



## Sakarya University Journal of Science

ISSN 1301-4048 | e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University |  
<http://www.saujs.sakarya.edu.tr/>

Title: Mechanochemical Conversion Of Domestic Celestite Mineral To Sr<sub>2</sub>O<sub>4</sub> In The Ammonium Oxalate Media

Authors: Mert Zorağa

Received: 2019-03-05 00:11:51

Accepted: 2019-04-12 16:14:46

Article Type: Research Article

Volume: 23

Issue: 5

Month: October

Year: 2019

Pages: 840-847

### How to cite

Mert Zorağa; (2019), Mechanochemical Conversion Of Domestic Celestite Mineral To Sr<sub>2</sub>O<sub>4</sub> In The Ammonium Oxalate Media. Sakarya University Journal of Science, 23(5), 840-847, DOI: 10.16984/saufenbilder.535643

### Access link

<http://www.saujs.sakarya.edu.tr/issue/44066/535643>

New submission to SAUJS

<http://dergipark.gov.tr/journal/1115/submission/start>

## Mechanochemical Conversion of Domestic Celestite Mineral to $\text{SrC}_2\text{O}_4$ in The Ammonium Oxalate Media

Mert Zoraga<sup>\*1</sup>

### Abstract

The main raw material used in the production of Sr metal and its compounds is  $\text{SrSO}_4$  (celestite) mineral and Turkey has valuable Sr mineral deposits. One of the important steps in the production of Sr compounds is the production of strontium oxalate compound that does not contain alkali compounds as contamination. Strontium is used as a primary raw material in the production of oxalate superconducting material and luminescence.

In this study, *in situ* conversion of  $\text{SrSO}_4$  into  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by ammonium oxalate is investigated and the effects of rotational speed, ball / sample ratio and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  /  $\text{SrSO}_4$  mole ratio on the conversion reaction were determined. It was found that the conversion of  $\text{SrSO}_4$  to  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  was increased with increasing mole ratio of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to  $\text{SrSO}_4$ . The maximum conversion, above 70 %, was achieved by using  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  /  $\text{SrSO}_4$  mole ratio: 1.5, rotation speed: 500 rpm and ball / sample ratio: 13.

**Keywords:** Celestite, strontium oxalate, mechanochemistry

### 1. INTRODUCTION

The main raw material used in the production of Sr metal and its compounds is the celestite mineral with the basic component of  $\text{SrSO}_4$ . Turkey has approximately 2.5 million tons of celestite reserves, which is one of the world's highest percentage of strontium-containing mineral deposits. The celestite mineral is enriched by Barit Maden Turk A.S. and converted into

celestite concentrate containing 95-97 %  $\text{SrSO}_4$  [1].

One of the important steps in the production of Sr compounds is to obtain the strontium oxalate compound without any alkali contamination. Strontium oxalate, Bi - Sr - Ca - Cu - oxide (BiSCCO) is used as a primary raw material for the production of superconducting and luminescent materials. Depending on the pH of the reagent solution used, there are different types of strontium oxalate such as anhydrous ( $\text{SrC}_2\text{O}_4$ ),

\* Corresponding Author: mzoraga@istanbul.edu.tr

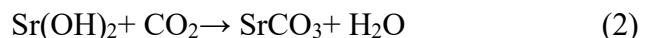
<sup>1</sup> Istanbul University-Cerrahpasa, Engineering Faculty, Metallurgical and Materials Engineering Department, Istanbul, Turkey. ORCID: 0000-0002-7723-728X

monohydrate ( $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ), dihydrate ( $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) and acid ( $\text{Sr}(\text{HC}_2\text{O}_4)$  ( $\text{C}_2\text{O}_4$ ) 0.5. $\text{H}_2\text{O}$ ). The studies in the literature have focused on the conversion of  $\text{SrSO}_4$  to  $\text{SrCO}_3$  by using different carbonate sources [2, 3]. There are few studies on the conversion of strontium oxalate. The current studies have focused on the thermal decomposition of strontium oxalate, co-precipitation of  $\text{H}_2\text{C}_2\text{O}_4$  and  $(\text{NH}_4)\text{C}_2\text{O}_4$  solutions from nitrate solutions and production of superconducting materials [4-6].

Kobe and Deiglmeier [7] examined the conversion of  $\text{SrSO}_4$  to  $\text{SrCO}_3$  using  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  solutions. It was determined that 96 % conversion was obtained depending on the experimental conditions. Iwai and Toguri [2] studied the conversion of  $\text{SrSO}_4$  in  $\text{Na}_2\text{CO}_3$  solution. They determined that  $\text{SrCO}_3$  is formed on the surface of  $\text{SrSO}_4$  particles and the rate of diffusion of the reactant from this porous product layer had controlled the reaction rate. Castillejos et al. [3] examined the effect of the solid - liquid ratio, pH value of the solution, temperature, stirring speed on conversion of the celestite concentrate to  $\text{SrCO}_3$  by using  $\text{Na}_2\text{CO}_3$  solution. It was reported that the reaction rate was controlled by the rate of diffusion of the  $\text{CO}_3^{2-}$  ions between the pores of the product layer.

During the application of the mechanochemical method defined as the progression of the chemical reaction with the help of mechanical energy, the dense product layer surrounding the reactant grains is broken and the new solid reactant surfaces are exposed. Thereby, the chemical reactions progresses in a shorter period. Obut et al. [8], Erdemoglu et al. [9] and Setoudeh et al. [10] showed that this situation was possible when  $\text{Na}_2\text{CO}_3$  solutions were used. Bingol et al. [11,12] compared the conversion of  $\text{SrSO}_4$  to  $\text{SrCO}_3$  by using  $(\text{NH}_4)_2\text{CO}_3$  reactant in both aqueous and anhydrous mechanochemical methods. It was found that 99.10 % and 98.10 % conversion values were achieved with aqueous and anhydrous mechanochemical method, respectively. Zhang and Saito [13] studied the production of  $\text{Sr}(\text{OH})_2$  from  $\text{SrSO}_4$  by anhydrous mechanochemical method using  $\text{NaOH}$ . They determined that  $\text{Sr}(\text{OH})_2$ , obtained as a result of

the reaction according to Reaction 1, transformed into  $\text{SrCO}_3$  easily with  $\text{CO}_2$  in air according to Reaction 2.



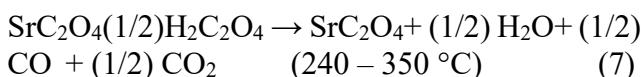
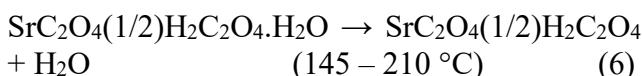
Setoudeh and Welham [14, 15] investigated the reduction of  $\text{SrSO}_4$  by using Al and Mg. In these highly exothermic reactions, when Mg was used, the reaction products were  $\text{SrS}$  and  $\text{MgO}$ . On the other hand, when Al was used, they determined that  $\text{Sr}_3\text{Al}_3\text{O}_5$ ,  $\text{SrAl}_4\text{O}_7$  and  $\text{SrAl}_2\text{O}_4$  compounds were formed depending on the grinding time of the mill as well as the  $\text{SrS}$  and  $\text{Al}_2\text{O}_3$  compounds.

Selim et al. [16] studied the precipitation of  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  by using  $\text{SrCl}_2$  and  $\text{Na}_2\text{C}_2\text{O}_4$  compounds. In their study, they examined the thermal decomposition of  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in different gas atmospheres (air,  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{CO}_2$ ) and found that dehydration occurred in two stages. The majority of the water was released at 180 °C and 5 % at 270 °C. They stated that the decomposition reaction of  $\text{SrC}_2\text{O}_4$  to  $\text{SrCO}_3$  occurred at a temperature range of 400 - 480 °C and the reaction was affected by the particle size and morphology of  $\text{SrCO}_3$ . Dollimore [6] studied the thermal decomposition of  $\text{SrC}_2\text{O}_4 \cdot 2,5\text{H}_2\text{O}$  and  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in  $\text{N}_2$  atmosphere. The samples were prepared by  $\text{Sr}(\text{NO}_3)_2$  and  $\text{H}_2\text{C}_2\text{O}_4$  solutions. It was reported that the dehydration reaction of  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  occurred in one stage, but the dehydration reaction of  $\text{SrC}_2\text{O}_4 \cdot 2,5\text{H}_2\text{O}$  was occurred gradually due to the crystal symmetry.

Knaepen et al. [4] used  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  solutions for the synthesis of different structures of strontium oxalate. They determined that two different forms of neutral strontium oxalate ( $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ ) and acid strontium oxalate ( $\text{SrC}_2\text{O}_4 \cdot y\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ ) were obtained depending on the concentration of  $\text{H}_2\text{C}_2\text{O}_4$  or  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . They stated that the thermal degradation of  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in the Ar atmosphere was carried out according to Reactions 3-5. The weight decreases as a result of the degradation where 9.50 %, 14.10 % and 22.70 % theoretical values were calculated, respectively for the Reactions 3-5.

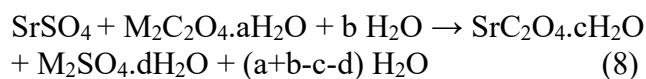


When the thermal decomposition of acid strontium oxalate under the same conditions were examined, they stated that the degradation reactions were carried out in four stages according to Reactions 6, 7, 4 and 5 respectively and the weight decrease was in accordance with the theoretical values of 7.90 %, 18.50 %, 11.40 % and 18.80 % respectively for the Reactions 6-7 and 4-5.



Christensen and Hazell [5] studied the thermal decomposition and crystal structures of the tetragonal SrC<sub>2</sub>O<sub>4</sub>.2D<sub>2</sub>O and triclinic SrC<sub>2</sub>O<sub>4</sub>.D<sub>2</sub>O prepared with Sr(NO<sub>3</sub>)<sub>2</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O and 99.70 % D<sub>2</sub>O. They determined that the dehydration step of the SrC<sub>2</sub>O<sub>4</sub>.xD<sub>2</sub>O compound was carried out at two temperatures: 180 °C and 300 °C while the SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O compound was dehydrated at 150 °C. When they examined the crystal structures of SrC<sub>2</sub>O<sub>4</sub>.2D<sub>2</sub>O and SrC<sub>2</sub>O<sub>4</sub>.D<sub>2</sub>O, they found that SrC<sub>2</sub>O<sub>4</sub>.2D<sub>2</sub>O was in tetragonal structure and that the Sr atom coordinated with eight O atoms from 6 oxalate and 2 water molecules. In addition, they determined that SrC<sub>2</sub>O<sub>4</sub>.D<sub>2</sub>O was triclinic, and that Sr atom coordinated with eight O atoms, 7 of which were oxalate and 1 was the water molecule. Price et al. [17] studied non-aqueous SrC<sub>2</sub>O<sub>4</sub> single crystal yield at 240 °C by hydrothermal method using FeC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O and SrCl<sub>2</sub>.6H<sub>2</sub>O to provide a sufficiently large single crystal formation suitable for crystal structure analysis instead of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O as oxalate source. As a result of their experimental studies, they stated that each Sr atom coordinates with eight O atoms and that the SrO<sub>8</sub> structure is in the square antiprism geometry. Bacce et al. [18] examined the thermal decomposition of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O and the effect of Eu<sup>3+</sup> addition by using conventional and ultrasonic mixing at 80 °C

using SrCl<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions. They stated that the ultrasonic mixing and Eu<sup>3+</sup> admixture reduced the particle size, provided uniform grains, and that the final reaction product was composed of SrCO<sub>3</sub>, SrO and Sr(OH)<sub>2</sub> mixture due to the fact that the water could not completely dissociate as a result of the decomposition in the air atmosphere at 1050 °C. Zhang et al. [19] studied the production of strontium oxalate and morphology in polymethacrylic acid (PMAA) solution at room temperature using SrCl<sub>2</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. In these experimental conditions, they determined that SrC<sub>2</sub>O<sub>4</sub> is formed in 6 – 7 μm dimensions and it has a biomimetic growth. Yu et al. [20] investigated the effect of polystyrene maleic acid (PSMA) on the production of SrC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O using SrCl<sub>2</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions. They stated that the crystals of SrC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O collapsed in the double pyramid structure at room temperature without using PSMA and when the PSMA was used, due to the concentration of the Sr<sup>2+</sup> ion with PSMA, the precipitation time increased and the morphology turned into a peanut structure by increasing the PSMA concentration. Obut [21] examined the effect of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions on the strontium oxalate conversion by using chemical purity SrSO<sub>4</sub> and concentrated celestite. They found that H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> had no effect on the conversion of SrSO<sub>4</sub> by using a stoichiometric amount of oxalate ion source according to the Reaction 8, but when using (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, SrCO<sub>4</sub> and celestite concentrate of chemical purity were obtained with 84.60 % and 74.70 % conversion respectively.



The mechanochemical method is more effective than chemical conversion owing to uncover new reaction areas on particle surface especially when a protective layer forms on the surface of solid particles. The aim of this study is to investigate the conversion of celestite to SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O by using mechanochemical method and to determine the effects of rotational speed, ball to sample ratio and concentration of the solution on the conversion reaction.

## 2. MATERIALS AND METHODS

### 2.1. Materials and Techniques

Celestite concentrate was obtained from Barite Maden Turk A.S. (Turkey). The celestite concentrate was wet sieved (Octagon 200) and -75 + 53 µm particle size fraction was collected. (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions, which were prepared by dissolving of chemically pure (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (Merck) in distilled water, were used in the conversion experiments. The simultaneous TG - DTA (TA - SDT Q600) device was used to determine the conversion of the solid reaction products. The characterization of the solid reaction products was carried out with X-ray powder diffractometer (XRD) (X Pert Pro) using Cu-Kα ( $\lambda = 1.54056 \text{ \AA}$ ) monochromatic X-ray. The results of the quantitative analysis of the celestite concentrate with the XRF device (Panalytical Axios - Minerals) are shown in Table 1.

Table 1. Chemical composition of celestite concentrate

Compound	Composition (wt %)
SrSO <sub>4</sub>	94.82
BaSO <sub>4</sub>	2.85
CaCO <sub>3</sub>	1.52
SiO <sub>2</sub>	0.43
Fe <sub>2</sub> O <sub>3</sub>	0.21
Al <sub>2</sub> O <sub>3</sub>	0.08
PbSO <sub>4</sub>	0.06
CuO, ZnO	< 0.02

### 2.2. Experimental Procedure

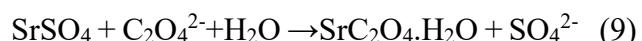
The experiments were carried out in MSE brand mills using 500 mL volumetric ceramic reaction chamber, 200 mm diameter ceramic balls and 250 mL (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution (AOX) and celestite concentrate. The MSE brand mill has rotating rollers that can be adjusted according to the chamber diameter to be used. It also provides effective milling and mixing by adjusting the rotation speed according to the chamber and ball diameter. SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub> conversion reaction yield were investigated by the following parameters: milling time: 3 - 8 h, ball / sample ratio: 9, 11 and 13; (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> / SrSO<sub>4</sub> mole ratio: 1.1, 1.3 and 1.5; and the rotational speed of

300, 400 and 500 rpm. After the conversion experiments, the solid-liquid separation was carried out by filtration and the solid reaction products were dried at 80 °C for 8 h. TG - DTA diagrams were obtained with 50 mg sample in alumina crucible and a blank alumina crucible as reference material, with a linear heating rate of 10 °C min<sup>-1</sup> and a flow rate of 100 mL min<sup>-1</sup> linear air flow.

## 3. RESULTS AND DISCUSSION

### 3.1. The conversion reaction mechanism of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>

The conversion reaction of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub> is a solid - liquid heterogeneous type reaction (Reaction 9):



The solubility product of SrSO<sub>4</sub> ( $K_{\text{sp},\text{SrSO}_4} = 2.8 \times 10^{-7}$ ) is greater than the solids product of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O ( $K_{\text{sp},\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}} = 5.6 \times 10^{-8}$ ) [9,21]. In this case, the solubility of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O in aqueous solutions ( $2.37 \times 10^{-4} \text{ mol L}^{-1}$ ) is less compared to the solubility of SrSO<sub>4</sub> ( $5.29 \times 10^{-4} \text{ mol L}^{-1}$ ), and this is the driving force for the conversion reaction. The molar volumes of SrSO<sub>4</sub> and SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O calculated by taking into account the densities and molar weights of  $46.38 \times 10^{-3} \text{ m}^3 \text{ kmol}^{-1}$  and  $71.18 \times 10^{-3} \text{ m}^3 \text{ kmol}^{-1}$  respectively. Since the molar volume of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O is greater than that of SrSO<sub>4</sub>, SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O, which forms the solid reaction product and surround the surfaces of unreacted SrSO<sub>4</sub> grains, is non-porous. When the solid product layer completely surrounds the surface of the solid reactant particles, it shows a protective behavior and does not allow ion diffusion, and as a result, the conversion reaction comes to a standstill and stops.

By applying the mechanochemical method, this protective product layer is broken, and a new unreacted surface is formed and thus the progression of the conversion reaction is ensured.

### 3.2. The Effects of Experimental Parameters

(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (AOX) in the solution of the reaction rate of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub> conversion to determine the effect of rotational speed of 300, 400, 500 rpm and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (AOX) / SrSO<sub>4</sub> = 1.1, 1.3 and 1.5 experiments for 8 hours were performed. In the experiments, 13.81, 11.69 and 10.13 g of concentrated celestite in the particle size range of -75 + 53 µm, 0.08 mol (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> by using 250 mL of solution obtained by dissolving the ball / sample = 9, 11 and 13 were studied. As shown in Figure 1, the rotational speed of 500 rpm is sufficient to break the protective SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O layer formed on the surface of SrSO<sub>4</sub> grains and under these conditions, the conversion rate has reached the highest value. In the experiments performed to determine the effects of other parameters on the conversion reaction rate, the rotational speed was kept constant at 500 rpm.

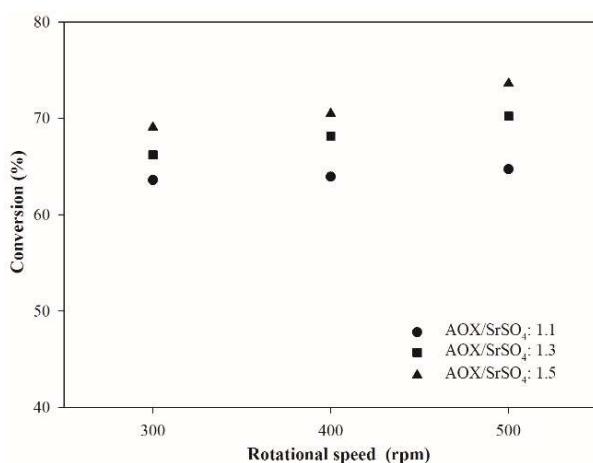


Figure 1. The effect of rotational speed on the conversion reaction to SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>

In order to determine the effect of AOX on the conversion of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>, experiments with AOX / SrSO<sub>4</sub> = 1.1, 1.3 and 1.5 were carried out. As shown in Figure 2, the conversion at 1.5 molar ratio was found to be over 70 %. The reaction takes place as a result of direct contact between the surface of the SrSO<sub>4</sub> and the AOX. Due to the high concentration of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions, ion exchange increases and the conversion of SrO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O is also increased with the increase in the AOX / SrSO<sub>4</sub> molar ratio

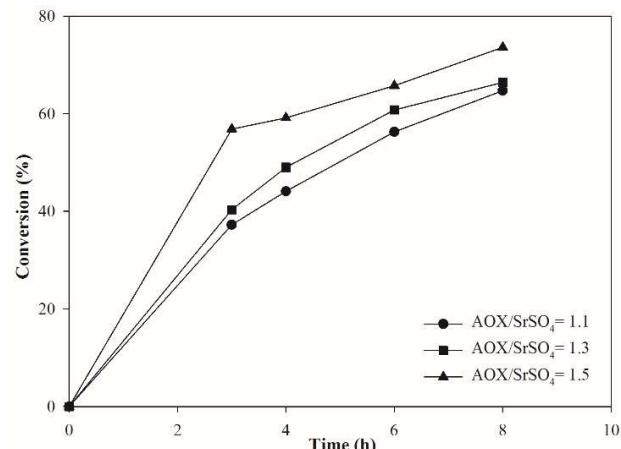


Figure 2. Effect of mole ratio of AOX / SrSO<sub>4</sub> on conversion reaction of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>

Experiments were carried out for 8 h to determine the effect of ball / sample ratio of 9, 11 and 13 and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (AOX) / SrSO<sub>4</sub> = 1.1, 1.3 and 1.5 on the reaction rate of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub> conversion. As shown in Figure 3, the conversion value increased with increasing the ball / sample and AOX/SrSO<sub>4</sub> ratios. In addition, AOX/SrSO<sub>4</sub> ratio has more significant effect on the conversion value at lower ball/sample ratios.

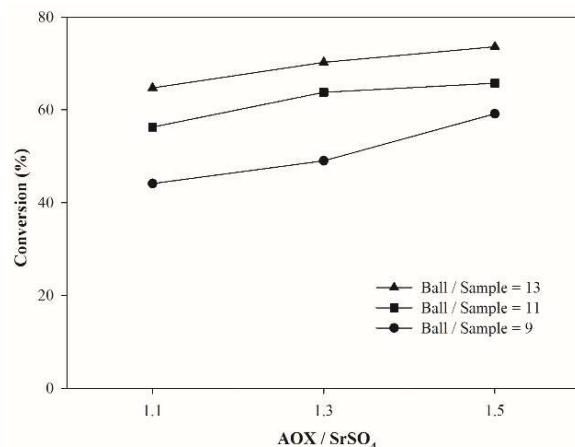


Figure 3. The effect of ball / sample ratio on the conversion reaction to SrSO<sub>4</sub> in SrC<sub>2</sub>O<sub>4</sub>

### 3.3. TG-DTA and XRD Analyzes

The conversion reaction of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub> were carried out to determine the effects of AOX on AOX / SrSO<sub>4</sub> = 1.1, 1.3 and 1.5 at different reaction times (3, 4, 6 and 8 hours) at 500 rpm rotational speed. The diagrams obtained from the simultaneous TG - DTA analysis of the solid

reaction products obtained are shown in Figures 4 and 5.

TGA analysis carried out in air atmosphere shows there weight loss steps (Figure 4). First weight loss step is between 90 - 305 °C due to the formation of SrC<sub>2</sub>O<sub>4</sub>, which was achieved by losing the crystal water of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O (Reaction 3). The second weight loss between 370 - 595 °C (Reaction 4), the third weight loss between 615 - 1100 °C show that SrCO<sub>3</sub> released CO<sub>2</sub> and converted into SrO (Reaction 5). Weight loss values are shown in Table 2. These values are different from the theoretical values. This difference shows that the sample is not composed only of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O, and some of the SrSO<sub>4</sub> remained unchanged.

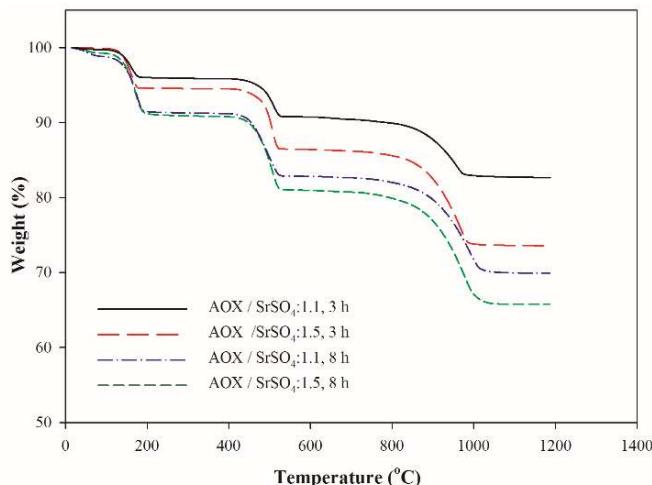


Figure 4. TG analyses of reaction products from conversion of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>

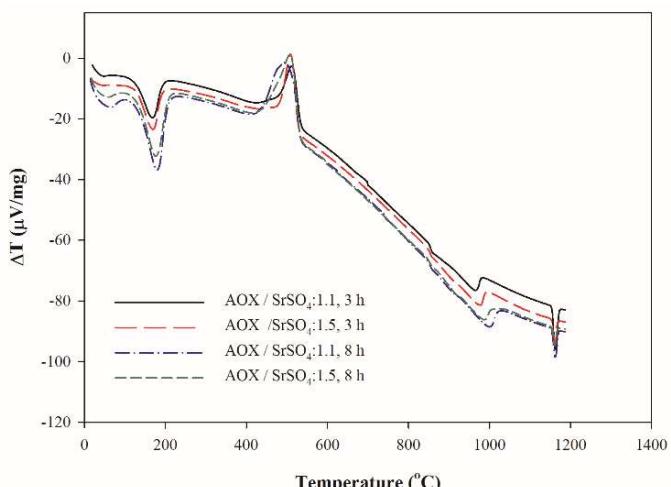


Figure 5. DTA analyses of reaction products from conversion of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>

The DTA diagram taken in the air atmosphere (Figure 5) shows the presence of three reactions. Peaks at 171 °C (endothermic peak), 502 °C (exothermic peak) and 980 °C (endothermic peak) are those of Reactions 3, 4 and 5, respectively. It belongs to the reversible allotrophic transformation of unreacted SrSO<sub>4</sub> in the severe and sharp endothermic peak sample seen at 1156 °C in the DTA diagram [22]. XRD diagram in Figure 6 shows that the substance consists of a mixture of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O (ICDD 20-1203) which is the reaction product of the unreacted SrSO<sub>4</sub> (ICDD 05-0593).

Table 2. The weight loss values obtained from the TG

Sample	First reaction step	Second reaction step	Third reaction step	Conversion, %
AOX / SrSO <sub>4</sub> : 1.5, 3 h	5.33	8.41	12.62	56.71
AOX / SrSO <sub>4</sub> : 1.5, 8 h	8.66	9.63	15.12	71.88
AOX / SrSO <sub>4</sub> : 1.1, 8 h	7.61	8.49	12.78	62.13
AOX / SrSO <sub>4</sub> : 1.1, 3 h	3.79	4.77	7.84	35.28
Theoric Value	9.30	23.76	46.48	

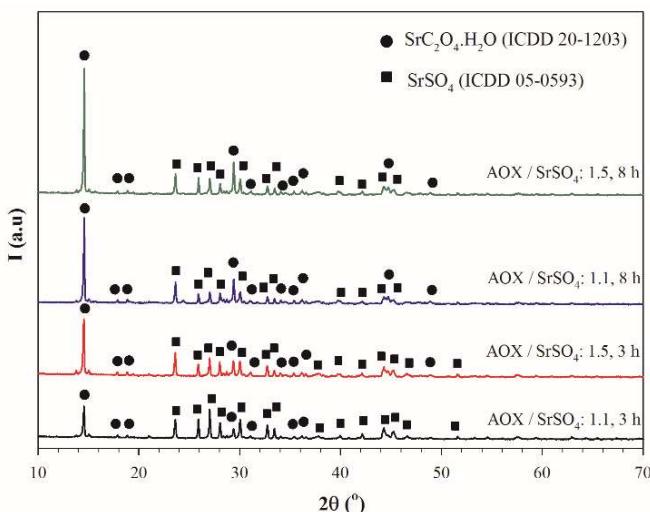


Figure 6. XRD analyses of reaction products

#### 4. CONCLUSIONS

The solubility of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O in aqueous solutions is less compared to the solubility of SrSO<sub>4</sub>, and this is the driving force for the conversion reaction.

Since the molar volume of SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O is greater than that of SrSO<sub>4</sub>, non-porous SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O solid product layer formed on the surface of SrSO<sub>4</sub> particles which shows a protective layer characteristic when it completely surrounds the surface of solid reactant grains. This layer, which does not allow ion diffusion, was broken by application of the mechanochemical method, where the formation of new reaction surface resulted in the progression of the conversion reaction.

The conversion of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O reached the highest value (above 70 %) under the relevant test conditions when working at a rotational speed of 500 rpm. When the reaction time or ball / sample ratio is increased according to the obtained test results, it is expected that the conversion will reach higher values.

Since the reaction was the result of direct contact between the AOX and SrSO<sub>4</sub>, it was determined that the conversion of SrSO<sub>4</sub> to SrC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O increased with the increase in mole ratio of AOX to SrSO<sub>4</sub>. The highest conversion value was above 70 % at AOX / SrSO<sub>4</sub>: 1.5 mole ratio.

#### REFERENCES

- [1] MTA, "Sivas ili maden ve enerji kaynakları," Retrieved 17 September 2018, from [http://www.mta.gov.tr/v3.0/sayfalar/bilgimerkezi/maden\\_potansiyel\\_2010/sivas\\_madenler.pdf](http://www.mta.gov.tr/v3.0/sayfalar/bilgimerkezi/maden_potansiyel_2010/sivas_madenler.pdf). 2010.
- [2] M. Iwai and J.M. Toguri, "The leaching of celestite in sodium carbonate solution," *Hydrometallurgy*, vol. 22, no. 1–2, pp. 87–100, 1989.
- [3] A.H. Castillejos, B. De La Cruz Del and S. Uribe, "The direct conversion of celestite to strontium carbonate in sodium carbonate aqueous media," *Hydrometallurgy*, vol. 40, no. 1–2, pp. 207–222, 1996.
- [4] E. Knaepen, J. Mullens, J. Yperman and L.C. Van Poucke, "Preparation and thermal decomposition of various forms of strontium oxalate1". *Thermochim. Acta*, vol. 284, no. 1, pp. 213–227, 1996.
- [5] A.N. Chritensen and R.G. Hazell, "Thermal analysis and crystal structure of tetragonal strontium oxalate dehydrate and of triclinic strontium oxalate hydrate," *Acta Chem. Scandin.*, vol. 52, pp. 508–512, 1998.
- [6] D. Dollimore, "The thermal analysis of strontium oxalate," *Thermochimica Acta*, vol. 92, no. 15, pp. 543–546, 1985.
- [7] A.K. Kobe and N.J. Deiglmeier, "Conversion from strontium sulfate by metathesis with alkali carbonate solution," *Ind. and Eng. Chem.*, vol. 35, no. 3, pp. 323–325, 1943.
- [8] A. Obut, P. Balaz and I. Girgin I, "Direct mechanochemical conversion of celestite to SrCO<sub>3</sub>," *Miner. Eng.*, vol. 19, no. 11, pp. 1185–1190, 2006.
- [9] M. Erdemoglu, S. Aydogan and M. Canbazoglu, "A kinetic study on the conversion of celestite (SrSO<sub>4</sub>) to SrCO<sub>3</sub> by mechanochemical processing,

- Hydrometallurgy, vol. 86, no. 1–2, pp.1–5, 2007.
- [10] N. Setoudeh, N.J. Welham and S.M. Azami, “Dry mechanochemical conversion of SrSO<sub>4</sub> to SrCO<sub>3</sub>,” J. Alloys Compd., vol. 492, no. 1–2, pp. 389–391, 2010.
- [11] D. Bingol, S. Aydogan and S.K. Bozbaş, “Optimization of the wet mechanochemical process conditions of SrSO<sub>4</sub> to SrCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by using response surface methodology,” Metall. Trans. B, vol. 43B, pp. 1214–1219, 2012.
- [12] D. Bingol, S. Aydogan and S.K. Bozbaş, “Production of SrCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by dry mechanochemical processing of celestite,” J. Ind. Eng. Chem., vol. 18, no. 2, pp. 834–838, 2012.
- [13] Q. Zhang and F. Saito, “Mechanochemical processing of celestine,” Chem. Eng. J., vol. 66, no: 1, pp. 79–82, 1997.
- [14] N. Steoudeh and N.J. Welham, “Ball milling induced reduction of SrSO<sub>4</sub> by Al,” Int. J. Miner. Process., vol. 98, no: 3–4, pp. 214–218, 2011.
- [15] N. Steoudeh and N.J. Welham, “Ball milling induced reduction of SrSO<sub>4</sub> by Mg,” Int. J. Miner. Process., vol. 104, pp. 49–52, 2012.
- [16] A.S. Selim and M. Abd-El-Khalik, “Thermal decomposition of strontium oxalate-effect of various atmospheres,” Powder Technol., vol. 20, no: 1, pp. 53–59, 1978.
- [17] D. J. Price, A.K. Powell and P.T. Wood, Hydrothermal crystallisation and X-ray structure of anhydrous strontium oxalate., Polyhedron, vol. 18, no: 19, pp. 2499–2503, 1999.
- [18] E. D. Bacce, A.M. Pires, M.R. Davalos and M. Jacelicci Jr, “Thermal decomposition and rehydration of strontium oxalate: morphological evolution,” Int. J. Inorg. Mater., vol. 3, no: 6, pp. 443–452, 2001.
- [19] D. Zhang, L. Qi, J. Ma and H. Cheng, “Biomimetic growth of strontium oxalate aggregates with unusual morphologies in the presence of poly(methacrylic acid),” Cryst. Eng. Comm., vol. 4, no: 88, pp. 536–538, 2002.
- [20] J. Yu, H. Tang and B. Cheng, “Morphological control of strontium oxalate particles by PSMA-mediated precipitation reaction,” Mater. Chem. Phys., vol. 9, no: 1, pp. 134–139, 2005.
- [21] A. Obut, “Interaction of celestine concentrate and reagent grade SrSO<sub>4</sub> with oxalate solution,” Acta Montan. Slovaca, vol. 17, no: 2, pp. 126–131, 2012.
- [22] J. Torres, J. Mendez and M. Sukiennik, “Transformation enthalpy of alkali-earth sulfates (SrSO<sub>4</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub>, BaSO<sub>4</sub>),” Thermochim. Acta, vol. 334, no: 1–2, pp. 57–66, 1999.