Effect of Mechanical Activation on the Synthesis of Strontium Carbonate via Black-Ash Process

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ABSTRACT

Celestite is the main raw material for producing strontium carbonate, which is widely used in color TV tubes, electroceramics, pyrotechnics, and zinc refining. The black-ash method is an economical route for this production, involving three steps: reducing celestite to strontium sulfide (SrS), dissolving SrS in hot water, and precipitating $SrCO_3$ from the solution. Although this process yields high-purity product, it consumes significant energy. In this study, mechanical activation was applied to reduce energy consumption by lowering the reduction temperature, improving dissolution, and shortening reaction time. Graphite was used as the reductant and sodium carbonate as the precipitant. TGA-DTA analysis determined the optimal milling time and reduction temperature. Celestite powder (76% purity) mixed with graphite was mechanically activated in a planetary mill, then heated at 900°C for one hour to convert $SrSO_4$ to SrS. The SrS was leached in 90°C water for one hour to separate gangue, and $SrCO_3$ was precipitated by adding sodium carbonate. The final product had 76.4% purity with over 99% recovery. Acid washing of the celestite increased product purity to 97.8%, showing that raw material purification greatly affects final quality.

***Keywords**: Celestite; SrS; Strontium Carbonate; Mechanical Activation; Carbothermic Reduction.*

1. INTRODUCTION

Celestite mineral predominantly consists of strontium sulfate ($SrSO_4$), which serves as the primary raw material for the production of strontium compounds [1]. Strontium carbonate ($SrCO_3$) is mainly employed in color television picture tubes for X-ray absorption [1]. Other applications include the production of permanent ceramic magnets, removal of lead from zinc sulfate solution in the zinc electrolysis process, production of metallic strontium, electroceramics, and oxide-based superconductors [2, 3]. Strontium carbonate itself is considered a precursor for the synthesis of other strontium compounds [4, 5]. Additional applications include the production of optical glasses, pyrotechnics, pigments, paints, and desiccants [5]. Global production of strontium carbonate ($SrCO_3$) has been reported at 245 thousand tons [6].

Strontium carbonate is obtained from celestite mineral via two major processes. The double decomposition method involves the direct dissolution of celestite with sodium carbonate, ammonium carbonate, or ammonium bicarbonate solutions, which may require purification depending on the initial celestite purity. The other method, known as the black ash process, involves carbothermic reduction to produce SrS and comprises three main stages: reduction, leaching, and precipitation. The conversion of strontium sulfate to SrS via carbothermic reduction at 1100–1300°C, leaching of SrS in water at 80°C, and precipitation of strontium carbonate ($SrCO_3$) from the strontium-bearing solution with sodium carbonate or CO_2 [1, 7, 8]. Compared to the double decomposition process, the black ash process offers higher product purity but entails higher energy consumption [7].

The fundamental conditions and details of carbothermic reduction were investigated by Erdemoglu and co-workers in 1998. The initial chemical reaction occurs at temperatures below 400°C (Eq. 1) [1].

$$SrSO4+4C\rightarrow SrS+4CO(1)SrSO4+4C\rightarrow SrS+4CO \quad (1)$$

Since both celestite and coke are solids, their inter-diffusion is limited, contact between them is poor, and the reaction proceeds slowly. With the formation of CO, this gas acts as the primary reducing agent, diffusing to the celestite surface not in contact with carbon. The gas-phase reaction (Eq. 2) occurs, producing CO_2, which subsequently reacts with carbon to regenerate CO (Eq. 3). Consequently, the gas-phase reaction is dominant, while the solid-state reaction (Eq. 1) is of lesser significance.

$$SrSO_4+4CO\rightarrow SrS+4CO_2 \quad (2)$$

$$CO2+C\rightarrow 2CO \quad (3)$$

Following the reduction reaction and SrS formation, if excess free carbon is present at elevated temperatures (e.g., above 1180°C), a partial reaction between SrS and carbon may occur, leading to the formation of SrC_2 (Eq. 4) [5].

$$SrS+2C\rightarrow SrC_2+S \quad (4)$$

In the work of Erdemoglu and co-workers in 1996, celestite with 95.5% purity and metallurgical coke with 97.82% purity were used. Reduction was carried out in a tube furnace under a nitrogen atmosphere. It was reported that complete conversion of $SrSO_4$ to SrS begins at temperatures exceeding 1200°C, and even with 50% excess coke, $SrSO_4$ and other sulfates remained present in the black ash. The quality of the reductant, particle size, temperature, and ore-to-reductant ratio affect the reduction process [7].

Mechanical activation has been successfully applied to enhance thermal processes of sulfide materials, including oxidation, decomposition in neutral atmospheres, and sublimation. Some advantages of mechanical activation include reduced reduction temperature, increased leaching rate and efficiency, preparation of water-soluble compounds, reduced reaction time, and the use of simpler and less expensive reactors [9, 10]. Consequently, the energy consumption of high-temperature processes such as carbothermic reduction of celestite is diminished [11]. Increasing

milling time may lead to agglomeration of fine particles during milling and sintering at relatively high temperatures during reduction, thereby eliminating the structural disorder effects in celestite and reducing the reduction efficiency [4].

Leaching of SrS in boiling water enhances strontium recovery. Other sulfides present in the black ash, such as BaS and CaS, dissolve simultaneously with SrS in hot water, reducing the purity of strontium carbonate. Precipitation with Na_2CO_3 yields higher precipitation rates and greater strontium recovery compared to CO_2, while CO_2 produces strontium carbonate of higher purity. Strontium recovery using Na_2CO_3 reaches a maximum within 2 minutes of carbonation and remains constant thereafter. Under laboratory conditions, a minimum of 25% excess sodium carbonate is sufficient for complete precipitation [12]. Prolonged holding time during this stage increases the crystal growth of strontium carbonate [8].

If the celestite ore has a purity below 90%, the resulting strontium carbonate product will have low economic efficiency [7]. Therefore, a beneficiation step is necessary to upgrade the celestite grade from medium- and low-grade ores prior to processing. Calcium is present as carbonate and sulfate in celestite ore. For calcium impurity removal, HCl at concentrations of 5–10% at ambient temperature is employed. Using this method, the calcium content is reduced from 0.75% to below 0.2% [13].

The present investigation focuses on the production of strontium carbonate from celestite ore via the black ash process, incorporating mechanical activation prior to the reduction stage.

2. MATERIALS AND METHODS

Celestite ore was obtained from the Dasht-e-Kavir mine in Semnan, Iran. The ore was initially crushed with a hammer to 3–5 cm pieces and subsequently milled using a shaker to particles below 100 μm. Graphite and celestite powder were mixed at a carbon-to-strontium sulfate molar ratio of 2:1 according to reaction (1). A planetary ball mill was employed for mechanical activation of the celestite–graphite mixture. Milling was performed at a rotational speed of 260 rpm with a ball-to-powder ratio of 30:1 for durations of 1 and 10 hours. After every 2 hours of milling, the apparatus was stopped for 15 minutes to prevent temperature rise. Three samples—unmilled, 1-hour milled, and 10-hour milled—were subjected to thermal analysis (TGA-DTA) at a heating rate of 10°C/min up to 900°C under air atmosphere. Reduction was conducted in a muffle furnace at 900°C for 1 hour, with charcoal powder placed around the crucible. One gram of the reduced mixture was leached in 100 cc of distilled water at 85–90°C, and the residue was separated from the SrS-containing solution by filter paper and washed several times with hot water. The residue was then dried in an oven at 110°C for 1 hour. The weight difference before and after leaching determined the leaching efficiency. Sodium carbonate, at twice the stoichiometric amount required by reaction (5), was added to 20 cc of distilled water, and the solution was heated to 90°C. This solution was stirred with a magnetic stirrer at 750 rpm for 10 minutes, during which the rapid formation of white powdery particles was observed. Due to the fine particle size of strontium carbonate, a settling time of 30 hours was allowed. The precipitate was separated by filter paper, washed several times with hot distilled water to remove sodium carbonate, and dried in an oven at 110°C for 1 hour.

$$SrS_{aq}+Na_2CO_{3aq}\rightarrow SrCO_{3s}+Na_2S_{aq} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Analysis of Celestite Ore Powder

XRD and XRF analyses were performed to determine the constituent phases and composition of the celestite ore. Based on the XRF results presented in Table 1, 93.42% SrO is present, equivalent to 76.1% strontium sulfate. These findings are consistent with the XRD results shown in Figure 1.

Table 1: XRF analysis of celestite ore powder

%SrO	$\%SO_3$	%CaO	%MgO	$\%SiO_2$	$\%Al_2O_3$	$\%Fe_2O_3$	$\%K_2O$	$\%P_2O_5$	$\%TiO_2$	$\%Na_2O$	%Cl	%LOI
93.42	33.18	4.38	3.54	2.83	2.40	0.60	0.15	0.09	0.08	0.08	0.08	5.29

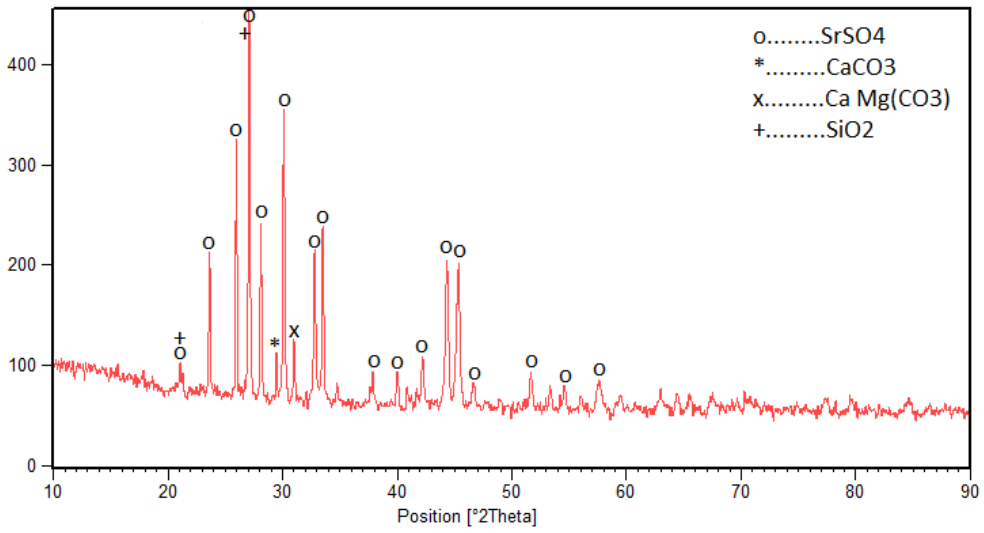

Figure 1: XRD pattern of celestite powder

3.2. TGA Thermal Analysis

TGA thermal analysis was employed to determine the thermal stability and weight loss associated with the carbothermic reduction reaction for the unmilled, 1-hour milled, and 10-hour milled celestite–graphite mixtures (Figure 2-a). The weight loss values for the three samples from the

TGA curves are presented in Table 2. Since the 1-hour milled sample exhibited weight loss comparable to the 10-hour milled sample, a milling time of 1 hour was adopted for subsequent experiments.

Figure 2-b shows the derivative weight loss curve (DTG), which more clearly delineates the reaction regions. For the unmilled sample, the onset temperature for weight loss corresponding to the reduction reaction is approximately 600°C. In contrast, after 1 and 10 hours of milling, the onset temperatures decreased to about 500°C. Thus, mechanical activation lowered the reaction onset temperature. It is also observed that the peak completion temperature for the 1-hour and 10-hour milled samples is 740°C. Therefore, to ensure complete reduction, a reduction temperature of 900°C was selected.

Figure 3 shows the DTA curves for the unmilled, 1-hour milled, and 10-hour milled mixtures, along with the graphite sample. Comparison of the DTA curves with the TGA-DTG results indicates that the endothermic peaks correspond to weight loss due to the reduction reaction. Since the DTA test was conducted in air, excess carbon combusts with atmospheric oxygen. Additionally, SrS (the reduction product) is unstable in the presence of oxygen and may undergo oxidation according to reactions (6) and (7). In the DTA curve, the exothermic peak for graphite combustion falls within approximately the same temperature range as the reaction peak for the 1-hour milled mixture. Considering these observations, it can be concluded that the exothermic oxidation of excess carbon and the endothermic reduction of celestite overlap, ultimately manifesting as an exothermic peak.

$$SrS+2O2=SrSO4 \qquad \Delta G=-882 \text{ kJ/mol} \qquad (6)$$

$$SrS+1.5O2=SrO+SO2 \qquad \Delta G=-399 \text{ kJ/mol} \qquad (7)$$

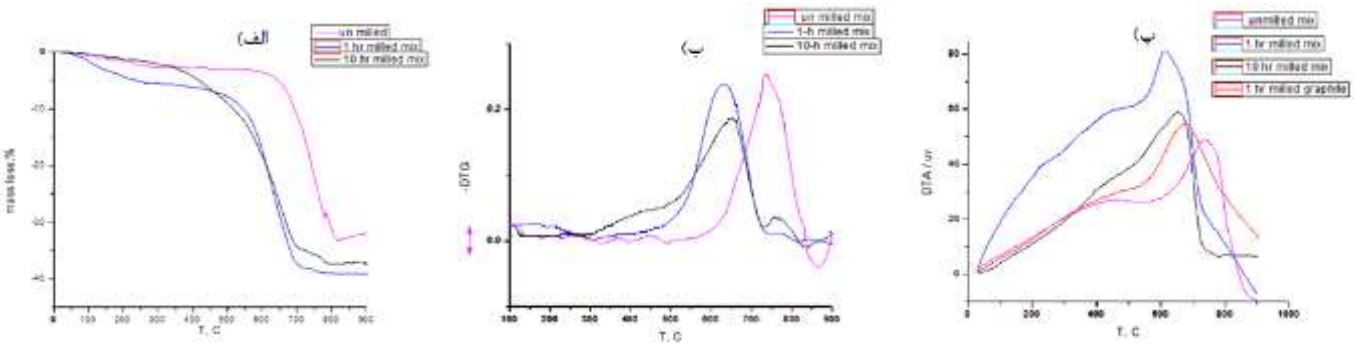

Figure 2: (a) TGA analysis; (b) DTG curves for unmilled, 1-hour ,and 10-hour milled mix samples, and (c) DTA analysis for unmilled, 1-hour milled mix samples ,and 10-hour milled mix samples; 1-hour milled graphite

Table 2: Results from TGA and DTG analyses

Milling time (hr)	Total weight loss in TGA (%)	Onset peak temperature in DTG (°C)	Completion peak temperature in DTG (°C)
0	32.9	600	860
1	40.6	500	740
10	38.1	300	740

3.3. Black Ash Process

The experimental results for reduction, leaching, and precipitation are presented in Table 3. The weight loss due to reduction, leaching efficiency, and final precipitate yield were higher for the 1-hour milled sample compared to the 10-hour milled sample.

Table 3: Experimental results of reduction, leaching, and precipitation tests

Condition	Weight loss in 3 g of initial mixture upon reduction (g)	Weight loss percentage upon reduction in furnace (%)	Leaching percentage in water (%)	Amount of precipitated $SrCO_3$ obtained from leaching of 1 g reduced mixture (g)
1 hr milling + reduction at 900°C + leaching	1.08	36	67	0.88
10 hr milling + reduction at 900°C + leaching	1.02	34	58	0.75

Table 4 presents the ICP analysis of the strontium carbonate product obtained under 1-hour milling conditions. Based on the strontium content determined by ICP (45.43%), the purity of the strontium carbonate product was calculated as 76.7%, and the strontium carbonate recovery exceeded 99%. Figure 3 shows the XRD pattern of the strontium carbonate product. As can be observed, the impurity levels in the sample were such that they were not detected as distinct phases in the XRD analysis.

Table 4: ICP analysis of strontium carbonate product

% Sr	% Ca	% Ba	% Na	% Mg
45.43	2.23	0.28	0.54	0.01

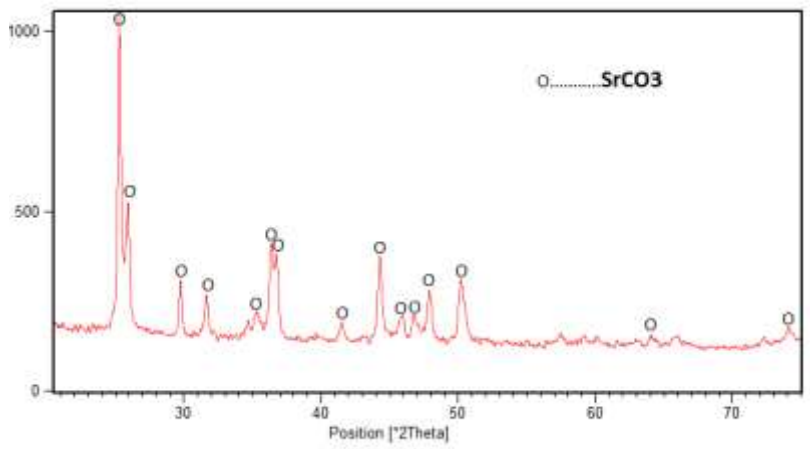

Figure 3: XRD pattern of strontium carbonate product

3.4. Beneficiation of Celestite Ore

Celestite powder was leached with 10% hydrochloric acid at a solid-to-liquid ratio of 1:2 for 1 hour at ambient temperature using a magnetic stirrer at 750 rpm. Table 5 presents the XRF results of the acid-leached celestite powder, showing that its purity increased to 96.9%. A milling time of 1 hour was selected, and the reduction, leaching, and precipitation steps were repeated as before. The strontium carbonate product purity reached 97.8%, with a recovery of 94%.

Table 5: XRF analysis of acid-leached celestite ore powder

%SrO	%SO_3	%CaO	%MgO	%SiO_2	%Al_2O_3	%Fe_2O_3	%BaO	%K_2O	%Na_2O	%Cl	%LOI
68.54	42.36	0.13	0.34	0.43	0.88	0.18	0.25	0.06	0.02	0.07	0.46

Table 6: XRF analysis of strontium carbonate product

%SrO	%SO_3	%CaO	%MgO	%Al_2O_3	%Fe_2O_3	%Na_2O	%LOI
84.62	0.07	0.40	0.47	0.56	0.09	0.59	13.20

4. CONCLUSIONS

1. Based on TGA-DTA results, the reduction reaction in the 1-hour and 10-hour mechanically activated samples commenced at lower temperatures compared to the unmilled sample.
2. According to the DTG curves, the formation temperature of SrS decreased in the 1-hour milled sample relative to the unmilled sample; however, extending the milling time from 1 hour to 10 hours did not cause a significant change in the SrS formation temperature.
3. The completion temperature of the reaction, as determined from the DTG curves, was identical for the 1-hour and 10-hour milled samples, measured at 740°C.
4. The leaching efficiency and precipitate yield obtained for the 1-hour milled sample were higher than those for the 10-hour milled sample.
5. In the case where the celestite ore powder was not acid-leached, the final strontium carbonate product exhibited a purity of 76.7%, with a conversion efficiency exceeding 99%.
6. Acid leaching increased the purity of celestite ore powder to 96.9%, yielding a strontium carbonate product with 97.8% purity and a conversion efficiency of 94%.

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