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RESEARCH ARTICLE

Examining the relationship between mechanical impact intensity and the decomposition temperature of celestite

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Abstract

The aim of this study was to investigate the impact of mechanochemical synthesis time on the decomposition of sulfated celestite ore and to understand the reactions, phases, and thermal transformations involved in the formation of strontium carbonate using various characterization techniques. The study found that the conversion rate of celestite ore to strontium carbonate increased with increasing mechanochemical synthesis duration, and that the peak intensities of SrCO3 were highest at 100 minutes but decreased at 200 minutes, indicating that the crystal structure was disrupted beyond a certain duration. The transformation temperatures in DTA curves also decreased with increasing synthesis duration due to the increase in energy of the particles. Overall, this study provides valuable insights into the mechanistic aspects of strontium carbonate decomposition.

1. Introduction

Strontium carbonate is a widely used compound in various industries, including electronics, ceramics, and metallurgy [1]. Traditional methods of producing strontium carbonate involve high-temperature processes, which are energy-intensive and environmentally harmful. Recently, researchers have been exploring new methods of producing strontium carbonate using mechanochemical synthesis [2].

Mechanochemical synthesis is a process that involves the use of mechanical energy to drive chemical reactions [3]. It is a promising method for producing strontium carbonate due to its simplicity, low energy consumption, and high yield. In this process, strontium oxide and carbon dioxide are mechanically milled together in the presence of a suitable catalyst to produce strontium carbonate. One of the key advantages of mechanochemical synthesis is that it can be carried out at room temperature, which eliminates the need for high-temperature furnaces and reduces energy consumption [4-6]. The process also produces less waste and is more environmentally friendly than traditional methods. Another advantage of mechanochemical synthesis is that it allows for the production of strontium carbonate with controlled particle size and morphology. This is important for applications such as catalysis, where particle size and morphology can have a significant impact on performance [7-9]. Despite the many advantages of mechanochemical synthesis, there are still some challenges that need to be addressed. For example, the process can be sensitive to the presence of impurities and requires careful control of the milling conditions to ensure consistent results. Nevertheless, ongoing research in this area is expected to lead to further improvements in the process [10, 11]. In summary, mechanochemical synthesis is a promising method for producing strontium carbonate with low energy consumption, high yield, and controlled particle size and morphology. As research in this area continues, we can expect to see the development of more efficient and effective methods for producing this important compound.

During mechanochemical synthesis, the mechanical energy generated by the milling process can induce structural changes in celestite, leading to the formation of intermediate phases and ultimately to the production of strontium carbonate. The milling process can also affect the size and morphology of the resulting particles, which can have important implications for the properties and performance of the final product [12, 13].

The extent and nature of the mechanical effects depend on several factors, including the type of milling equipment used, the milling time, and the milling intensity. These factors can be optimized to control the properties of the final product and to minimize the formation of unwanted byproducts [14]. Understanding the mechanical effects of mechanochemical synthesis is important for the development of efficient and effective methods for producing strontium carbonate. Further research is needed to elucidate the underlying mechanisms of the process and to optimize the milling conditions for the production of high-quality strontium carbonate [15, 16].

The aim of this study is to investigate the effects of mechanical activation on the transformation temperature of celestite during mechanochemical synthesis. The study will focus on the relationship between the mechanical intensity of the milling process and the transformation temperature of celestite to strontium carbonate.

2. Materials and methods

The celestite ore used in all experimental studies was obtained free of charge from Barit Maden Turk A.Ş. The chemical analysis of the celestite ore used in all experiments was determined by atomic absorption spectrometry (AAS) and presented in Table 1. As shown in the table, the structure of the celestite ore contains three different sulfate compounds: $SrSO_4$, $CaSO_4$, and $BaSO_4$. The concentrated celestite ore was found to

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contain 95.5% by weight of strontium sulfate ($SrSO_4$) compound. In addition to $SrSO_4$, calcium sulfate ($CaSO_4$) was also found in the ore, accounting for 3% by weight.
A mixture of strontium sulfate ($SrSO_4$) and ammonium carbonate $(NH_4)_2CO_3$ was prepared according to Equation 1 for investigating the mechanochemical conversion of celestite ore to strontium carbonate.

$$SrSO4 + (NH_4)_2CO_3 \rightarrow SrCO_3 + (NH_4)_2SO_4 \quad (1)$$

A 1:1 stoichiometric ratio was used for $SrSO_4$ and $(NH_4)_2CO_3$, and the mechanochemical synthesis process was carried out for 10, 100, and 200 minutes using a 5 mm diameter WC ball, a 1:10 powder-to-ball ratio, and a constant rotation speed of 450 rpm. The experiment was conducted at the Department of Metallurgy and Materials Engineering in Karadeniz Technical University, using a Fritsch Premium Line 5 planetary ball mill.

The particle morphologies and energy dispersive X-ray (EDX) analysis of the resulting SrCO3 powders were observed using a Zeiss EVO LS10 scanning electron microscope (SEM). Phase transformation temperatures of the SrCO3 powders obtained were determined using a Linseis PT1600 DSC/DTA/TG device, with differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) methods. The thermal analyses were conducted between 30-1200 °C at a heating rate of 30 °C/min.

Table 1. Composition of the celestite ore

Compound	Weight percent (%)
$SrSO_4$	95,5
$CaSO_4$	3,0
$BaSO_4$	0,5
SiO_2	0,5
Fe_2O_3	0,5

3. Results and discussion

In our study, concentrated celestite ore, obtained free of charge from Barit Maden Turk A.S., was used as the source of strontium carbonate. Scanning electron microscope (SEM) images of the concentrated celestite ore taken from different sieve ranges are presented in Figure 1. Upon examination of the SEM images, it was observed that the dominant particle shape of the powder was generally round and angular. Considering that using such widely distributed ore could result in an inhomogeneous particle size distribution in the production of $SrCO_3$, celestite ore in the -1000/+125 µm sieve range was preferred in this study.

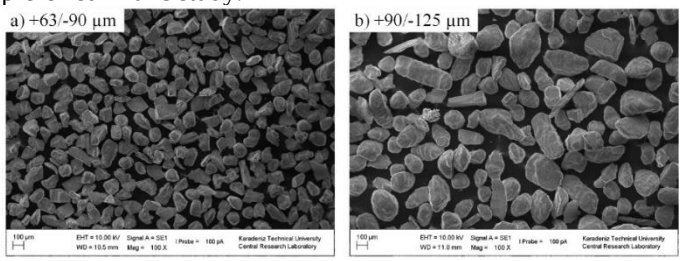

Figure 1. Scanning electron microscope (SEM) images of concentrated celestite ore obtained from different sieve intervals.

The study utilized differential thermal analysis (DTA) to investigate the temperature-induced phase transitions of celestite ore (Figure 2). The DTA curve of the ore exhibited three distinct endothermic peaks. The first peak corresponds to the thermal decomposition temperature range of $CaCO_3$, which is present along with $CaSO_4$ in the ore's structure. This decomposition reaction starts at 670 °C and completes at 832 °C (peak 1). The second endothermic peak, which is of low intensity, represents the phase transition of SrCO3, another impurity present in the celestite ore. This transition is shown by peak 2, beginning at 835 °C and ending at 920 °C, where the α-$SrCO_3$ phase transforms to β-$SrCO_3$ phase. The third and most intense endothermic peak depicts the thermal decomposition of $SrCO_3$ in the ore. As per the thermal reaction associated with peak 3, it initiates at 1130 °C and completes at 1200 °C.

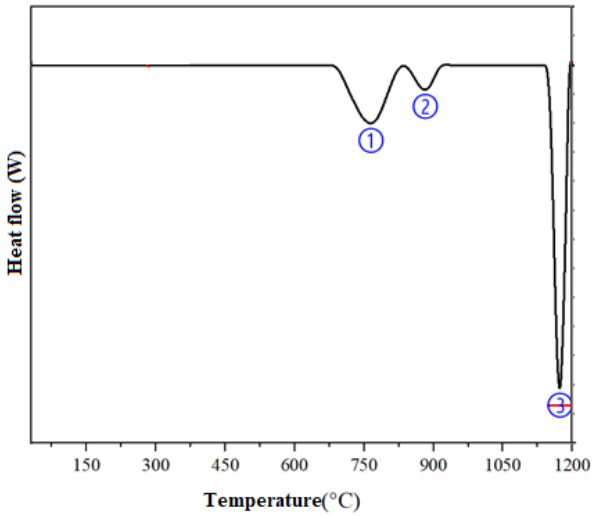

Figure 2. DTA analysis of domestic celestite ore

The SEM and EDS analysis results presented in Figure 3 provide important information regarding the progress of the mechanochemical synthesis process. The EDS analysis confirms that unreacted strontium sulfate is still present in the powder mixture after 10 minutes of synthesis. This is indicated by the EDS results obtained from Points 1 and 2 in Figure 3, which both show a high percentage of strontium and sulfur, but a low percentage of carbon and oxygen. However, point 3 in Figure 3 shows a higher percentage of carbon, oxygen, and lower percentage of sulfur, indicating that some progress towards the formation of strontium carbonate has been made in this area. Overall, these results suggest that a longer mechanochemical synthesis time is required to achieve complete conversion of sulfated celestite to strontium carbonate.

Based on the EDS analysis results shown in Figure 4, it can be observed that the percentage of S element (% wt.) in the strontium carbonate ($SrCO_3$) compound produced through a 1:1.0 stoichiometric ratio of $SrSO_4$:$(NH4)_2CO_3$ and 200 min of mechanochemical synthesis is significantly lower compared to the results obtained from the 10-minute synthesis process. The EDS analysis indicates that the S percentage (% wt.) for point 1, 2, and 3 points are 0.15%, 0.18%, and 0.25%, respectively. These values are considerably lower than the S percentage (% wt.) obtained for points 1, 2, and 3 in the 10-minute synthesis process, which were 15.20%, 16.13%, and 4.05%, respectively. This suggests that the sulfate compound in the original structure has been successfully converted into a carbonate compound through the 200-minute mechanochemical synthesis process.

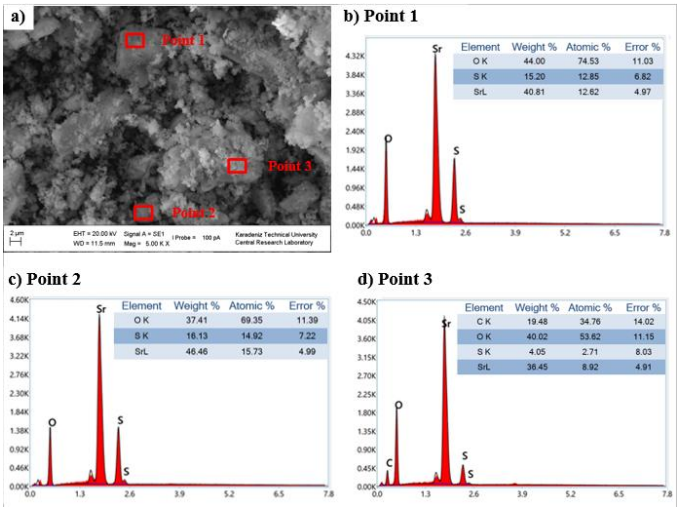

Figure 3. EDS results of powders subjected to 10 minute mechanochemical synthesis.

In summary, the analysis and interpretation of the SEM and EDS results indicate that a longer duration of mechanochemical synthesis is necessary to achieve complete conversion of sulfated celestite to strontium carbonate. The decrease in sulfur content in the strontium carbonate compound produced after 200 minutes of synthesis confirms successful conversion and supports the efficacy of the extended synthesis time in promoting the desired chemical transformation. Based on the SEM images and EDS analysis, it is evident that a 10-minute synthesis duration is not sufficient to achieve complete conversion of sulfated celestite to strontium carbonate. This suggests that an extended synthesis duration leads to a more complete conversion of $SrSO_4$ to SrCO3. The EDS analysis in Figure 4 further supports this observation, as the sulfur content (% wt.) decreases significantly in the strontium carbonate samples synthesized for 100 and 200 minutes compared to the 10-minute synthesis process. This confirms that the sulfate compound in the original structure is successfully transformed into the carbonate compound through the longer mechanochemical synthesis durations.

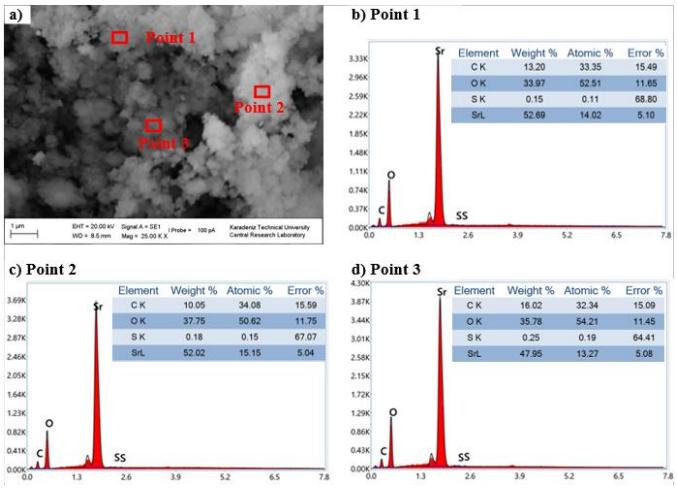

Figure 4. EDS results of powders subjected to 200 minute mechanochemical synthesis.

Particles ranging in size from approximately 10 µm to 100 µm were obtained after a 10-minute synthesis process. These particles exhibited sharp and irregular shapes, indicating the presence of $SrCO_3$ on their outer shells and the occurrence of breakage during the process. According to the particle size distribution, the average particle size decreased to 6.721 µm after a 10-minute mechanochemical synthesis. This suggests a reduction in particle size compared to the initial sample. Strontium carbonate particles produced through mechanochemical synthesis for 100 minutes exhibited an average particle size of 4.257 µm. This indicates further reduction in particle size compared to the 10-minute synthesis. The strontium carbonate particles obtained after 200 minutes of mechanochemical synthesis. The prolonged synthesis duration resulted in a significant decrease in particle size, making it challenging to identify individual particle shapes. Overall, the results indicate that increasing the duration of mechanochemical synthesis led to a decrease in the particle size of the strontium carbonate particles. The particles became smaller and exhibited a more homogeneous size distribution with longer synthesis durations.

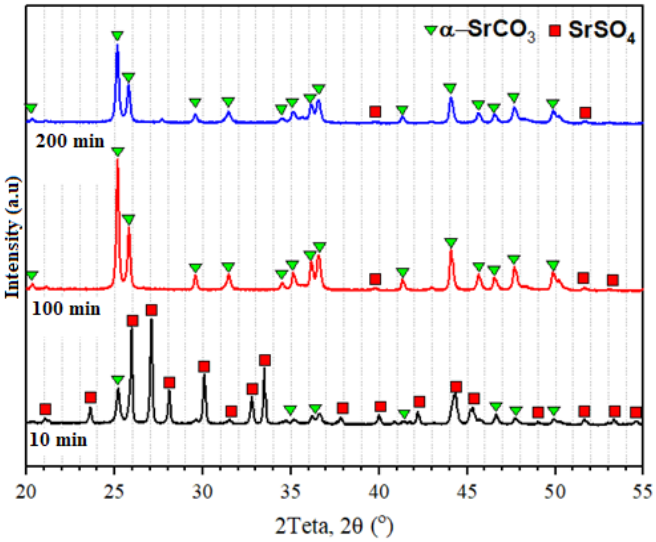

Figure 5. The X-ray diffraction patterns obtained after mechanochemical synthesis with different times.

Figure 5 displays the X-ray diffraction patterns obtained at different synthesis times (10 min, 100 min, and 200 min) for a 1:1.0 stoichiometric ratio of $SrSO_4$:$(NH_4)_2CO_3$ using mechanochemical synthesis. At 10 minutes of synthesis, the pattern showed peaks for both $SrSO_4$ and $SrCO_3$. However, increasing the synthesis time to 100 minutes led to approximately 86% of the celestite ore converting into $SrCO_3$ (determined by Rietveld refinement analysis), and this percentage increased to 92% after 200 minutes of synthesis. The X-ray diffraction patterns revealed that the $SrCO_3$ peaks increased at 100 minutes of synthesis but decreased at 200 minutes, suggesting that extended synthesis times beyond a certain point cause structural distortions and a decrease in crystal size for $SrCO_3$. This variation in X-ray diffraction patterns due to synthesis time was observed for other stoichiometric ratios as well.

DTA and TGA analyses were performed to determine the thermal decomposition temperatures of $SrCO_3$ in transformation processes carried out at synthesis durations. DTA and TGA analyses applied to $SrCO_3$ compounds produced by

mechanochemical transformation performed at 1:1.0 stoichiometric ratio of $SrSO_4$:$(NH_4)_2CO_3$ and for 10, 100, and 200 minutes are presented in Figure 6 and Figure 7, respectively. Two different endothermic peaks were observed in the DTA graph showing the phase transformation and thermal decomposition of $SrCO_3$ for each synthesis duration at 1:1.0 stoichiometric ratio (Figure 6). No transformation peaks related to different compositions were detected outside these endothermic peaks. The transformation temperatures in DTA curves for different synthesis durations were found to decrease with increasing synthesis duration. The temperature at which strontium carbonate begins to thermally decompose was determined as 1000°C for the shortest synthesis duration, while this temperature decreased to 885°C and then to 800°C as the synthesis duration increased. The increase in the energy of the particles in the mechanochemical synthesis process (due to the decrease in particle size) with the synthesis duration causes the thermal decomposition temperature of strontium carbonate to change. The lower intensity of endothermic peak number 2, which was the main focus for the 10-minute synthesis duration, compared to the other synthesis durations (100 and 200 minutes) indicates a lower amount of $SrCO_3$ formation. This confirms the findings from SEM and XRD analyses. When the TGA curve for different synthesis durations was examined for the fixed stoichiometry of 1:1.0 (Figure 7), the lowest weight loss (%6.5) was observed again for the 10-minute synthesis duration, which confirms the DTA data. The conversion rate of the sulfate compound in celestite to strontium carbonate and the weight loss in the same proportion increase with the increase in mechanochemical synthesis duration. The instant total weight loss at 1200°C for the maximum synthesis duration of 200 minutes is approximately 15.1%. One study, which is related to the celestite ore, results revealed a significant decrease in the reaction temperature as the milling time increased. Specifically, after 1 minute of disc milling, the reaction temperature decreased from 973°C to 892°C. Similarly, with 45 minutes of planetary ball milling, a reduction in the reaction temperature was observed. This finding suggests that longer milling durations promote more efficient carbothermic reduction, leading to a lower required reaction temperature [17].

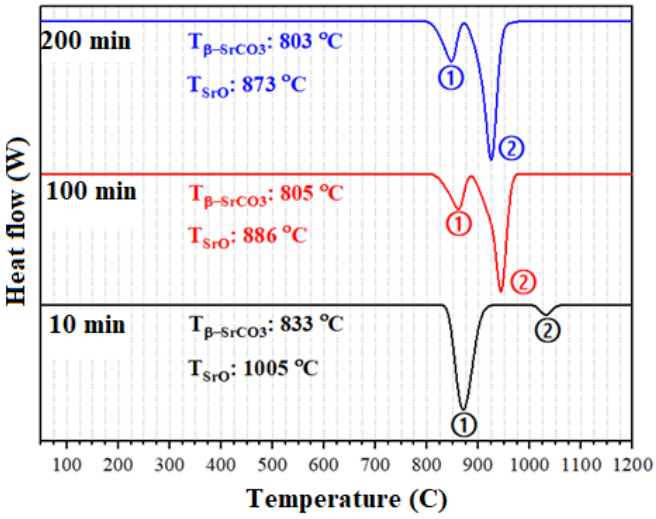

Figure 6. DTA curves obtained after the mechanochemical synthesis process at different times.

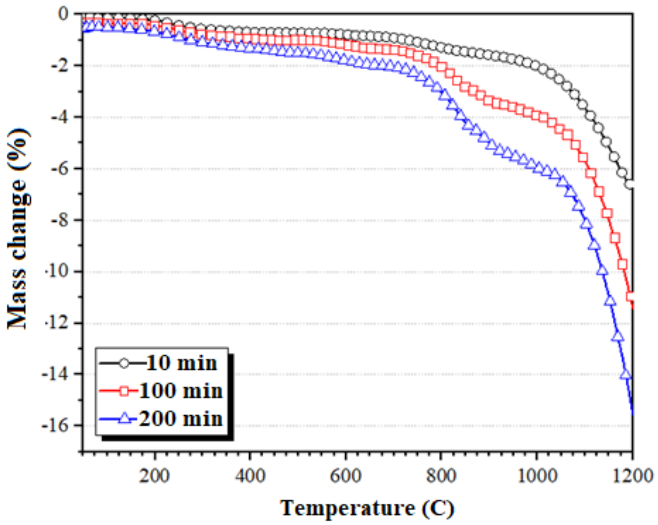

Figure 7. TGA curves obtained after the mechanochemical synthesis process at different times.

Mechanochemical synthesis is a promising method for the production of advanced materials due to its low cost, high efficiency, and environmentally friendly nature. In this process, the reactants are subjected to mechanical force and deformation, leading to solid-state reactions that result in the formation of new materials. However, the reaction temperature and time are important factors that can affect the outcome of the reaction. In this discussion, we will focus on the mechanism behind the decrease in reaction temperature with an increase in mecanochemical synthesis time.

First, it is important to understand the concept of milling energy, which refers to the amount of energy imparted to the reactants during the milling process. The milling energy can affect the reaction kinetics and the thermodynamics of the system. In the case of mechanochemical synthesis, the milling energy can cause deformation and defects in the crystal structure of the reactants, leading to an increase in the reactivity of the system.

The decrease in reaction temperature with an increase in mechanochemical synthesis time can be attributed to several factors. One of the main factors is the increase in surface area of the reactants as a result of the milling process. The increased surface area leads to a higher concentration of reactive sites, which can promote the reaction at lower temperatures [18, 19]. Another factor is the formation of defects and dislocations in the crystal structure of the reactants during the milling process. These defects can serve as nucleation sites for the reaction, reducing the activation energy required for the reaction to occur [20]. Additionally, the deformation of the crystal structure can lead to the formation of non-equilibrium phases, which may have lower reaction temperatures compared to the equilibrium phases. Furthermore, the increase in milling time can lead to the formation of reactive intermediates, such as metastable phases, that can promote the reaction at lower temperatures. These intermediates may have different chemical and physical properties compared to the starting materials and can act as catalysts for the reaction. Finally, the increase in milling time can lead to the formation of amorphous phases, which have higher reactivity compared to crystalline phases. The amorphous phases have a disordered atomic structure, which can provide more reactive sites for the reaction to occur. The amorphous phases can also have a lower activation energy for the reaction,

leading to a decrease in the reaction temperature. In summary, the decrease in reaction temperature with an increase in mechanochemical synthesis time can be attributed to several factors, including the increase in surface area, the formation of defects and dislocations, the formation of reactive intermediates, and the formation of amorphous phases. These factors can all contribute to the increased reactivity of the system, leading to a decrease in the activation energy and the reaction temperature. Understanding these mechanisms is important for the design and optimization of mechanochemical synthesis processes for the production of advanced materials.

4. Conclusions

The main objective of this study was to investigate how mechanochemical synthesis time affects the decomposition of sulfated celestite ore and the formation of strontium carbonate, using various characterization techniques. The results indicate that after 100 minutes of synthesis time, approximately 86.1% of celestite ore is transformed to $SrCO_3$, which increases to 92.2% after 200 minutes of synthesis time. The intensity of $SrCO_3$ peaks also increases at 100 minutes of synthesis time but decreases at 200 minutes, suggesting a disruption in the crystal structure and a reduction in crystal size. The transformation temperatures in DTA curves decrease with increasing synthesis duration due to the increase in energy of particles during the mechanochemical synthesis process. Additionally, the conversion rate of sulfate compound in celestite to strontium carbonate and the weight loss in the same proportion increase with an increase in mechanochemical synthesis duration. These findings provide valuable insights into the mechanistic aspects of strontium carbonate decomposition.

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Author contributions

Kürşat İçin: Conceptualization; Data curation; Formal analysis; Sümran Bilgin: Funding acquisition, Investigation; Sefa Emre Sünbül: Methodology; Sultan Öztürk Project administration, Resources, Supervision.

References

1. Için, K., Öztürk, S., Çakıl, D. D., Sünbül, S. E., Ergin, İ., Özçelik, B., Investigation of nano-crystaline strontium hexaferrite magnet powder from mill scale waste by the mechanochemical synthesis: Effect of the annealing temperature. Materials Chemistry and Physics **2022,** 290, 126513
2. Yan, F., Zhang, X., Asselin, E., Duan, D., Li, Z., Preparation of strontium carbonate via celestite leaching in NaHCO3 using two interconnected reactors. Hydrometallurgy **2021,** 204, 105729
3. Liu, X., Li, Y., Zeng, L., Li, X., Chen, N., Bai, S., He, H., Wang, Q., Zhang, C., A Review on Mechanochemistry: Approaching Advanced Energy Materials with Greener Force. **2022,** 34 (46):2108327
4. Ardila-Fierro, K. J., Hernández, J. G., Sustainability Assessment of Mechanochemistry by Using the Twelve Principles of Green Chemistry. **2021,** 14 (10):2145-2162
5. Dayani, N., AmirArjmand, A., Nouri-Khezrabad, M., Hasani, S., High-efficiency mechanochemical synthesis of Strontium carbonate nanopowder from Celestite. **2021,** 18 (1):24-31
6. El-Sadek, M. H., Farahat, M. M., Ali, H. H., Zaki, Z. I., Synthesis of SrTiO3 from celestite and rutile by mechanical activation assisted Solid-State reaction. Advanced Powder Technology **2022,** 33 (5):103548
7. Erdemoğlu, M., Aydoğan, S., Canbazoğlu, M., A kinetic study on the conversion of celestite (SrSO4) to SrCO3 by mechanochemical processing. Hydrometallurgy **2007,** 86 (1):1-5
8. Obut, A., Baláž, P., Girgin, İ., Direct mechanochemical conversion of celestite to SrCO3. Minerals Engineering **2006,** 19 (11):1185-1190
9. Bingöl, D., Aydoğan, S., Bozbaş, S. K., Production of SrCO3 and (NH4)2SO4 by the dry mechanochemical processing of celestite. Journal of Industrial and Engineering Chemistry **2012,** 18 (2):834-838
10. Bowmaker, G. A., Solvent-assisted mechanochemistry. Chemical Communications **2013,** 49 (4):334-348
11. Martín-Perales, A. I., Balu, A. M., Malpartida, I., Luque, R., Prospects for the combination of mechanochemistry and flow applied to catalytic transformations. Current Opinion in Green and Sustainable Chemistry **2022,** 38, 100714
12. Takacs, L., The historical development of mechanochemistry. Chemical Society Reviews **2013,** 42 (18):7649-7659
13. Black, A. L., Lenhardt, J. M., Craig, S. L., From molecular mechanochemistry to stress-responsive materials. Journal of Materials Chemistry **2011,** 21 (6):1655-1663
14. Tole, I., Habermehl-Cwirzen, K., Rajczakowska, M., Cwirzen, A. Activation of a Raw Clay by Mechanochemical Process—Effects of Various Parameters on the Process Efficiency and Cementitious Properties Materials [Online], **2018**
15. Bingöl, D., Aydoğan, S., Bozbaş, S. K., Optimization of the Wet Mechanochemical Process Conditions of SrSO4 to SrCO3 and (NH4)2SO4 by Using Response Surface Methodology. Metallurgical and Materials Transactions B **2012,** 43 (5):1214-1219
16. Tiwary, R. K., Narayan, S. P., Pandey, O. P., Preparation of strontium hexaferrite magnets from celestite and iron ore fines by mechanochemical route. Mineral Processing and Extractive Metallurgy **2009,** 118 (4):201-204
17. Sezer, R., Hızlı, İ. G., Bilen, A., Ertürk, S., Arslan, C. J. M. B., Effect of Mechanical Activation on Roasting of Celestite Ore. **2017,** (11):53-59
18. Tan, Q., Li, J., Recycling Metals from Wastes: A Novel Application of Mechanochemistry. Environmental Science & Technology **2015,** 49 (10):5849-5861
19. Tsuzuki, T., McCormick, P. G., ZnO nanoparticles synthesised by mechanochemical processing. Scripta Materialia **2001,** 44 (8-9):1731-1734
20. Wang, R., Zhu, Z., Tan, S., Guo, J., Xu, Z., Mechanochemical degradation of brominated flame retardants in waste printed circuit boards by Ball Milling. Journal of hazardous materials **2020,** 385, 121509