

Received March 6, 2018; reviewed; accepted May 17, 2018

Mechano-chemical conversion of celestite in highly concentrated sodium carbonate media

Raşit Sezer ^{1,2}, Cüneyt Arslan ²

¹ Karadeniz Technical University

² Istanbul Technical University

Corresponding author: rasisetzer@gmail.com (Raşit Sezer)

Abstract: An effect of high-energy ball milling on the mechano-chemical conversion of celestite to strontium carbonate (SrCO_3) was studied. A celestite ore was ground by a planetary ball mill in a highly concentrated sodium carbonate (Na_2CO_3) solution. The experimental study was carried out to determine the effects of milling time (15, 30, and 45 min) and Na_2CO_3 concentration (1, 1.25, and 1.5 M) on the particle size and SrCO_3 percentage of the product. A celestite/ball weight ratio was selected as 1/10 and the volume of carbonate solution was calculated for the stoichiometric amount of sulfate in celestite, as constant. After filtering, washing and drying the precipitated SrCO_3 sludge was analyzed by XRD, SEM-EDS. Powders were leached in HCl solution and analyzed by AAS in order to determine the SrCO_3 amount in the product. A response surface methodology was applied via the Box-Behnken method for the results of particle size and SrCO_3 percentage. Regression model coefficients were 98.61 and 98.14%, which were the results of compatibility as experimentally obtained and predicted by the model, respectively. The maximum amount of SrCO_3 , 96.84% and the minimum particle size, 10.297 μm were obtained with the maximum values of the parameters, 45 min, 1.5 M Na_2CO_3 , and 450 rpm.

Keywords: celestite, wet milling, direct conversion, response surface methodology, strontium carbonate

1. Introduction

Strontium carbonate is the most common strontium compound for the production of electroceramics, oxide superconductors, special glasses, strontium metal and the strontium compounds such as strontium chloride (SrCl_2), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), strontium hydroxide ($\text{Sr}(\text{OH})_2$), etc. (Habashi, 1997). The only commercial mineral of strontium is celestite (SrSO_4) (Doğan et al., 2004). Strontium carbonate is produced by two different methods; black ash and direct conversion methods. In the black ash method, the celestite is reduced with coke and strontium sulfide is obtained at 1000 – 1200 °C. The reduced ore is dissolved in water at about 85 – 90 °C. Then, dissolved strontium is precipitated by the carbonating agents such as sodium carbonate (Na_2CO_3), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) or carbon dioxide (CO_2) (Erdemoğlu and Canbazoglu, 1998; Erdemoğlu et al., 2006; Meng et al., 2009). Second method is direct conversion, which is an ion exchange reaction of SrSO_4 with any carbonate. There are several studies about these two commercial methods.

Previous studies, related to the conversion of celestite to SrCO_3 , have been carried out by dissolving and carbonating of celestite in molten alkali salts at elevated temperatures. Taking advantage of the solubility of SrSO_4 in NaCl, the ion exchange reaction occurs with Na_2CO_3 and K_2CO_3 , to form SrCO_3 . SrCO_3 can be produced with a yield of 99.34 % at 840 °C by mixing celestite with NaCl and Na_2CO_3 (Booth and Pollard, 1948). It has been found that in the presence of alkali halides such as LiBr and NaBr in the NaCl salt at 850 °C, celestite is converted to SrCO_3 with Na_2CO_3 and K_2CO_3 , but the alkali halides do not react (Busey and Pollard, 1948).

Studies on the production of SrCO_3 in carbonate solutions have been based on examining the behavior of celestite in Na_2CO_3 and $(\text{NH}_4)_2\text{CO}_3$ solutions. SrCO_3 formation is possible under basic

conditions ($\text{pH} > 7.75$) in aqueous solutions of celestite mineral in air. Martínez and Uribe (1995) found that celestite could react with CO_3^{2-} ions formed by dissolution of CO_2 gas from air, in the aqueous media (Martínez and Uribe, 1995). The conversion of SrSO_4 to SrCO_3 takes place on the surface and as the reaction progresses, the thickness of the SrCO_3 layer on the surface increases (Sanchez-Pastor et al., 2007). Diffusion of sulfate ions in the strontium carbonate layer on the surface determines the rate of reaction (Iwai and Toguri, 1989; Zoraĝa et al., 2016). According to the studies on the conversion kinetics carried out by different researchers; the mixing speed and the increase of the solution temperature were found to increase the reaction speed while the increase of the ore size and solid/liquid ratio slowed down the reaction (Bingöl et al., 2010; Carrillo et al., 1995; Castillejos et al., 1996; Iwai and Toguri, 1989; Martínez and Uribe, 1995; Zoraĝa and Kahruman, 2014; Zoraĝa et al., 2016). In addition, while the concentration of Na_2CO_3 is sufficient to satisfy the stoichiometric requirement, the concentration of SO_4^{2-} ions has a negative effect on the reaction rate beyond 1 M. Conversion of CO_3^{2-} ions to HCO_3^- ions slows down the reaction when the pH value of the solution is lowered under $\text{pH} < 9$ (Castillejos et al., 1996). Suarez-Orduna et al. (2004) and Rendon-Angeles et al. (2006) studied the behavior of single crystal celestite ore in Na_2CO_3 , K_2CO_3 , NaOH and NaF solutions at hydrothermal conditions and at temperatures between 150 and 250 °C. The SrCO_3 formed in the carbonate solutions was found to be identical in shape and size to the original celestite (Suárez-Orduña et al., 2004; Suárez-Orduña et al., 2007). Despite the fact that in the NaF solution the crystals completely converted to SrF_2 , but in the hydroxide solution, the $\text{Sr}(\text{OH})_2$ crystals formed immediately as transparent powder due to the continuous dissolution/recrystallization mechanism in the hydrothermal fluid (Rendon-Angeles et al., 2006).

Mechano-chemical processes reduce the crystal activation of minerals by high-energy milling and reduce the activation energy required for reaction (Baláž et al., 2014). There are only a few studies available in the literature for the production of SrCO_3 from celestite, using devices such as planetary type ball mills and attritors. In the studies carried out, the conversion ratio of SrSO_4 to SrCO_3 was investigated by changing the grinding parameters such as celestite/carbonate ratio, solid/liquid ratio, grinding speed, and time in dry or aqueous Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ media. (Erdemoĝlu et al., 2007; Obut et al., 2006). Celestite ore can be converted to SrCO_3 by washing with pure water after grinding with sodium carbonate in planetary type ball mill. Conversion starts with 10 min high-energy grinding and the conversion ratio increases to 90 % after 30 minutes (Setoudeh et al., 2010). A conversion rate of 98 % can be obtained after washing of 180 min dry-milled celestite and $(\text{NH}_4)_2\text{CO}_3$ where it is possible to achieve a conversion rate of 99.08 % after 75 min of wet milling (Bingöl et al., 2012a; Bingöl et al., 2012b).

Zhang and Saito (1996) reported SrCO_3 precipitation by keeping the mixture of celestite and NaOH , which was 120 min milled in a planetary type ball mill, in pure water for up to 1 week. It was found that after grinding, the powders were converted to $\text{Sr}(\text{OH})_2$ and after that SrCO_3 was formed due to the dissolution of CO_2 of the air (Zhang and Saito, 1997). In a similar work, Turianicová et al. (2013) investigated the ability of celestite to convert to SrCO_3 in the presence of LiOH and NaOH , in CO_2 atmosphere. No reaction was observed in the presence of LiOH , even though celestite reacted with CO_2 and NaOH during dry milling and converted to SrCO_3 . However, thanks to the Li_2CO_3 occurrence, SrSO_4 in celestite has been converted to SrCO_3 during the washing (Turianicová et al., 2013).

Although strontium sulfate and strontium carbonate both have low solubility in water, driving force of conversion is that the solubility constant of strontium carbonate (K_{sp} : 5.6×10^{-10}) is lower than the solubility constant of strontium sulfate (K_{sp} : 3.44×10^{-7}) (Haynes, 2014). Celestite is converting to strontium carbonate in aqueous sodium carbonate solution according to the following equation;



CO_3^{2-} ions that are released by the complete dissolution of the Na_2CO_3 react with the Sr^{2+} ions passing through the solution by the partial dissolution of the SrSO_4 , and thus the SrCO_3 solid particles are precipitated. The conversion reaction occurs on the surface of celestite particles via the diffusion of the CO_3^{2-} ion passing through the porous SrCO_3 layer. Total conversion of celestite takes quite long time in conventional celestite leaching in aqueous sodium carbonate media. This process requires very high carbonate concentrations (Castillejos et al., 1996; Iwai and Toguri, 1989). Thanks to mechano-chemical process, however, high conversions can be achieved in shorter times with lower carbonate concentrations (Baláž, 2003).

In this study, conversion of celestite (as received) to SrCO_3 by high-energy wet milling in Na_2CO_3 solution was investigated in the light of particle size and SrCO_3 percentage of the product. The effects of milling speed (150 – 450 rpm), carbonate concentration (1 – 1.5 M), and milling time (15 – 45 min) in sodium carbonate solution were investigated. Although there are some studies on mechano-chemical conversion of celestite, in those studies, the solid/liquid ratio was selected considerably low and the particle size change was not investigated. On the other hand, starting particle size of celestite is chosen smaller, mostly finer than 250 microns, where < 2 mm ore is used in this study. This paper researches the particle size variation and SrCO_3 percentage of the product that was high-energy milled in highly concentrated aqueous media with high solid/liquid ratio (25/136). A three-level Box-Behnken design, response surface methodology was adopted to assess the effect of parameters on the particle size and SrCO_3 percentage, which are very important specifications for further processes.

2. Materials and methods

Celestite ore with < 2 mm particle size, kindly provided by Barit Maden Türk A.Ş., has 95 % SrSO_4 , 3 % CaSO_4 , and other impurities. Each experimental run starts with introducing 25 g celestite and 136 cm^3 sodium carbonate (Na_2CO_3) solution into the milling jar that is made out of tungsten carbide (WC). Total weight of WC balls is 250 g, each having a diameter of 10 mm. The concentration of the carbonate solution is adjusted to 1, 1.25, and 1.5 M, which are the multiples of stoichiometric carbonate needs for celestite conversion. Fritsch Pulverisette 6 planetary ball mill was used for high-energy milling. Milling speeds are 150, 300, and 450 rpm; times are 15, 30 and 45 min, between every 5 min of milling, 2 min break was taken for cooling.

After milling process, solid and the liquid phases were separated by centrifuging. Solids were washed four times with 200 cm^3 of distilled water and dried at 105 °C for 24 hours. Dried solids were analyzed by X-Ray Diffractometer (PANalytical X'pert Pro) to determine chemical structures and Zeiss Evo LS100 scanning electron microscope (SEM) with Bruker Quantax energy dispersive spectrometer (EDS) was used for morphological investigation of powders. To determine the percentage of strontium carbonate (SrCO_3), Perkin Elmer AAnalyst 400 atomic absorption spectrometer (AAS) was used. One gram of each milled solid was dissolved in 100 cm^3 1 M HCl solution and then the ratio of the soluble SrCO_3 was calculated from [Sr] data of AAS analyses of the leach solution.

The conversion efficiency of strontium sulfate (SrSO_4) to strontium carbonate (SrCO_3) was optimized by the response surface methodology using Box-Behnken Design (BBD), which is a collection of mathematical and statistical technique to model and analyze the engineering problems. Optimization of the various process parameters can be made as a result of the responses. The statistical software MINITAB 17 was used for evaluation of the data. Milling time, X_1 (15 – 45 min), sodium carbonate concentration, X_2 (1 – 1.5 M) and the milling speed, X_3 (150 – 450 rpm) were selected as independent variables. The values of the parameters are given in Table 1 with their coded levels.

Table 1. Experimental parameters

Variables	Values		
	Low (-1)	Medium (0)	High (+1)
X_1 Milling time (min)	15	30	45
X_2 Sodium carbonate concentration (M)	1	1.25	1.5
X_3 Milling speed (rpm)	150	300	450

Assuming that all variables are measurable, the response surface can be expressed by the following equation;

$$Y = f(X_1, X_2, X_3, \dots, X_k) \quad (2)$$

where Y is the response of the system, and X_i is the variables of action, called factors.

In response surface methodology, the purpose is to optimize the response variable (Y), which is the maximum value of the SrCO_3 percentage and the moderate particle size of the product. Independent variables are assumed to be continuous and controllable by experiments with negligible errors. It is necessary to find an appropriate approach for the real functional relationship between the dependent

variables and the response surface. A second-order mathematical model is built, which can be expressed by the following equation;

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where Y is the response, X_i means the coded values of process parameters. β is an intercept coefficient, β_i is linear coefficient, β_{ii} is quadratic coefficient, β_{ij} is interaction coefficient, and ε is a random error. The second order model to be determined in the β coefficients is obtained by the least squares. Eq.3 matrix can be written in general form (Eq. 4).

$$Y = bX + \varepsilon \quad (4)$$

Y is defined as a matrix of measured values from independent variables (X), coefficients (b) and the errors (ε).

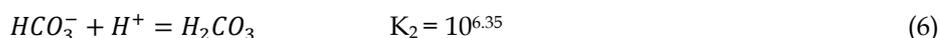
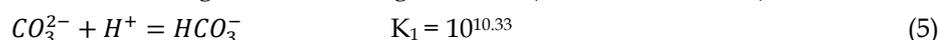
The quality of the fit and the significance of the polynomial model can be identified by the coefficient of determination (R^2) and the P-values.

3. Results and discussion

3.1. Mechano-chemical conversion

In this study, the effect of different grinding times, speed, and carbonate concentration on the mechano-chemical transformation and the particle size of celestite were investigated. The volume of milling liquid is defined from Eq.1 by calculating the stoichiometric need of 1 M sodium carbonate solution to satisfy for conversion of 25 g strontium sulfate to strontium carbonate. Three different concentrations; 1, 1.25, and 1.5 M are the multiples of the calculated carbonate need. The temperature of the system never exceeded 30 °C. After milling process, the solid/liquid separation was done by centrifuging and measured pH value of the liquid phase was between 10 and 11.

When sodium carbonate is dissolved in water, a partial amount of carbonate ions transforms to polybasic acid and bicarbonate according to the following reactions (Carrillo et al., 1995);



Mole fractions of the polybasic acid, carbonate, and bicarbonate ions are constant at constant pH, even if the total concentration changes. Accordingly, the relative molar fractions of CO_3^{2-} , HCO_3^- and H_2CO_3 in equilibrium depend on the pH of the solution, are shown in Fig. 1. Calculation from Eq. 5, $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ is 0.21 and $[\text{H}_2\text{CO}_3]/[\text{HCO}_3^-]$ is $10^{-4.65}$ from Eq. 6 when pH is 11. This means that, in the working solution, there is only a small amount of H_2CO_3 , that is quite negligible and, actual CO_3^{2-} ion concentration is more than 80 % of total concentration, which is valid for all total concentration and the whole reaction period.

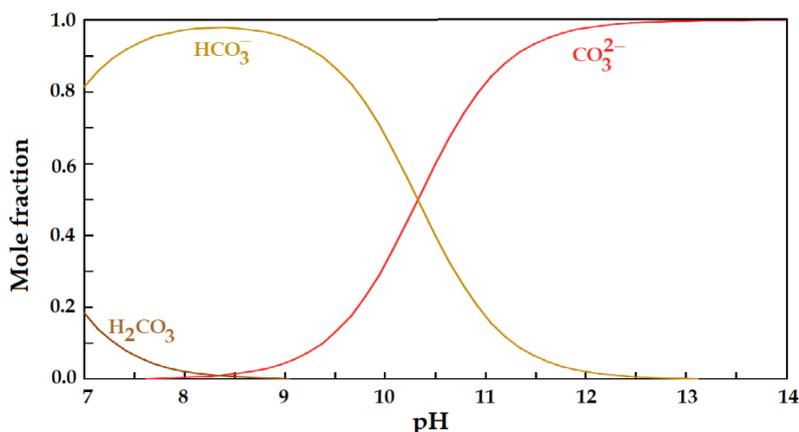


Fig. 1. Relative mole fractions of CO_3^{2-} , HCO_3^- and H_2CO_3 depending on pH at 25 °C (Castillejos et al., 1996)

Washed and dried solid powders were analyzed by SEM-EDS to determine the conversion of SrSO_4 morphologically (Fig. 2). Shape of the original celestite mineral is angular (Fig. 2a). As the milling speed,

time, and carbonate concentration increase, the amount and number of sharp-angled SrSO_4 grains decreased, as well as fine rounded SrCO_3 grains (usually appear as lighter particles in the images) became widespread (Fig. 2b – d). Through wet milling in carbonate media, the celestite particles are crumbled and the surface area for the reaction expands. In addition, SrCO_3 powders, formed on the surface of celestite, are disintegrated from the surface via crushing by milling media so that the new SrSO_4 surface is released for continuing the reaction, which is explained in Fig. 3.

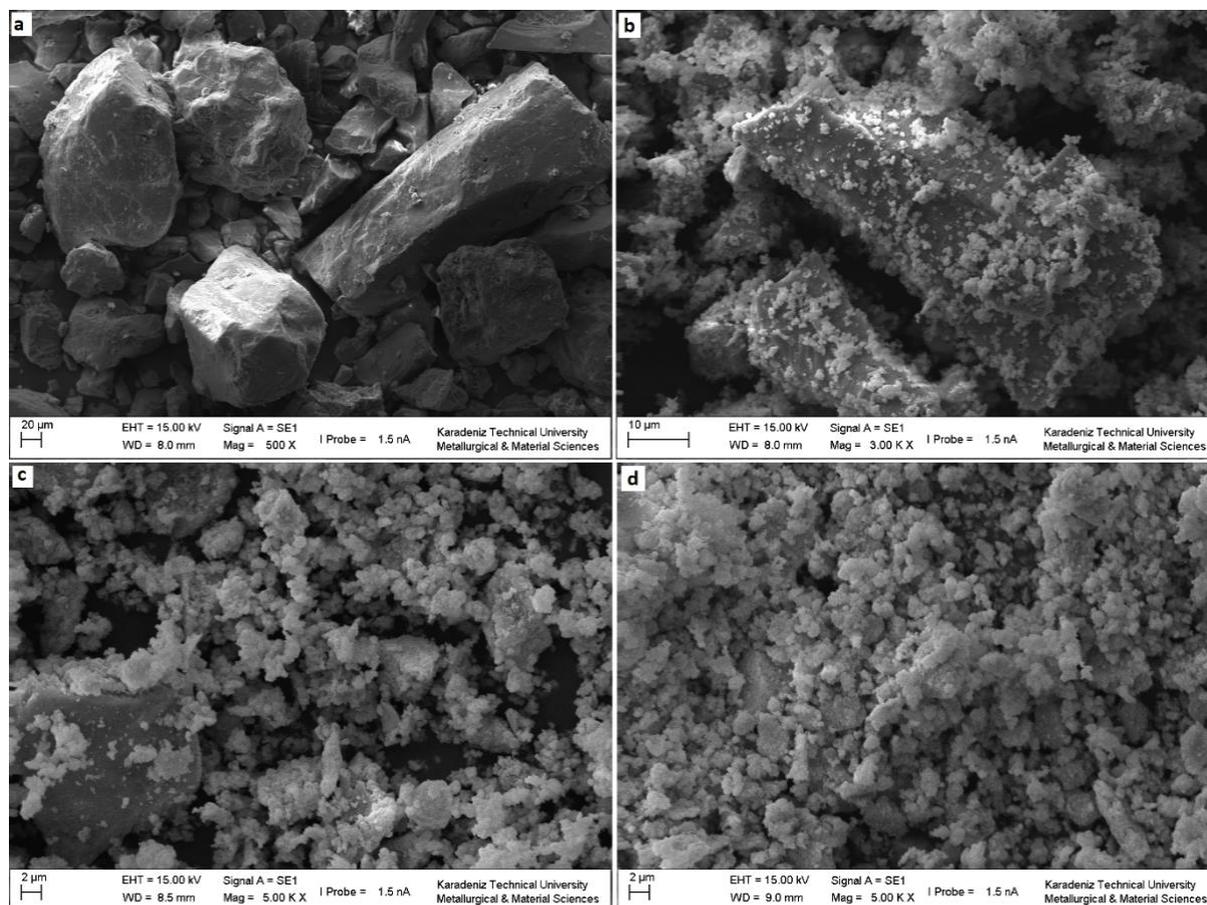


Fig. 2. SEM images of (a) the original celestite and wet milled powders (b) 1M, 150 rpm, 15 min, (c) 1.25 M, 300 rpm, 30 min, (d) 1.5 M, 450 rpm, 45 min

Some researchers have noted that the conversion of celestite to strontium carbonates in carbonate solutions is in accordance with the shrinking core model (Bingöl et al., 2010; Carrillo et al., 1995; Castillejos et al., 1996; Iwai and Toguri, 1989; Zorağa and Kahruman, 2014). According to this model, SrSO_4 in the celestite reacts with the carbonate ions in the solution and form a porous SrCO_3 layer on the particle surface (Fig. 3b). The SrCO_3 shell continues to grow as the SrSO_4 in the core reacts with the carbonate ions in the solution. The slowest phase of the process is that the reactant CO_3^{2-} ions pass through the shell to reach the internal SrSO_4 core and the product SO_4^{2-} ions pass away shell towards the solution. Therefore, the conversion becomes progressively more difficult, even if the CO_3^{2-} concentration in the solution is very high. However, in the mechano-chemical conversion, the particle is broken by the action of the impact, which causes new surfaces to emerge and so the reaction continues easily. In addition, the shell layer is thinned by breaking off the SrCO_3 layer formed on the surface (Fig. 3c). The conversion reaction occurs rapidly on the newly formed celestite surfaces and under the thinned shells (Fig. 3d). With repeated crashes, the whole process repeats itself (Fig. 3e). The surface area for the conversion reaction is enlarged thanks to the scaling and the thinning of the shells. Therefore, the total reaction time is tremendously shortened and even lower carbonate concentrations can be studied.

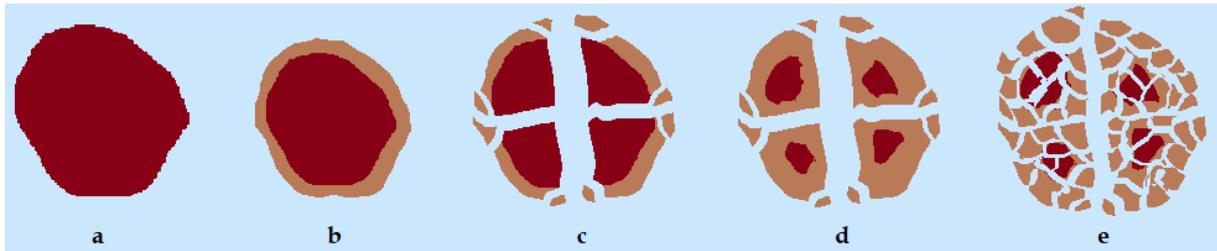


Fig. 3. Schematic view of the mechano-chemical conversion process

According to the XRD analyses, intensities of the peaks belong to SrSO_4 are decreasing during the mechano-chemical conversion (Fig. 4). XRD analysis of the celestite as-received has only SrSO_4 peaks where the highest intensity is on 25.906° that is 2θ of (0 0 2) plane. While increasing the time and speed of milling and carbonate concentration, the peaks that belongs to SrCO_3 start to appear. Results of the experiment with maximum values (1.5 M, 450 rpm, and 45 min) show that the majority of the peaks belongs to SrCO_3 and the peaks of SrSO_4 almost completely disappear because of complete conversion of SrSO_4 to SrCO_3 .

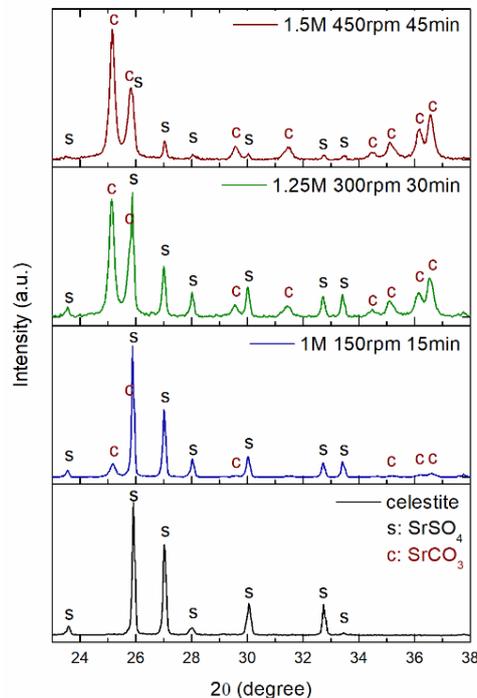


Fig. 4. XRD patterns of celestite and wet milled powders

3.2. Response Surface Methodology

The experimental design is produced by the response surface methodology with using Box-Behnken method. Fifteen experiments were done according to three factors, each of which has three coded levels to determine the responses (SrCO_3 % and d_{90}). The percentage of SrCO_3 was calculated from AAS analysis of 1 g wet milled powder that is leached in 100 cm^3 1 M HCl solution (Eq. 7). Where X_{Sr} is the value measured by AAS (g/L), M_{SrCO_3} is the molecular weight of SrCO_3 and M_{Sr} is the molecular weight of strontium.

$$\text{SrCO}_3\%_{\text{Wt.}} = \frac{X_{\text{Sr}} \cdot 0.1}{1} \cdot \frac{M_{\text{SrCO}_3}}{M_{\text{Sr}}} \cdot 100 \quad (7)$$

The second-order regression models are established from the observed experimental results (SrCO_3 % and d_{90}). The responses of any parameter combinations of the coded levels of milling time (X_1), carbonate concentration (X_2) and milling speed (X_3) can be calculated from the model equation (Eq. 8 and 9), where Y_1 is SrCO_3 % and Y_2 is particle size of 90 % of the product (d_{90}). The coded and the actual

levels of experiments produced by Box-Behnken design is given in Table 2 with results of SrCO₃ % and d₉₀; observed from experiments and the predicted from the regression model.

$$Y_1 = 72.807 + 12.499X_1 + 1.751X_2 + 16.120X_3 - 4.158X_1^2 - 2.793X_2^2 - 8.741X_3^2 + 0.505X_1X_2 - 0.593X_1X_3 + 0.743X_2X_3 \quad (8)$$

$$Y_2 = 16.53 - 7.077X_1 + 1.088X_2 - 11.139X_3 + 2.00X_1^2 - 0.06X_2^2 + 7.01X_3^2 - 0.96X_1X_2 + 5.35X_1X_3 - 0.15X_2X_3 \quad (9)$$

Table 2. Box-Behnken design layout with coded and actual with observed results (SrCO₃ % and d₉₀)

Exp. No.	Level of parameter						SrCO ₃ %		d ₉₀ (μm)	
	Coded			Actual			Observed	Predicted	Observed	Predicted
	X ₁	X ₂	X ₃	X ₁ /(min)	X ₂ /(M)	X ₃ /(rpm)				
1	-1	-1	0	15	1	300	52.60	52.11	21.533	23.506
2	+1	-1	0	45	1	300	74.80	76.10	12.955	11.272
3	-1	+1	0	15	1.5	300	55.90	54.60	25.919	27.602
4	+1	+1	0	45	1.5	300	80.12	80.61	13.501	11.528
5	-1	0	-1	15	1.25	150	30.63	30.70	51.434	49.108
6	+1	0	-1	45	1.25	150	58.60	56.88	22.931	24.261
7	-1	0	+1	15	1.25	450	62.40	64.12	17.466	16.134
8	+1	0	+1	45	1.25	450	88.00	87.93	10.349	12.675
9	0	-1	-1	30	1	150	43.72	44.14	33.033	33.386
10	0	+1	-1	30	1.5	150	44.93	46.16	35.223	35.866
11	0	-1	+1	30	1	450	76.13	74.90	12.056	11.412
12	0	+1	+1	30	1.5	450	80.31	79.89	13.637	13.284
13	0	0	0	30	1.25	300	73.12	72.81	15.771	16.530
14	0	0	0	30	1.25	300	72.60	72.81	17.291	16.530
15	0	0	0	30	1.25	300	72.70	72.81	16.528	16.530

The analysis of variance for regression model with the linear, square and interaction contributions is given in Table 3. As a significance test, the P-values of model, linear and square effects are lower than the confidence level ($P < 0.05$). Hence, linear and square effects of the parameters are statistically confident. The linear effect contribution s of the parameters is quite significant, which are 90.35 % and 80.51 % for SrCO₃ % and d₉₀, respectively.

Table 3. ANOVA results for regression model

Source	SrCO ₃ percentage				Particle size (d ₉₀)			
	Degree of freedom	Adjusted sum of square	P - Value	Contribution %	Degree of freedom	Adjusted sum of square	P - Value	Contribution %
Regression Model	9	3698.07	0.000	99.64	9	1712.25	0.001	98.27
Linear	3	3353.12	0.000	90.35	3	1402.78	0.000	80.51
Square	3	340.32	0.001	9.17	3	191.35	0.013	10.98
Interaction	3	4.63	0.654	0.12	3	118.12	0.035	6.78
Error	5	13.32		0.36	5	30.04		1.72
Total	14	3711.39		100	14	1742.29		100

According to the model equation (Eq. 8) for SrCO₃ %, the linear effect of the main variables (X₁, X₂, and X₃) are positive while the quadratic effects (X₁², X₂², and X₃²) are negative, which clearly explains the signs in front of the coefficients. Additionally, it can be seen from Table 4 and model equation that milling time coefficient (12.499) and milling speed coefficient (16.120) affect the result (SrCO₃ %) because the coefficients are quite higher than the coefficient of carbonate concentration (1.751). According to model equation (Eq. 9) for particle size (d₉₀), linear effects of milling speed and milling time are negative, which means that they decrease the particle size owing to the energy of milling. It can also be seen from Table 4 and model equation that milling time coefficient (7.077) and milling speed coefficient (11.139)

affect the result (d_{90}) mainly because the coefficients are quite higher than the coefficient of carbonate concentration (1.088).

Table 4. Estimated regression coefficients and test of statistical significance for analysis of model terms

Term	SrCO ₃ percentage			Particle size (d_{90})		
	Coefficient	Standard error of coefficient	P-Value	Coefficient	Standard error of coefficient	P-Value
Constant	72.807	0.943	0.000	16.53	1.42	0.000
X ₁	12.499	0.577	0.000	-7.077	0.867	0.000
X ₂	1.751	0.577	0.029	1.088	0.867	0.265
X ₃	16.120	0.577	0.000	-11.139	0.867	0.000
X ₁ * X ₁	-4.158	0.850	0.004	2.00	1.28	0.177
X ₂ * X ₂	-2.793	0.850	0.022	-0.06	1.28	0.967
X ₃ * X ₃	-8.741	0.850	0.000	7.01	1.28	0.003
X ₁ * X ₂	0.505	0.816	0.563	-0.96	1.23	0.469
X ₁ * X ₃	-0.593	0.816	0.500	5.35	1.23	0.007
X ₂ * X ₃	0.743	0.816	0.405	-0.15	1.23	0.906

Dual effects of the variables on the SrCO₃ percentage and the particle size evaluation of the product, while the third variable is at the center value, are shown via contour and surface plots in Fig. 5 and 6. The effects of milling time and milling speed on the particle size evaluation are higher at low efficiency rather than high efficiency and they are the most effective parameters, similarly witnessed on particle size. Carbonate concentration has a slight effect on conversion at low milling speed and times. However, this slight effect becomes more important at higher values of milling time and speeds, owing to the consumption of CO₃²⁻ ions by the conversion reaction.

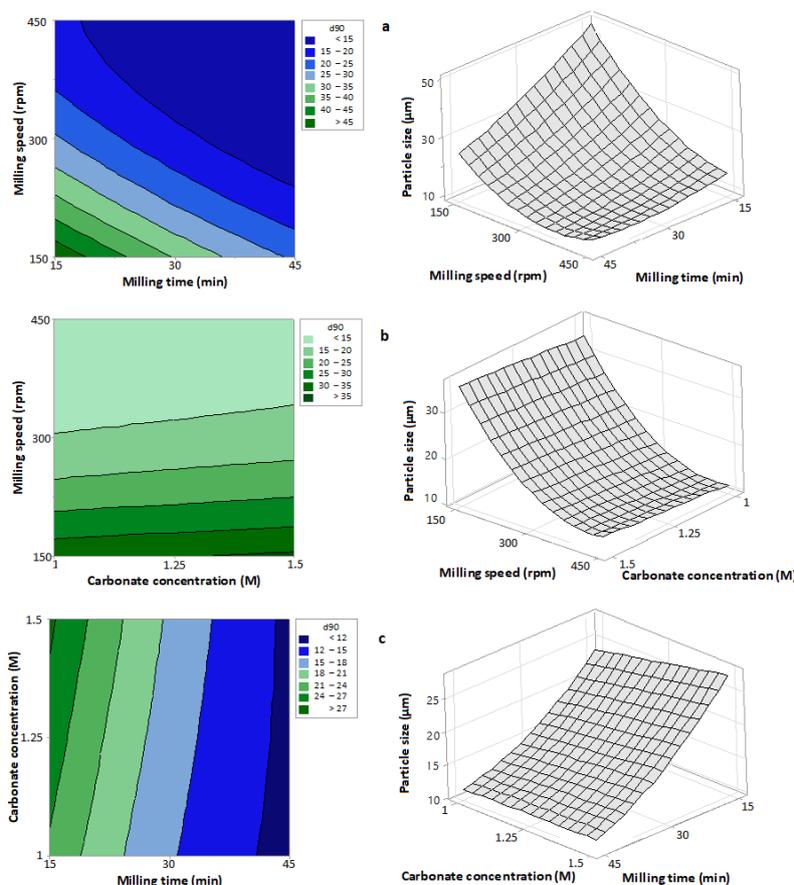


Fig. 5. Contour and surface plots reflecting the simultaneous dual effect of variables on particle size (d_{90}). a) milling time and milling speed, b) carbonate concentration and milling speed, c) milling time and carbonate concentration. Third variables are held at the center level; 30 min, 1.25 M and 300 rpm

The two most effective parameters, milling speed and time, are working together for reducing the particle size (Fig. 6a). Increases at low values are especially more effective in decreasing the particle size. When the dual effects of carbonate concentration, with the milling speed (Fig. 6b) or with milling time (Fig. 6c) are examined, the increase of carbonate concentration has a slight effect on the particle size. This slight effect thanks to the disintegration of SrCO_3 particles occurred by mechano-chemical conversion. Mechano-chemical conversion is a process, where chemical reaction and milling are working together. Milling makes the main job of grinding the particles. So milling time and speed have the major effect. Nevertheless, SrCO_3 shell, occurred by the chemical reaction, can be disintegrated easily.

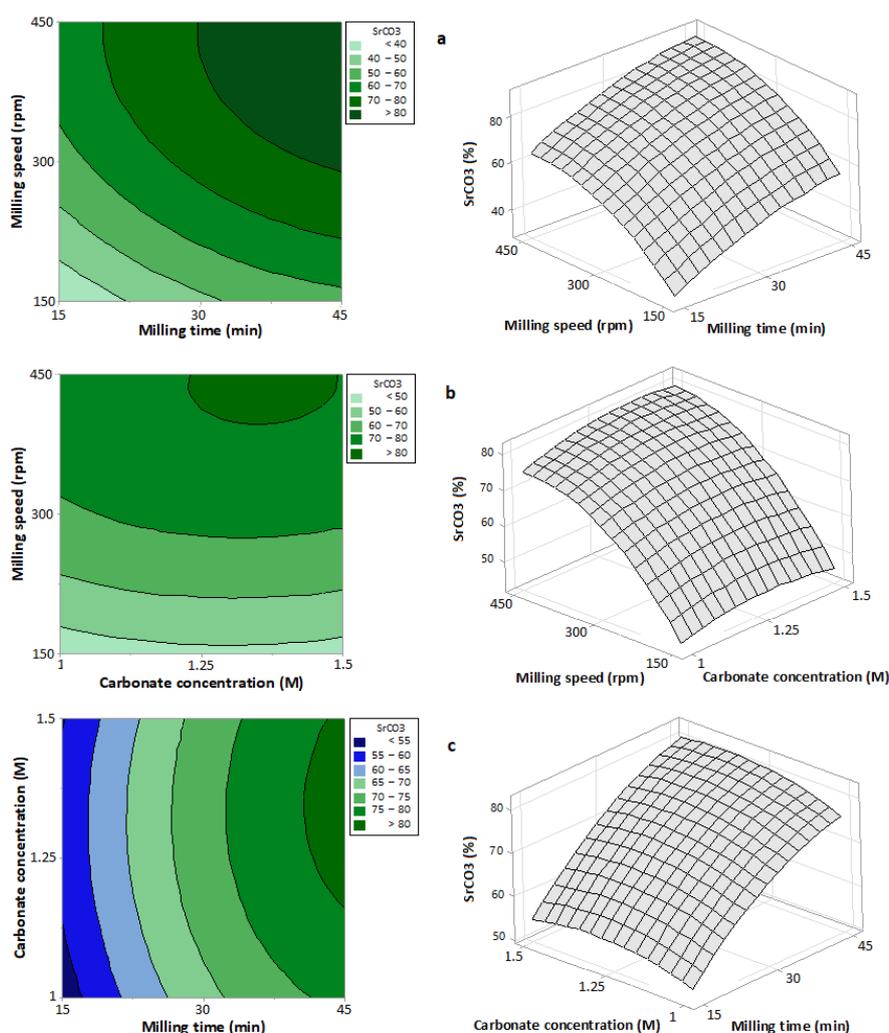


Fig. 6. Contour and surface plots reflecting the simultaneous dual effect of variables on SrCO_3 percentage. a) milling time and milling speed, b) carbonate concentration and milling speed, c) milling time and carbonate concentration. Third variables are held at the center level; 30 min, 1.25 M and 300 rpm

To verify and test the regression model, further experiments were done including the maximum and the minimum values. Table 5 shows the parameters of the verification experiments with observed and predicted results. The maximum conversion efficiency (96.84 %) was observed with the highest experimental parameters (Exp. No. 20). With the benefit of mechano-chemical conversion a product of SrCO_3 96.84 % is obtained at the parameters: 1.5 times of stoichiometrically needed Na_2CO_3 , room temperature, 45 min processing time. In order to attain this kind of efficiency in classical hydrometallurgical method, however, one needs to employ greater numbers for these parameters. For instance, Bingöl et al. (2010) reported that 97.36 % conversion can be obtained when the solution temperature is 60 °C, process time is 180 min, $\text{Na}_2\text{CO}_3/\text{SrSO}_4$ ratio is 4. Similarly, Castillejos et al. (1996)

noted a total conversion of SrSO_4 with 10 % excess Na_2CO_3 at 75 °C. Starting material celestite has to be fine (< 250 micron) in the conventional hydrometallurgical method, while it can be used as received (< 2 mm), as practiced in this study (mechano-chemical method).

Table 5. Verification experiments with observed results (% SrCO_3 and d_{90})

Exp. No.	Level of parameter						SrCO ₃ %		Particle size (d_{90})	
	Coded			Actual			Observed	Predicted	Observed	Predicted
	X ₁	X ₂	X ₃	X ₁ (min)	X ₂ (M)	X ₃ (rpm)				
16	-1	-1	-1	15	1	150	29.30	28.41	52.116	46.852
17	0	-1	-1	30	1	150	47.00	47.95	33.962	33.386
18	-1	0	0	15	1.25	300	54.64	56.15	24.587	25.609
19	+1	-1	+1	45	1	450	86.3	82.14	11.275	12.644
20	+1	+1	+1	45	1.5	450	96.84	88.14	10.297	12.595

The relationship between the experimental and predicted results are presented in Fig. 7. According to the model run, adjusted R^2 is 0.9961 for SrCO_3 percentage and is 0.9814 for particle size (d_{90}). The regression model has excellent correlation between the observed and predicted results for both model runs and verification runs except for the maximum level. Unfortunately, there is a large residue for the maximum level experiment that has 8.7 residues between actual and predicted result of SrCO_3 , 96.84 %, and 88.14 %, respectively.

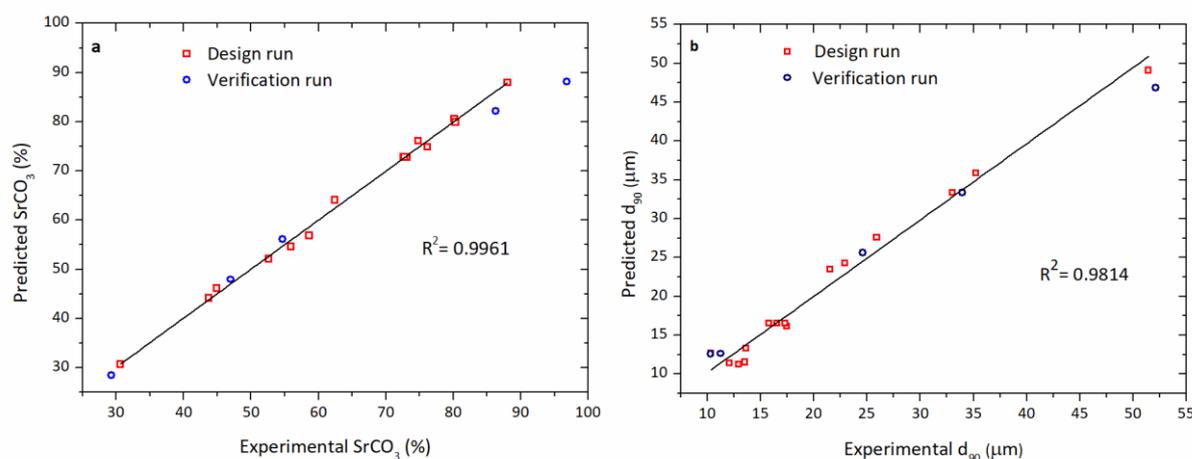


Fig. 7. Relationship between experimental and the predicted results for a) SrCO_3 % and b) d_{90}

4. Conclusions

Mechano-chemical conversion of celestite to strontium carbonate in highly concentrated sodium carbonate media by planetary ball mill was investigated via response surface methodology. Celestite was converted to SrCO_3 very efficiently, requiring no size reduction process, such as crushing, grinding, sieving etc. High efficiencies were obtained, as similar to the hydrometallurgical routes, in shorter periods, with less Na_2CO_3 amounts, and at low temperatures. The effects of milling time, carbonate concentration, and milling speed on particle size and SrCO_3 percentage of the product were investigated. Milling speed and milling time are the most effective parameters for both SrCO_3 percentage and the particle size evaluation. There is no significant effect of initial sodium carbonate concentration, but the concentration slightly affects the SrCO_3 percentage and the particle size of the product at only higher milling speed and extended milling time. By increasing the milling parameters, particle size decreases and the amount of SrCO_3 increases. The maximum efficiency of SrCO_3 (96.84 %) and the minimum particle size (10.297 μm) were obtained with the maximum values of the parameters; 45 min, 1.5 M, and 450 rpm. Regression models are compatible with experimental results, except the ones attained at the highest valued parameters.

Acknowledgments

This work was supported by Scientific and Research Council of Turkey (TUBITAK) [grant number 115M631].

References

- BALÁŽ, P., 2003. *Mechanical activation in hydrometallurgy*. International Journal of Mineral Processing, 72(1-4), 341-354. doi:http://dx.doi.org/10.1016/S0301-7516(03)00109-1
- BALÁŽ, P., BALÁŽ, M., BUJŇÁKOVÁ, Z., 2014. *Mechanochemistry in technology: from minerals to nanomaterials and drugs*. Chemical Engineering & Technology, 37(5), 747-756. doi:10.1002/ceat.201300669
- BİNGÖL, D., AYDOĞAN, S., GÜLTEKİN, S. S., 2010. *Neural model for the leaching of celestite in sodium carbonate solution*. Chemical Engineering Journal, 165(2), 617-624. doi:http://dx.doi.org/10.1016/j.cej.2010.10.007
- BİNGÖL, D., AYDOĞAN, S., BOZBAŞ, S., 2012. *Optimization of the wet mechanochemical process conditions of SrSO₄ to SrCO₃ and (NH₄)₂SO₄ by using response surface methodology*. Metallurgical and Materials Transactions B, 43(5), 1214-1219. doi:10.1007/s11663-012-9687-6
- BİNGÖL, D., AYDOĞAN, S., BOZBAŞ, S. K., 2012. *Production of SrCO₃ and (NH₄)₂SO₄ by the dry mechanochemical processing of celestite*. Journal of Industrial and Engineering Chemistry, 18(2), 834-838. doi:http://dx.doi.org/10.1016/j.jiec.2011.11.145
- BOOTH, H. S., POLLARD, E. F., 1948. *Conversion of celestite to strontium carbonate*. Industrial & Engineering Chemistry, 40(10), 1986-1988. doi:10.1021/ie50466a031
- BUSEY, H. M., POLLARD, E. F., 1948. *Conversion of Strontium Sulfate to Carbonate in Molten State - Effect of Alkali Halides*. Industrial & Engineering Chemistry, 40(10), 1988-1990. doi:10.1021/ie50466a032
- CARRILLO, F. R. P., URIBE, A. S., CASTILLEJOS, A. H. E., 1995. *A laboratory study of the leaching of celestite in a Pachuca tank*. Minerals Engineering, 8(4-5), 495-509. doi:http://dx.doi.org/10.1016/0892-6875(95)00012-F
- CASTILLEJOS, A. H. E., DE LA CRUZ DEL, F. P. B., URIBE, A. S. (1996). *The direct conversion of celestite to strontium carbonate in sodium carbonate aqueous media*. Hydrometallurgy, 40(1-2), 207-222. doi:http://dx.doi.org/10.1016/0304-386X(94)00060-G
- HABASHI, F. (1997). *Alkaline Earth Metals*. Handbook of Extractive Metallurgy Volume 4. Germany: WILEY-VCH.
- DOĞAN, H., KORAL, M., & KOCAKUŞAK, S., 2004. *Acid leaching of Turkish celestite concentrate*. Hydrometallurgy, 71(3-4), 379-383. doi:10.1016/S0304-386X(03)00089-6
- ERDEMOĞLU, M., AYDOĞAN, S., CANBAZOĞLU, M., 2007. *A kinetic study on the conversion of celestite (SrSO₄) to SrCO₃ by mechanochemical processing*. Hydrometallurgy, 86(1-2), 1-5. doi:http://dx.doi.org/10.1016/j.hydromet.2006.10.001
- ERDEMOĞLU, M., & CANBAZOĞLU, M., 1998. *The leaching of SrS with water and the precipitation of SrCO₃ from leach solution by different carbonating agents*. Hydrometallurgy, 49(1-2), 135-150. doi:http://dx.doi.org/10.1016/S0304-386X(98)00018-8
- ERDEMOĞLU, M., SARIKAYA, M., CANBAZOĞLU, M., 2006. *Leaching of Celestite with Sodium Sulfide*. Journal of Dispersion Science and Technology, 27(4), 439-442. doi:10.1080/01932690500357230
- HAYNES, W. M., 2014. *CRC Handbook of Chemistry and Physics* (W. M. Haynes Ed. 95th ed.). Boca Raton: CRC Press
- IWAI, M., TOGURI, J. M. (1989). *The leaching of celestite in sodium carbonate solution*. Hydrometallurgy, 22(1-2), 87-100. doi:http://dx.doi.org/10.1016/0304-386X(89)90043-1
- MARTÍNEZ, A. L., URIBE, A. S., 1995. *Interfacial properties of celestite and strontianite in aqueous solutions*. Minerals Engineering, 8(9), 1009-1022. doi:http://dx.doi.org/10.1016/0892-6875(95)00064-W
- MENG, J., LIU, G., ZHAO, H., WANG, L., YU, J., 2009. *Mechanism study on carbon reducing reaction in the preparation process of strontium carbonate (SrCO₃)*. Asia-Pacific Journal of Chemical Engineering, 4(5), 586-589. doi:10.1002/apj.291
- OBUT, A., BALÁŽ, P., GIRGIN, İ., 2006. *Direct mechanochemical conversion of celestite to SrCO₃*. Minerals Engineering, 19(11), 1185-1190. doi:http://dx.doi.org/10.1016/j.mineng.2005.11.001
- RENDON-ANGELES, J. C., PECH-CANUL, M. I., LOPEZ-CUEVAS, J., MATAMOROS-VELOZA, Z., YANAGISAWA, K., 2006. *Differences on the conversion of celestite in solutions bearing monovalent ions under hydrothermal conditions*. Journal of Solid State Chemistry, 179(12), 3645-3652. doi:10.1016/j.jssc.2006.07.043
- SANCHEZ-PASTOR, N., PINA, C. M., FERNANDEZ-DIAZ, L., 2007. *A combined in situ AFM and SEM study of the interaction between celestite (001) surfaces and carbonate-bearing aqueous solutions*. Surface Science, 601(14), 2973. doi:http://dx.doi.org/10.1016/j.susc.2007.05.002

- SETOUDEH, N., WELHAM, N. J., AZAMI, S. M., 2010. *Dry mechanochemical conversion of SrSO₄ to SrCO₃*. Journal of Alloys and Compounds, 492(1-2), 389-391. doi:<http://dx.doi.org/10.1016/j.jallcom.2009.11.114>
- SUÁREZ-ORDUÑA, R., RENDÓN-ANGELES, J. C., LÓPEZ-CUEVAS, J., YANAGISAWA, K., 2004. *The conversion of mineral celestite to strontianite under alkaline hydrothermal conditions*. Journal of Physics: Condensed Matter, 16(14), S1331-S1344. doi:10.1088/0953-8984/16/14/046
- SUÁREZ-ORDUÑA, R., RENDÓN-ANGELES, J. C., YANAGISAWA, K., 2007. *Kinetic study of the conversion of mineral celestite to strontianite under alkaline hydrothermal conditions*. International Journal of Mineral Processing, 83(1-2), 12-18. doi:<http://dx.doi.org/10.1016/j.minpro.2007.03.003>
- TURIANICOVÁ, E., OBUT, A., ZORKOVSKÁ, A., BALÁŽ, P., MATIK, M., BRIANČIN, J., 2013. *The effects of LiOH and NaOH on the carbonation of SrSO₄ by dry high-energy milling*. Minerals Engineering, 49, 98-102. doi:10.1016/j.mineng.2013.05.017
- ZHANG, Q., SAITO, F., 1997. *Mechanochemical processing of celestine*. Chemical Engineering Journal, 66(1), 79-82. doi:[http://dx.doi.org/10.1016/S1385-8947\(96\)03181-6](http://dx.doi.org/10.1016/S1385-8947(96)03181-6)
- ZORAĞA, M., KAHRUMAN, C., 2014. *Kinetics of conversion of celestite to strontium carbonate in solutions containing carbonate, bicarbonate and ammonium ions and dissolved ammonia*. Journal of the Serbian Chemical Society, 79(3), 345-359. doi:10.2298/jsc130307066z
- ZORAĞA, M., KAHRUMAN, C., YUSUFOĞLU, I., 2016. *Conversion kinetics of SrSO₄ to SrCO₃ in solutions obtained by dissolving/hydrolyzing of equimolar amounts of NH₄HCO₃ and NH₄COONH₂*. Hydrometallurgy, 163, 120-129. doi:<http://dx.doi.org/10.1016/j.hydromet.2016.03.021>