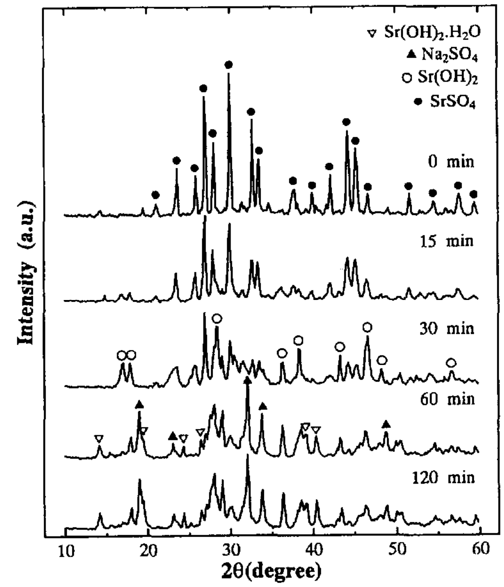

Fig. 2. XRD patterns of the mixtures of celestine and NaOH milled for different times (Cu Kα).

However, it is well known that $Sr(OH)_2$ reacts very easily with CO_2 gas, i.e.

$$Sr(OH)_2 + CO_2 = SrCO_3 + H_2O \quad (2)$$

Fig. 3 shows XRD patters of the mixtures exposed to air for 2 days after milling for different times. From the figure, it can be seen that the peak intensities of the $Sr(OH)_2$ hydrate decrease as milling progresses, while the peak heights of the $SrCO_3$ increase with increasing milling time. This implies

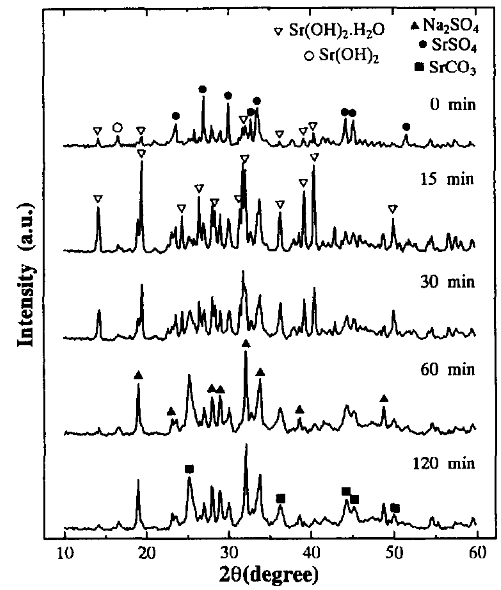

Fig. 3. XRD patterns of the mixtures of celestine and NaOH exposed for 2 days after milling for different times (Cu Kα).

that $Sr(OH)_2$ and its hydrate are transformed into the carbonate form, by reacting with CO_2 gas from air. It is easily deduced from Fig. 3 that the amount of $SrCO_3$ increases with increasing milling time. Thus, the amount of $SrCO_3$ in the exposed mixture after milling is closely related to the exposure treatment as well as the milling operation. In the present case, the milling of the mixture seems to play a significant role in accelerating the reaction rate, by increasing the fresh surface area of the reacting compounds.

3.2. Sulfur content

Fig. 4(a) shows the percentage of SO_4 anion in the filtrate to SO_4 in celestine subjected to the exposure operation for 1 week vs. the milling time. Around 68% of insoluble SO_4 in celestine is transferred into the soluble form simply by the mixing operation. Furthermore, more than 95% of the insoluble SO_4 is transferred into the soluble form by milling for about 120 min. Therefore, ball milling is necessary to achieve a high reaction rate.

Fig. 4(b) shows the concentration of $SrSO_4$ that remained in the recovered products obtained from the mixtures exposed for 1 week vs. the milling time. About 39% of the $SrSO_4$ is included in the product after washing of the unmilled mixture. The concentration decreases to around 4% after 60 min of milling, suggesting that insoluble sulfate is changed into soluble form by the milling operation. However, no further decrease in the yield is observed, so that around 60 min of milling may be enough time to finish the substitution reaction under the present conditions.

3.3. $SrCO_3$ content in the product

Fig. 5 shows the yield of $SrCO_3$ in the residues after washing the milled samples exposed for different times as a function of the milling time. The curves shown in the figure are extrapolated from the measured values with ±5% accuracy. In the case of the unexposed mixture, the yield is independent of the milling time and remains almost constant at around 10%. When the unexposed mixtures are dispersed in water, $Sr(OH)_2$ and Na_2SO_4 dissolve simultaneously in the water, forming Sr cations and SO_4 anions. This ionization results in the reverse reaction to form $SrSO_4$ precipitates. This reverse reaction is the reason why the yield for the unexposed mixtures shows such a low value. The yield increases with increasing exposure time. This means that $Sr(OH)_2$ is carbonated by reacting with CO_2 gas from air. After 48 h of exposure, the yield starts from about 50% and reaches more than about 80% after 60 min of milling. A similar trend can be seen for the mixtures exposed for 96 h. The yield values are much higher than those of the mixtures exposed for 48 h. Although the data are scattered, over 90% $SrCO_3$ can be concentrated in the product within 60 min of milling.

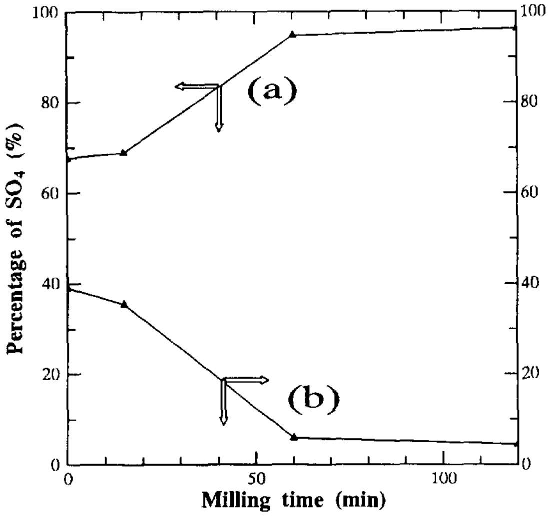

Fig. 4. Changes (a) in the percentage of SO_4 anion in the filtrate to SO_4 in the celestine and (b) in the concentration of $SrSO_4$ in the residue with milling time.

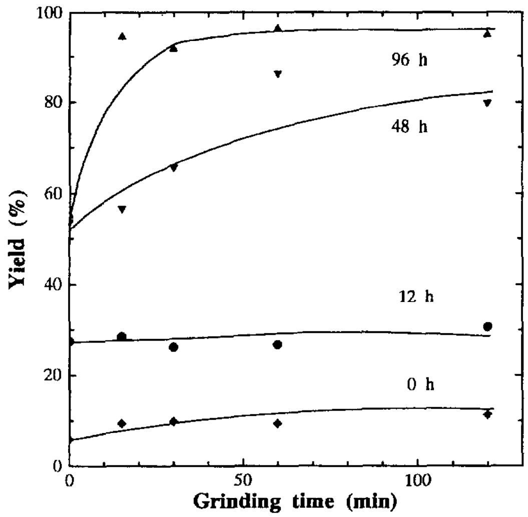

Fig. 5. Yield of Sr extracted by 1 N HCl solution vs. milling time, depending on the exposing time.

4. Concluding remarks

The experimental results in the present work can be summarized as follows.

(1) Room temperature milling of celestine and dry NaOH powder mixtures enables us mechanochemically to produce $Sr(OH)_2$ and Na_2SO_4 in the product. In the present case, the milling and mixing operation for the mixture play significant roles in accelerating the reaction rate, by increasing the fresh surface area of the reacting compounds.

(2) $Sr(OH)_2$ is easily changed into its hydrate form and both compounds are transformed into $SrCO_3$ by reacting with CO_2 gas from air.

(3) $SrCO_3$ in the product is recovered by washing Na_2SO_4 out with distilled water. About 4 days of exposure treatment for the mixtures milled for 60 min enables us to concentrate more than about 90% $SrCO_3$ in the final powder product.

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