

# Effect of Mechanical Activation and Excess Graphite on the Formation of $\text{SrCO}_3$ from Celestite via Black-Ash Method

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**Abstract:** Celestite ore, the primary mineral for producing strontium compounds, particularly strontium carbonate, is processed using the black ash method, which involves carbothermic reduction, water leaching, and carbonation. This study aims to investigate the combined effect of mechanical activation and additional graphite on strontium carbonate's recovery rate and purity. Celestite ore with a strontium sulfate content of 79% was obtained from the Dasht-e-Kavir mine. Acid washing with 10% hydrochloric acid significantly reduced carbonate impurities, resulting in a celestite purity of 96.9%. Mixtures of celestite and graphite with varying amounts of graphite were prepared with and without milling. The mixtures were roasted at 900°C for 1 hour to form strontium sulfide, followed by hot water leaching. After filtration, sodium carbonate was added to the leachate containing SrS, resulting in the formation and precipitation of white strontium carbonate crystals. The results showed that adding graphite increased the recovery rate in unmilled specimens. However, the recovery rate decreased significantly when 1 and 10 hours of milling were applied in the presence of excess graphite. Conversely, in the absence of additional graphite, milling for 1 and 10 hours increased the strontium recovery rate to over 95%. Furthermore, the analysis of strontium carbonate obtained from the sample with the highest recovery rate showed a purity of over 99.9%.

**Keywords:** Celestite, Black ash, Mechanical activation, Graphite, Strontium carbonate.

## 1. INTRODUCTION

Celestite ore is the primary source for the production of strontium carbonate, which is used in various applications such as color TV picture tubes, ceramic magnets, pyrotechnics, pigments, driers, and the production of strontium metal [1]. In 2001, approximately 85% of all strontium was consumed in the glass and ceramics industry, mainly in television faceplate glass and ceramic ferrite magnets [2]. The required purity of strontium carbonate for use in the glass and ceramic industries is at least 96%, while for the production of strontium metal, it is 99% [3].

In terms of celestite ore concentration, Dogan et al. [4] found that hydrochloric acid is the most effective acid for removing calcium from celestite. The use of 5-10% hydrochloric acid at room temperature reduced calcium content from 0.75% to less than 0.2%. To produce high-purity strontium carbonate, the iron content in celestite should be less than 0.1%. The direct conversion and black ash methods are the most common techniques for producing strontium carbonate. In the direct conversion method, celestite powder reacts with sodium carbonate [5] or ammonium

carbonate [6] at temperatures above 90°C to form strontium carbonate. In the black ash method, celestite is roasted with coke at temperatures above 1000°C Eq. (3). The resulting product, known as black ash, mainly contains soluble strontium sulfide. After leaching and removing insoluble compounds, the solution reacts with carbon dioxide or sodium carbonate to precipitate strontium carbonate [7, 8]. One advantage of the black ash method is the easy removal of iron through filtration of the residue. This method produces strontium carbonate of chemical-grade purity, with a minimum purity of 98%, while the direct conversion method produces strontium carbonate of technical-grade purity, with a minimum purity of 97% [2].



Erdemoglu et al. [7] examined the effects of temperature, time, and coke quantity on the carbothermic conversion of celestite. They reported the optimal values as follows: temperature (1200°C), reduction time (30 minutes), and coke addition (1.5 times the stoichiometric value). Reduction between 900°C and 1000°C primarily occurred through CO generated from the Boudouard reaction. They suggested that at around 1000°C, excess CO, which does not

contribute to the reduction process, may convert to CO<sub>2</sub> and free carbon through the Boudouard reaction. The partial reaction between free carbon and SrS leads to the formation of strontium carbide. Increasing the amount of coke resulted in a higher rate of carburization of alkaline earth metals while decreasing the purity of strontium carbonate.

Erdemoglu and Canbazoglu [8] evaluated the leaching of SrS with water and the precipitation of SrCO<sub>3</sub> from the leachate. Celestite was roasted with coke, using 50% excess compared to the stoichiometric equation Eq. (1), at 1300°C for 2 hours to produce strontium sulfide. In the carbonation stage, the optimum carbonation time was found to be 2 minutes. The amount of sodium carbonate used was 1.5 times the stoichiometric value according to Eq. (2). They also studied the solubility of SrS and SrO in water, finding that the highest solubility was 80 g/L at boiling temperature, while the solubility decreased at lower temperatures. At low temperatures, strontium oxide exhibited lower solubility compared to strontium sulfide [9].

$\text{SrS}_{(\text{aq})} + \text{Na}_2\text{CO}_{3(\text{aq})} \rightarrow \text{SrCO}_{3(\text{s})} + \text{Na}_2\text{S}_{(\text{aq})}$  (2)

The high temperature involved in the process has disadvantages, such as high energy consumption, sintering of reactants and products, and material selection challenges for reactor construction [10]. Mechanical activation reduces the temperature required for carbothermic reduction of minerals [11, 12, 13]. Some advantages of mechanical activation include lower reaction temperature, increased dissolution rate, and shorter reaction times [1]. Erdemoglu et al. [1] investigated the effect of mechanical activation on the reduction temperature of celestite with coke. They observed that 1 hour of milling decreased the formation temperature of SrS from 957°C to 900°C, while 24, 72, and 120 hours of milling reduced the formation temperature of SrS to nearly 700°C. Milling for up to 120 hours resulted in enhanced mass loss due to improved contact surfaces between celestite and coke particles, which accelerated the solid-state reaction for conversion. Roasting the milled mixture at high temperatures activated the sintering process, negating the celestite structure disorder's effect and delaying the reduction reaction. Ong and Yang [14] milled graphite under a neutral atmosphere, air, and oxygen. In the presence of oxygen, oxidation occurred on the graphite surface along the

graphene edges, preventing the graphite from breaking and becoming amorphous. At a certain milling time, the specific surface area of graphite was higher in the neutral atmosphere compared to air and oxygen.

In this study, we simultaneously investigated the effects of varying graphite amounts and milling times on the recovery of strontium and the purity of strontium carbonate. Graphite served as the reducing agent, and a CO atmosphere was created by surrounding the celestite-graphite reaction chamber with charcoal powder.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Materials and Devices

Celestite ore with a purity of 79% was obtained from the Dasht-e-Kavir mine in Semnan, Iran. The purification of celestite was carried out using hydrochloric acid (purity 37%). Ultra-pure graphite (Merck, Germany) with a grain size below 50 µm was used. Charcoal powder was utilized to create a reductive atmosphere around the crucible environment. Sodium carbonate (purity 99.9%) was used for carbonation.

X-ray fluorescence (XRF) (model PW1480, Philips, Netherlands, voltage 40 kV, current 30 mA, with a copper anode) was used to determine the elements. X-ray diffraction (XRD) (Explorer model, manufactured by CNR company in Italy, copper anode lamp with wavelength  $\lambda = 1.54 \text{ \AA}$ , voltage 40 kV, and current 30 mA) was applied to determine the phase analysis. An inductively coupled plasma spectrometer (ICP-OES) (model 11076/IR/KW17, Germany) was used to determine the percentage of elements.

### 2.2. Design of Experiments

First, the celestite ore was crushed with a hammer and powdered in a shaker. Particle size was measured according to the ASTM E-11 standard, which indicated that 90.34% of particles were below 74 µm. XRD analysis of the raw celestite is shown in Fig. 1, indicating the presence of strontium sulfate, calcite, dolomite, and silica phases. XRF analysis of the raw celestite is represented in Table 1, revealing that the amount of SrO is 44.5 wt%. Accordingly, the strontium sulfate amount can be calculated to be 79 wt%, which equals the sum of SrO and SO<sub>3</sub> in XRF analysis. It means that the only sulfate phase existing in the ore is SrSO<sub>4</sub>.

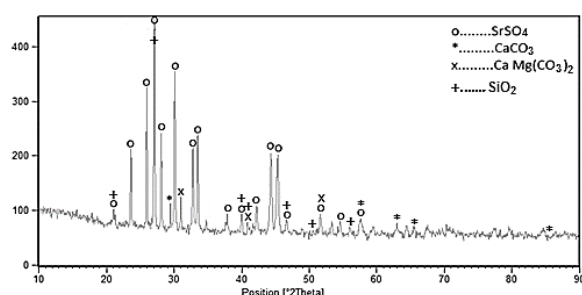


Fig. 1. XRD analysis of the raw celestite powder

The results in Table 1 indicate that in addition to dolomite, calcite, and silica, which were identified in XRD analysis, elements such as barium, iron, aluminum, and fluorine are present in the raw celestite. These elements were not detected by XRD due to their small amounts.

For purification, the raw celestite powder was washed with 10 wt% hydrochloric acid with a solid-to-liquid ratio of 1:20 g/mL for 1 h on the magnetic stirrer at room temperature. Table 2 indicates the XRF analysis results of the concentrated celestite. As a result of acid washing, fluorine, copper oxide, manganese oxide, and titanium oxide have been completely removed, and the amounts of CaO and MgO compounds, which were in the form of carbonate compounds in celestite ore, have been reduced. Comparing Table 1 and Table 2 shows that the purity of  $\text{SrSO}_4$  has increased from 79% to 96.9% due to acid washing.

Graphite in the ratios of 1, 1.5, and 2 times the stoichiometric values, according to Eq. (1), was mixed with celestite. Then, the celestite-graphite mixture was milled at different times (1 and 10 h), with a ball-to-powder ratio of 30, and a rotation speed of 260 rpm in the air atmosphere. The ball's diameters were 17, 13, and 7 mm. According to the programming capability of the planetary ball mill, the milling process was stopped for 15 minutes after each 2 h of milling to prevent the temperature increase in the milling chamber.

Nine samples of the celestite-graphite mixture were prepared in an un-milled and milled state (milled for 1 and 10 h). The effects of milling time

and additional graphite on the strontium recovery rate and the strontium carbonate purity were investigated. In the coding of the samples, symbols 1C, 1.5C, and 2C correspond to graphite addition as 1, 1.5, and 2 times the stoichiometric value, respectively. Symbols 0h, 1h, and 10h correspond to the milling times of 0 (un-milled), 1, and 10 h, respectively.

In the carbothermic reduction stage, the alumina crucible containing the mixture of celestite and graphite powder was buried in a crucible of charcoal powder (Fig. 2). The volume of the crucible was  $30 \text{ cm}^3$ , and the volume of the other crucible was  $100 \text{ cm}^3$ . In each reduction test, 3 g of the mixture was used. Then crucibles were placed in a Muffle furnace at a temperature of  $900^\circ\text{C}$  for 1 h.

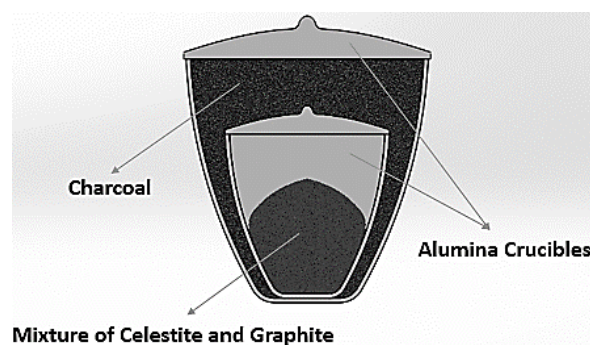


Fig. 2. Experimental setup for placing celestite and graphite mixture in a charcoal bed

The following equation was used to calculate the mass loss:  $W_R$  is the mixture's mass after roasting, and  $W_0$  is the mass before roasting.

$$\text{Mass Loss\%} = ((W_0 - W_R)/W_0) \times 100\% \quad (3)$$

Afterwards, 1 g of the obtained black ash was leached in 100 mL of distilled water and stirred magnetically for 1 h at a temperature of  $97^\circ\text{C}$ . Insoluble compounds were removed from the solution via filtration using Whatman No. 42 filter paper (2.5-micron pores). The leach residue was dried in an oven at  $110^\circ\text{C}$  for 1.5 h and then weighed to determine the dissolution amount. The dissolution rate was calculated as follows:

$$\% \text{Solubility} = (1 - L) \times 100\% \quad (4)$$

Table 1. XRF analysis of the raw celestite powder

Phase	SrO	SO <sub>3</sub>	CaO	MgO	BaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	CuO	Cl	F	LOI
%wt	44.55	34.44	4.43	0.51	0.2	0.82	0.19	0.19	0.06	0.03	0.03	0.59	0.07	5.13	3.35

Table 2. XRF analysis of the concentrated celestite powder

Elements	SrO	SO <sub>3</sub>	CaO	MgO	BaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl	LOI
%wt	54.68	42.36	0.13	0.34	0.25	0.34	0.88	0.18	0.16	0.06	0.07	0.46

Where L is the mass of the leach residue after leaching 1 g of the black ash in hot water, measured in grams. During filtration, the temperature of the leach liquor may decrease, causing the dissolved SrS to solidify into  $\text{Sr}(\text{OH})_2$ , which can affect the recovery rate. Erdemoglu and Canbazoglu [8] reduced the temperature of the solution containing SrS to ambient temperature and separated the solid strontium hydroxide.

The carbonation stage was performed on a hot plate to prevent the temperature drop of the solution containing SrS. In this stage, sodium carbonate was added to the solution containing SrS at a temperature of  $97^\circ\text{C}$ , using two times the stoichiometric value according to Eq. (2). The mixture was stirred for 10 minutes with a magnetic stirrer. White particles of strontium carbonate were immediately observed after adding sodium carbonate to the solution. The retention time for the complete precipitation of the particles was 40 h. After filtration, the strontium carbonate precipitate was dried in an oven at  $110^\circ\text{C}$  for 1.5 h and then weighed. Each experiment was repeated at least two times to increase the reliability of the measurements.

The strontium recovery rate and the purity of the final precipitate were calculated according to Eq. (5) and Eq. (6), respectively. In the equations, A, B, C, and D refer to the percentage of strontium in the final precipitate (%), the mass of the final precipitate (g), the mass of strontium in the final precipitate (g), and the theoretical mass of total strontium in the black ash (g), respectively.

$$\% \text{Sr Recovery} = C/D \times 100\%; (C = A \times B) \quad (5)$$

$$\% \text{SrCO}_3 \text{ in final precipitate} = A \times M_{\text{SrCO}_3}/M_{\text{Sr}} \quad (6)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Milling of the Mixture of Celestite and Graphite

The mixture of celestite and graphite was milled for 1 and 10 hours. Graphite was added stoichiometrically (sample 1h-1C) and also in 2 times the stoichiometrically required amount (samples 1h-2C and 10h-2C). Fig. 3 illustrates the X-ray diffraction of the milled mixture of celestite and graphite. With an increase in the graphite content from 1h-1C to 1h-2C, the intensity of the carbon peak enhanced. As the milling time increased from 1h-2C to 10h-2C, the intensity of

the carbon and strontium sulfate peaks decreased. The reduction in peak intensity due to milling is attributed to the disordering of celestite and graphite structures and their amorphization [1]. It was observed that the decrease in the intensity of the carbon peak is greater than that of strontium sulfate. The higher rate of graphite amorphization is caused by its laminated structure with weak Van der Waals bonds [12].

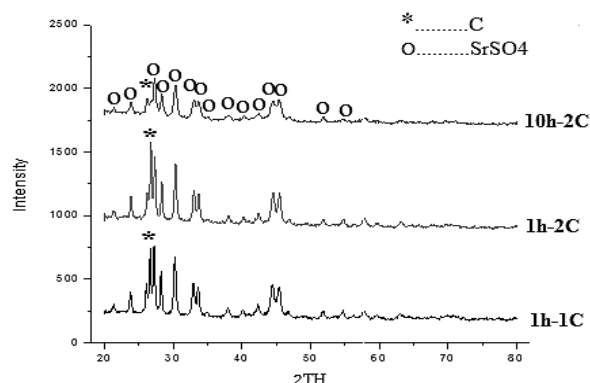


Fig. 3. X-ray diffraction pattern of the mixture of celestite and graphite after milling for 1 and 10 h

#### 3.2. Roasting of the Milled Mixture of Celestite and Graphite

XRD analysis of raw celestite demonstrates that the main impurities are calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), and silica ( $\text{SiO}_2$ ) compounds (Fig. 1). However, according to the XRF analysis of the concentrated celestite (Table 2), the amounts of CaO and MgO have decreased through acid washing. CaO and MgO only exist in carbonate form.

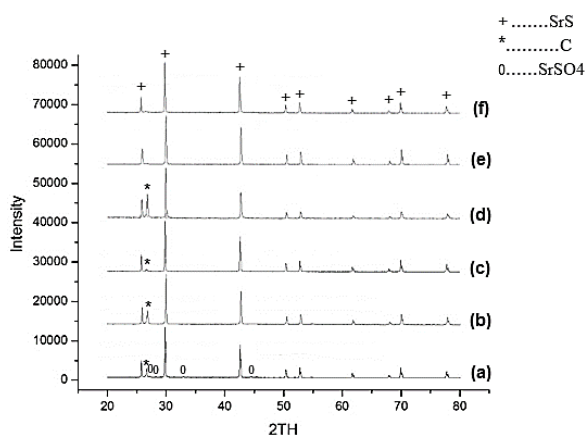
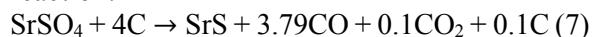
It is reported that the calcination temperature of dolomite is  $777.8^\circ\text{C}$ , and for calcite, it is  $834^\circ\text{C}$ , as determined by DTA analysis under  $\text{N}_2$  gas pressure [15]. The milled and unmilled mixture of celestite and graphite was roasted at  $900^\circ\text{C}$  for 1 hour. Fig. 4 illustrates the XRD patterns of the roasted mixtures (black ash).

As indicated, sample 0h-1C shows the presence of SrS,  $\text{SrSO}_4$ , and carbon peaks after roasting. By increasing the graphite content from sample 0h-1C to 0h-2C, all peaks of  $\text{SrSO}_4$  faded, while the carbon peak intensity increased. These results can be explained by the fact that additional carbon was used to further reduce  $\text{SrSO}_4$  and form SrS [7].

By applying 1 hour of milling in sample 1h-1C, all  $\text{SrSO}_4$  was converted to SrS, and the intensity of the carbon peak decreased. This indicates that



milling can facilitate the reduction of  $\text{SrSO}_4$ , leading to a higher consumption of carbon compared to sample 0h-1C. However, carbon remains in the black ash, which may be attributed to the partial formation of  $\text{CO}_2$  instead of  $\text{CO}$ . Calculations using FactSage software indicate that the presence of carbon is due to the formation of  $\text{CO}_2$ , as shown in the following reaction:

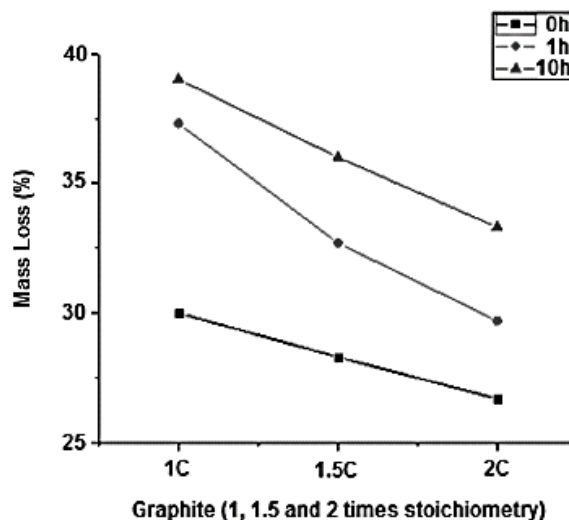


**Fig. 4.** XRD analysis of celestite-graphite black ash after roasting at  $900^\circ\text{C}$  for 1 h. a) sample 0h-1C, b) sample 0h-2C, c) sample 1h-1C, d) sample 1h-2C, e) sample 10h-1C, and f) sample 10h-2C

With an increase in the graphite content from sample 1h-1C to 1h-2C, the intensity of the carbon peak further increased. Additionally, no new phase, such as carbide, was observed in the XRD diffraction pattern. In samples 10h-1C and 10h-2C, the graphite peak in the black ash has been removed. It is reported that the significant decrease in the amount of carbon in the black ash is related to carbon gasification [7].

Fig. 5 shows the mass loss of the milled mixture of celestite and graphite after roasting at  $900^\circ\text{C}$ . The mass loss is mainly attributed to the gas production during roasting, as mentioned in Eq. (6). Therefore, the mass loss can be considered as a criterion for the reaction progress and SrS formation. As shown in Fig. 5, the mass loss decreases with the addition of graphite from the stoichiometric ratio (denoted by 1C) to samples with 1.5 and 2 times the stoichiometric ratio (denoted by 1.5C and 2C). This implies that although the addition of carbon may assist in the reduction progress, it decreases the percentage of mass loss due to the increase in

total mass. Moreover, the results indicate that milling has increased the mass loss, as it activates the reactants and facilitates the reaction progress.



**Fig. 5.** Mass loss of the celestite and graphite mixture after heating at  $900^\circ\text{C}$  for 1 h. Mixtures are in un-milled condition (black line), and milled conditions for 1 h (red line), and 10 h (blue line)

### 3.3. Leaching of the Roasted Mixture and Precipitation of $\text{SrCO}_3$

Fig. 6(a) demonstrates the solubility of the roasted mixture for both un-milled and milled conditions. The solubility increases with longer milling times. Milling helps activate the reactants and promotes the formation of SrS. However, the addition of more graphite reduces the solubility due to the presence of insoluble graphite residue. Additionally, higher amounts of graphite can lead to sintering during roasting, preventing the reduction of  $\text{SrSO}_4$  and resulting in reduced dissolution.

Fig. 6(b) displays the mass of  $\text{SrCO}_3$  precipitate for un-milled and milled conditions. It shows that the precipitation of  $\text{SrCO}_3$  increases with longer milling times, which is attributed to the higher solubility of the milled samples. However, the addition of graphite harms the final  $\text{SrCO}_3$  precipitation because the agglomeration of graphite during milling and sintering during roasting hinder the dissolution of SrS. Fig. 7 presents the XRD pattern of the  $\text{SrCO}_3$  precipitate from the 10h-1C sample, which exhibited the highest precipitation. As depicted, the only detectable phase is  $\text{SrCO}_3$  with an orthorhombic structure.



**Fig. 6.** a) Solubility of the roasted mixture in hot water in various milling conditions. b) Mass of the final  $\text{SrCO}_3$  precipitate after the addition of  $\text{Na}_2\text{CO}_3$  to the solution. Roasted mixtures are in un-milled condition (black line), and milled conditions for 1 h (red line), and 10 h (blue line)



**Fig. 7.** XRD analysis of the final  $\text{SrCO}_3$  precipitate of the sample 10h-1C

Table 3 provides the results of the ICP analysis for the final  $\text{SrCO}_3$  precipitate of the 10h-1C sample. It indicates that the impurity levels are negligible. The purity of the final  $\text{SrCO}_3$  precipitate can be calculated using Eq. (6), and in this case, it was found to be almost 100%.

### 3.4. The Recovery Rate of Strontium

According to Fig. 8, the recovery of strontium was influenced by both milling conditions and the addition of graphite. The recovery rate, calculated using Eq. (5), was found to be approximately 95% for the samples 1h-1C and 10h-1C. This indicates that milling for up to 1 hour had a significant impact on the strontium

recovery. However, further milling (up to 10 hours) did not result in an increased recovery rate. Milling can effectively grind and activate the celestite particles, increasing the effective surface area of the reactants. This enhanced surface area facilitates the roasting reaction, leading to the formation of more soluble  $\text{SrS}$ . Consequently, less unreacted celestite remains in the roasted product, reducing strontium losses during the leaching process and improving the overall recovery.

On the other hand, the addition of graphite in amounts exceeding the stoichiometric value increased the recovery of strontium when milling was not applied. Excess graphite promotes the progress of the roasting reaction, resulting in the formation of more  $\text{SrS}$ . As a result, strontium losses during the leaching step are reduced.

However, when excess graphite is used and milling is applied, it tends to agglomerate and cover the celestite particles during the milling process. Consequently, after roasting, the celestite particles become embedded in the excess graphite and cannot be dissolved during leaching. This leads to the presence of unreacted celestite in the leaching waste, resulting in a decrement in the recovery rate.

**Table 3.** The results of ICP analysis of the final  $\text{SrCO}_3$  precipitate of the sample 10h-1C

Element	Sr	Na	Ba	Ca	Fe
wt%	60.62	0.0013	0.0010	0.0003	0.0078

In summary, milling for up to 1 hour improves strontium recovery by increasing the effective surface area of the reactants. Excess graphite, when not combined with milling, enhances the recovery rate by promoting the roasting reaction. However, the combination of excess graphite and milling negatively affects the recovery rate by preventing the dissolution of celestite particles during leaching.

#### 4. CONCLUSIONS

The present work investigated the formation of strontium carbonate from celestite using the black ash method. The process involved roasting a powder mixture of celestite and graphite, followed by leaching the roasted powder in hot water to dissolve the strontium sulfide. Impurities were removed as waste through filtration, and then sodium carbonate was added to the solution containing strontium sulfide, resulting in the formation and precipitation of white crystals of strontium carbonate. The final product was filtered and dried for further analysis.

The study examined the impact of different amounts of graphite and milling times on the recovery and purity of the strontium carbonate. When milling was not applied, adding graphite increased the recovery rate. However, when excess graphite was present and milling was conducted for 1 and 10 hours, the recovery rate significantly decreased. This suggests that milling under conditions with excess graphite is not suitable for achieving a high strontium recovery rate. On the other hand, in the absence of additional graphite, milling for 1 and 10 hours increased the recovery rate to around 95%.

The analysis of the strontium carbonate obtained from the 10h-1C sample revealed a purity above 99.9%.

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