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Wet mechanochemical processing of celestine using $(NH_4)_2CO_3$

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ABSTRACT

In this study, traditional (univariate) method of processing to the wet mechanochemical treatment were applied to obtain both $SrCO_3$ and $(NH_4)_2SO_4$ from celestite $(SrSO_4)$-$(NH_4)_2CO_3$-H_2O mixtures in a planetary ball mill. X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and chemical analysis were used to analyze products formed during wet milling. A hydrometallurgical process was carried out to examine milling time, ball to grinding material mass ratio, $(NH_4)_2CO_3$ to $SrSO_4$ mole ratio and rotational speed of the mill in a planetary mill. Under optimum conditions, a conversion approaching 100% of $SrCO_3$ was obtained.

Keywords: ammonium sulfate, celestine, strontium carbonate, wet mechanochemical conversion

$(NH_4)_2CO_3$ kullanılarak sölestinin yaş mekanokimyasal işlenmesi

ÖZ

Bu çalışmada, yaş mekanokimyasal işlem bir planetary bilyalı değirmende sölestin $(SrSO_4)$-$(NH_4)_2CO_3$-H_2O karışımından $SrCO_3$ ve $(NH_4)_2SO_4$ elde etmek için geleneksel (tekli) yöntemle uygulandı. X-ışını kırınımı, Fourier dönüşümlü kızılötesi spektroskopi, taramalı elektron mikroskobu ve kimyasal analiz yaş öğütme sırasında oluşan ürünleri analiz etmek için kullanıldı. Hidrometalurjik işlem, bir planeter değirmende öğütme süresi, bilya ile öğütülmüş malzeme kütle oranı, $(NH_4)_2CO_3$ ile $SrSO_4$ mol oranı ve değirmen dönme hızını incelemek için gerçekleştirildi. Optimum koşullar altında, $SrCO_3$'ın %100'e yaklaşan bir dönüşümü elde edildi.

Anahtar Kelimeler: amonyum sülfat, sölestin, stronsiyum karbonat, yaş mekanokimyasal dönüşüm

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1. INTRODUCTION

Celestine, the sulfate of strontium, is the major source of strontium and its compounds. Strontium is much less toxic than either lead or barium. The principal uses of strontium are in the manufacture of strontium carbonate and nitrate. $SrCO_3$ is used principally in the manufacture of glass for TV picture tubes and ceramic ferrites for magnets. Strontium nitrate is used for safety flares and other pyrotechnics; it imparts a brilliant red color to the flame [1]. Minor applications of strontium compounds are in ceramics, depilatories, and medicine. The processes used to obtain $SrCO_3$ from celestine are the black ash method [2–5] and the direct converting method [6–9]. However, these two processes are now in question because of problems either arising from matrix and grade of celestine or problems that occur during the energy–intensive carbothermic reduction of celestine (CO_2 release) and carbonation of sulfidized solution (H_2S release) in the black ash method, or iron problems and low $SrCO_3$ grade in the direct converting method.

There are a number of studies using ammonium carbonate ($(NH_4)_2CO_3$) [10] and ammonium bicarbonate (NH_4HCO_3) [11,12] instead of Na_2CO_3 for conversion. Both the production ammonium sulfate and strontium carbonate were realized from celestine by Piedrafita [13] and Kocakuşak et al. [14]. According to the following reaction, strontium carbonate (solid) and ammonium sulfate (soluble) are obtained from celestine with ammonium carbonate [13,14].

$$SrSO_4(s)+(NH_4)_2CO_3(s)=SrCO_3(s)+(NH_4)_2SO_4(aq) \quad (1)$$

According to the above conversion reactions, 1.527 tons of $SrCO_3$ and 1.365 tons of $(NH_4)_2SO_4$ can theoretically be produced as a result of processing 2 tons of celestine concentrate (95% $SrSO_4$). In addition, both nitrogen and sulfur requirements of soil and neutralization of alkaline soil can provide by using $(NH_4)_2SO_4$ [15].

The activation by mechanical energy has applications in many fields ranging from waste processing to the production of advanced materials [16]. Mechanochemical conversion of celestine to $SrCO_3$ was performed using high-energy mills by many researchers [17–20]. Mechanochemical processes use mechanical energy to activate chemical reactions and structural changes. However, the conversion of celestine with $(NH_4)_2CO_3$ was firstly investigated dry and wet mechanochemical treatments by using response surface methodology in a planetary mill by the present authors [21–23].

At present study, the production conditions of $SrCO_3$ (product) and $(NH_4)_2SO_4$ (byproduct) from celestine were investigated by applying the traditional (univariate) method of processing to the wet mechanochemical treatment using $(NH_4)_2CO_3$ in a planetary ball mill. The results of dry [21] and wet methods were evaluated by comparison.

2. EXPERIMENTAL

2.1. Material

Natural celestine concentrate from Barit Maden Türk A.Ş. (Sivas, Turkey), reagent grade anhydrous $(NH_4)_2CO_3$ (Sigma-Aldrich), boiled-cooled deionized water, and HCl solution were used in this study. The chemical composition of the celestine is 95.64% $SrSO_4$, 0.35% $BaSO_4$, 1.49% $CaSO_4 \cdot 2H_2O$, and other minor minerals [21,23].

2.2. The wet milling procedure

The wet mechanochemical conversion via Fritsch Pulverisette 6 models of planetary type ball mill was performed using 250 cm^3 ZrO_2 vessels including celestine, $(NH_4)_2CO_3$, and 20 mL boiled-cooled deionized water with 51 ZrO_2 balls (171.91 g) of 10 mm diameter at milling time, 10–90 min; mass ratio of ball to milled materials, 5–40; $(NH_4)_2CO_3$ to $SrSO_4$ mole ratio, 1–4; rotational speed of mill, 100–500 rpm; and milling atmosphere, air. Due to the lower solubility of $SrCO_3$ ($K_{sp}= 5.6x10^{-10}$) than $SrSO_4$ ($K_{sp}= 3.44x10^{-7}$), the general conversion reaction (Eq. 1) proceed toward the right [24].

The wet conversion experiments were performed according to the flowsheet in Figure 1. The mill was stopped during conversion treatments for 3 min per 15 min period to protect against overheating in reversed rotational speed mode. After milling, the milled material subjected to solid/liquid separation by centrifugation (10 min at 1000 rpm). Tests were reported as the average of the two results. The variation between runs was <0.5%. The conversion percentages were calculated using the amount of unreacted $SrSO_4$ in solids (by washing with 1 N HCl) and the amount of sulfate (by turbidimetric method with Shimadzu UV-2450 spectrophotometer) in liquids.

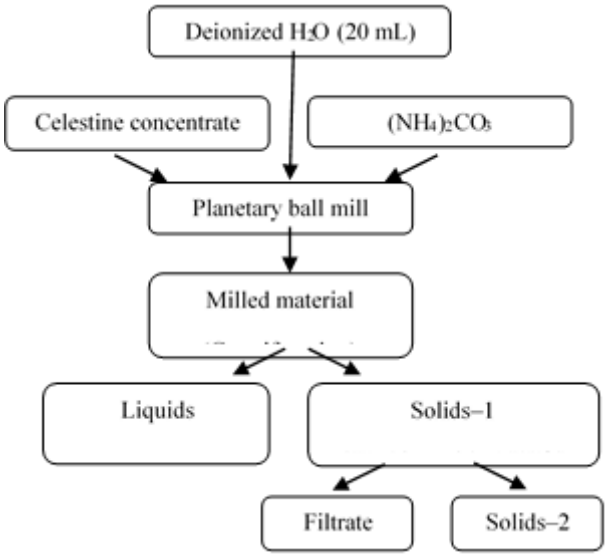


Figure 1. The flowsheet of wet conversion experiments (Yaş dönüşüm deneylerinin akım şeması)

2.3. Characterization

The compositions of the celestine concentrate and the reaction products were analyzed using SHIMADZU XRD-6000 model of X-ray diffraction (XRD), Bruker Tensor 27 model of Fourier transform infrared (FTIR) spectroscopy, and JEOL JSM-6060 model of a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Milling time

The effect of milling time was investigated in the range of 10–90 min in a planetary type ball mill. The celestine concentrate for different periods of time was mechanochemically treated with $(NH_4)_2CO_3$ and H_2O. The test conditions were a 10 ball-to-milled material mass ratio, 2 $(NH_4)_2CO_3$-to-$SrSO_4$-mole ratio, and a 400–rpm mill rotational speed. As seen in Figure 2, a milling time longer than 75 min did not significantly affect conversion. Our previous research results[21] showed that the best conversion of celestine to strontianite was obtained during dry milling after a 180–min activation time of longer than wet milling time.

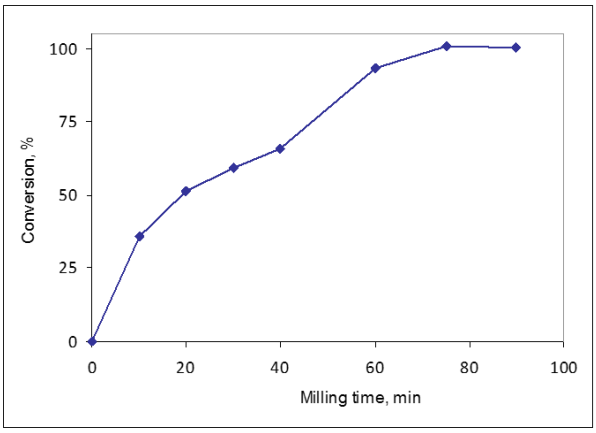


Figure 2. The effect of grinding time to wet conversion (Öğütme süresinin yaş dönüşüme etkisi)

3.2. Ball/grinding material ratio (w/w)

The effect of ball/grinding material ratio (w/w) was examined in the range of 5–40. The tests were performed in conditions of 75 min of milling time, $(NH_4)_2CO_3/SrSO_4$ mole ratio (2/1), and 400–rpm of the rotational speed of mill. Figure 3 shows the variation in conversion of celestine to $SrCO_3$ as a function of ball/grinding material ratio. The conversion of celestine increased up to mass ratio of 10. Thereafter, the conversion declined slightly in consequence of reduced contact between the ball and a small amount of grinding material.

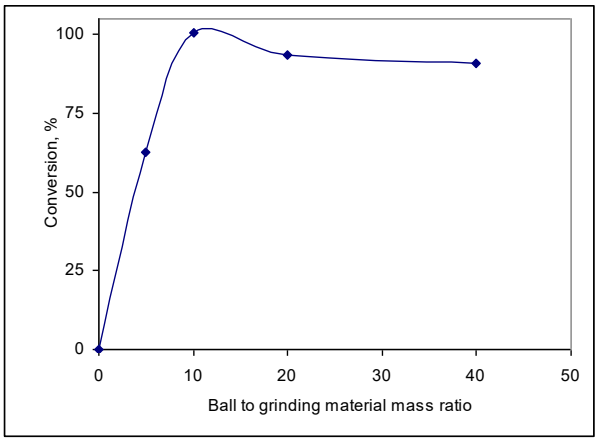


Figure 3. The effect of ball/grinding material ratio (w/w) to wet conversion (Bilya/öğütme malzemesi oranının yaş dönüşüme etkisi)

3.3. The $SrSO_4/(NH_4)_2CO_3$ mole ratio

The effect of $SrSO_4/(NH_4)_2CO_3$ mole ratio on wet conversion was investigated using 1, 1.1, 1.3, 1.5, 1.75, 2, 3, and 4 mole ratios of $SrSO_4$ to $(NH_4)_2CO_3$. 75 min grinding time, 10 ball/grinding material ratio (w/w), and a 400 rpm mill rotational speed were selected as experimental conditions. As shown in Figure 4, the

conversion of celestine to $SrCO_3$ was not exactly in 75 min at stoichiometric amount of $(NH_4)_2CO_3$. The conversion of celestine to $SrCO_3$ increased with an increase of $(NH_4)_2CO_3$. Bingöl et al. (2012a) noted that "Conversion occurs dynamically as a result of mechanochemical contact between the surface of the celestine and the reaction media". The ion exchanges increase due to a high amount of $(NH_4)_2CO_3$. The amount of required $(NH_4)_2CO_3$ for conversion must be excess of the stoichiometric amount required. The high conversion was reached a 2-$(NH_4)_2CO_3/SrSO_4$ mole ratio. The conversion decreased at higher mole ratio than 2 of $(NH_4)_2CO_3/SrSO_4$ mole ratio can be explained by taking into account of insufficient contact between balls and grinding material [23]. Mole ratio is an important factor for wet mechanochemical conversion.

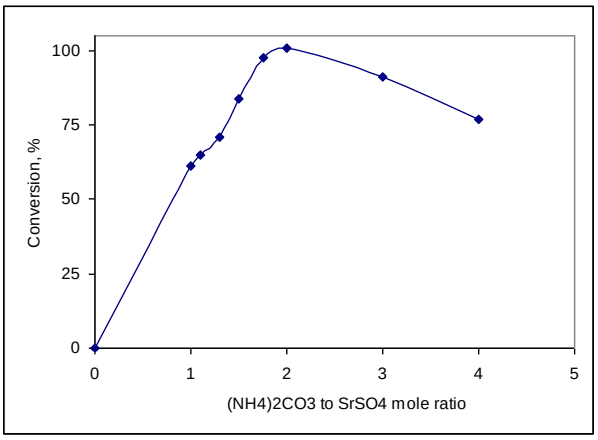


Figure 4. Effect of the $(NH_4)_2CO_3$ to $SrSO_4$ mole ratio on wet conversion ($(NH_4)_2CO_3/SrSO_4$ mol oranının yaş dönüşüme etkisi)

3.4. The rotational speed of mill

The effect of mill rotational speed for 100, 200, 300, 400, and 500 rpm is shown in Figure 5 (milling time: 75 min, ball/grinding material ratio (w/w): 10, and $(NH_4)_2CO_3/SrSO_4$ mole ratio: 2. The rotational speed of mill was observed to increase up to 400 rpm; later, the conversion decreased. Increasing mill speed increases impact energy between particles. At higher rotational speed of mill, the conversion was slightly decreased because of insufficient contact between the balls and grinding material.

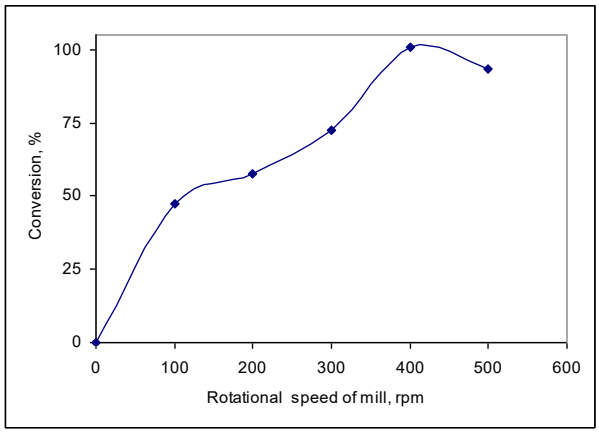


Figure 5. Effect of the rotational speed of mill on wet conversion (Değirmen dönüş hızının yaş dönüşüme etkisi)

Obut et al. [17] have shown that the conversion of celestine with Na_2CO_3 was 93.0% after 20 min by wet milling; whereas we reached about 100% after 75 min using $(NH_4)_2CO_3$ in a planetary ball mill by wet mechanochemical conversion. It should be noted that we used different mole ratios $(NH_4)_2CO_3$ to $SrSO_4$ and different milling runs with a ball to milled material mass ratio of 10.

3.5. FT-IR analysis

For observing structural changes, IR spectra of celestine (a) and the product of wet mechanochemical treatment (b) shows in Figure 6 (milling time: 75 min, ball/milled material ratio (w/w): 10, $(NH_4)_2CO_3/SrSO_4$ mole ratio: 2, mill rotational speed: 400–rpm). In Figure 6a, the bands at 992 and 1070 cm^{-1} are characteristic of the sulfate group in celestine. The peak at 856 cm^{-1} as well as the broad band at 1437 cm^{-1}, seen in Figure 6b, defines the carbonate group in formed $SrCO_3$ [25–27]. Thus, FT–IR analysis supports the realization of the conversion to $SrCO_3$ of celestine by wet mechanochemical processing.

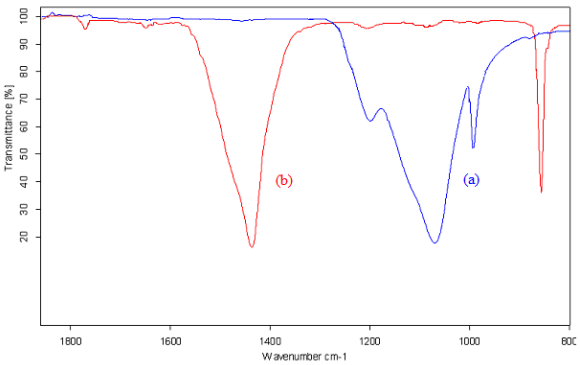


Figure 6. FT-IR spectra of (a) celestine concentrate and (b) the product of mechanochemical treatment ((a) sölestin konsantresi ve (b) mekanokimyasal işlem sonrası ürünün FT-IR spektrumu)

Figure 7 shows the FT-IR spectra of pure $(NH_4)_2SO_4$ crystal and $(NH_4)_2SO_4$ crystal obtained from $(NH_4)_2SO_4$ solution after wet conversion. As can be seen, the spectra of $(NH_4)_2SO_4$ crystal obtained from the leach solution (Figure 7b) are identical to the spectra of pure $(NH_4)_2SO_4$ crystal (Figure 7a). The bands 608 and 1065 cm^{-1} are assigned to the stretch of SO , and the bands 1403 and 3199 cm^{-1} are assigned to the stretch of NH [28]. However, the bands of the NH symmetric bending absorption and SO stretching absorption of SO can be assigned at 1458 and 1105 cm^{-1}, respectively. The wavenumber of the NH band is relatively lower by approximately 30–60 cm^{-1} than those in pure $(NH_4)_2SO_4$ crystal, proposing that a strong hydrogen bond between of NH and SO may form [29].

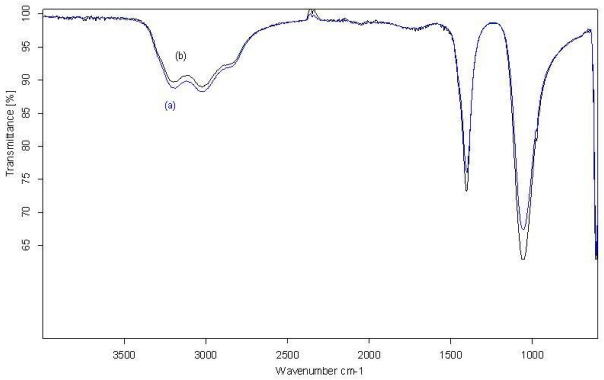
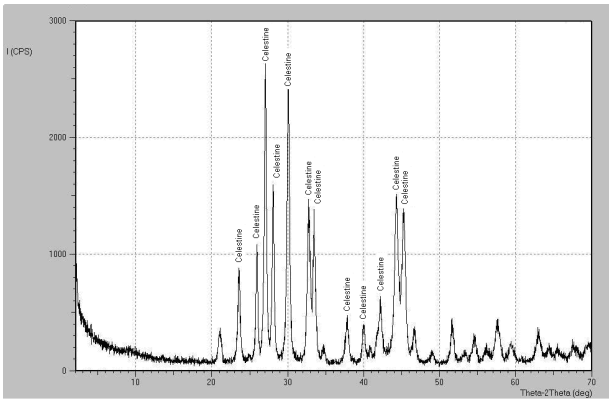


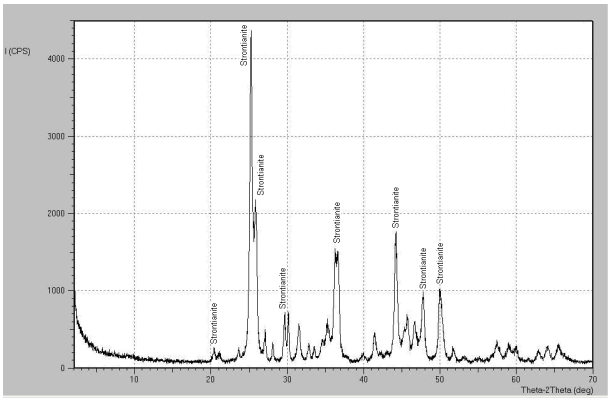
Figure 7. FT-IR spectra for (a) pure $(NH_4)_2SO_4$, (b) $(NH_4)_2SO_4$ crystal obtained from the leach solution after wet mechanochemical conversion ((a) saf $(NH_4)_2SO_4$ ve (b) yaş mekanokimyasal dönüşümden sonra liç çözeltisinden elde edilen $(NH_4)_2SO_4$ kristalinin FT-IR spektrumu)

3.6. XRD analysis

Conversion of celestine into $SrCO_3$ was also investigated by XRD analyses [Cu Kα: 0.154 nm]. Structural changes in the raw celestine and the treated celestine could be showed in Figures 8 (a) and (b), respectively. The major phase in the concentrate was celestine ($SrSO_4$) [PDF No: 5-593] (Figure 8a). The XRD pattern of the product of mechanochemical treatments is given in Figure 8b. The phase in the product is strontianite ($SrCO_3$) [PDF No: 5-418].



(a)

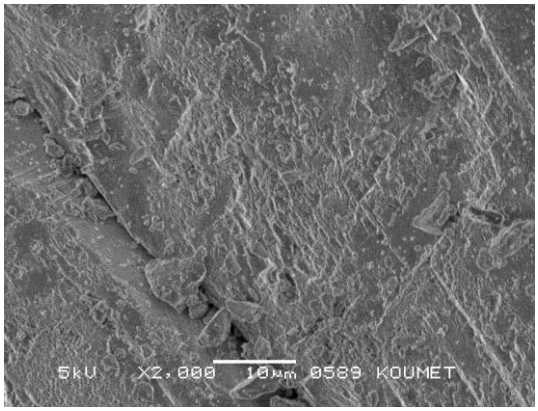


(b)

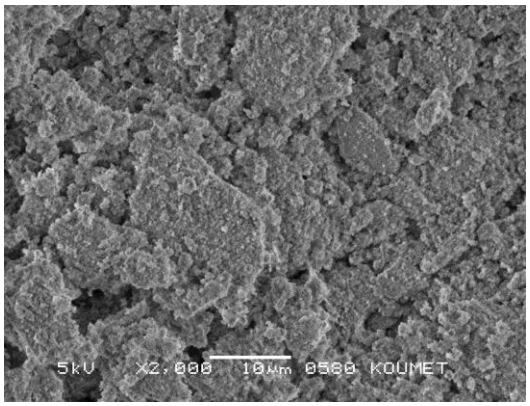
Figure 8. XRD patterns of (a) the raw celestine and (b) the product of mechanochemical treatment ((a) ham sölestin ve (b) mekanokimyasal işlem sonrası ürünün XRD paterni)

3.7. SEM analysis

The surface morphology of the raw celestine and product were observed using SEM analysis. In Figures 9 (a) and (b), SEM analysis of the celestine concentrate and the product are shown. The celestine concentrate consists of angular particles and facet surfaces (Figure 9a), but the product contains spheric particles and agglomerates (Figure 9b).



(a)



(b)

Figure 9. SEM photos of (a) celestine concentrate and (b) the product of mechanochemical treatment ((a) ham sölestin ve (b) mekanokimyasal işlem sonrası ürünün SEM görüntüleri)

4. CONCLUSION

The conversion of celestine to $SrCO_3$ can be obtained via wet mechanochemical treatment using $(NH_4)_2CO_3$ in a planetary mill. The reaction products, $SrCO_3$ and $(NH_4)_2SO_4$, were obtained as a result of using $(NH_4)_2CO_3$. The conversion of celestine to $SrCO_3$ was essentially complete within 75 min. The conversion was nearly 100% at the milling time of 75 min, ball/grinding material ratio (w/w) of 10, $(NH_4)_2CO_3/SrSO_4$ mole ratio of 2, and a mill rotational speed of 400 rpm. However, our previous research results showed differences in the mechanochemical conversion of celestine by dry and wet methods. Our previous research [21] results showed that the percentage of conversion of dry milled solids ($SrSO_4$–$SrCO_3$ mixture) was 98 after 180 min dry milling in a planetary ball mill, whereas in present our work the percentage reached about 100 less than as 75 min in a wet planetary ball mill. Similar results were also found using the RSM model [23]. It is demonstrated that the effect of milling time on the changes during wet milling that leads to the conversion of celestine to $SrCO_3$ was the most important difference between dry and wet methods. The conversion time for wet milling was an advantage in that it was less than for dry milling.

Acknowledgements

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