

Carbothermic Reduction of Mechanically Activated Mixtures of Celestite and Carbon

N.Setoudeh, M. Ali Askari Zamani and N.J.Welham

Abstract—The effect of dry milling on the carbothermic reduction of celestite was investigated. Mixtures of celestite concentrate (98% SrSO_4) and activated carbon (99% carbon) was milled for 1 and 24 hours in a planetary ball mill. Un-milled and milled mixtures and their products after carbothermic reduction were studied by a combination of XRD and TGA/DTA experiments. The thermogravimetric analyses and XRD results showed that by milling celestite-carbon mixtures for one hour, the formation temperature of strontium sulfide decreased from about 720°C (in un-milled sample) to about 600°C, after 24 hours milling it decreased to 530°C. It was concluded that milling induces increasingly thorough mixing of the reactants to reduction occurring at lower temperatures

Keywords—Activated carbon, Celestite, Ball milling, Carbothermic reduction, Strontium sulfide.

1. INTRODUCTION

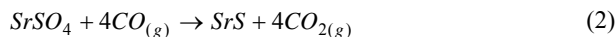
THERE are two commercial processes to manufacture SrCO_3 from celestite [1-2]. In the black ash process, SrSO_4 is reduced with coke (or coal) at temperatures generally over than 1000°C to produce water soluble SrS [2-4]. The sulfide is then leached in hot water and strontium carbonate is precipitated using soda ash, ammonium bicarbonate and/or CO_2 [5-6]. In the second process, finely powdered celestite is reacted with hot sodium carbonate solution (>90°C) to obtain SrCO_3 and by-product sodium sulfate by a double decomposition reaction [7-9]. Although the black ash method produces a higher purity SrCO_3 product it is more energy intensive than the double decomposition process. Other than these two above commercial methods and their modifications, there are several reports of the conversion celestite to SrCO_3 by other methods including the high temperature and high pressure reaction between celestite and either sodium or potassium carbonate [10] and direct leaching of celestite with Na_2S to produce SrCO_3 [11].

Fundamental conditions of the carbothermic reduction have been investigated and discussed in detail by Erdemoglu et al. [12-13] and Sonawane et al. [4] There are some articles about carbothermic reduction of SrSO_4 in isothermal conditions at

different temperatures [4,12-13]. The previous results showed that the first chemical reaction occurring at low temperatures (>400°C) is the solid-state reaction given as [4, 12-13].



Since the mineral celestite and coke are solids which do not easily fuse, contact between them is poor and the reaction is slow. With the formation of product SrS at the mineral surface, the solid-solid reaction is inhibited. The CO generated diffuses and reacts with celestite which is not in contact with carbon, according to:



The CO_2 diffuses back into the carbon to generate more CO , according to the “Boudouard” reaction:



In the solid-state reaction of celestite, CO is a gaseous intermediate and since the interface between gaseous CO and solid SrSO_4 takes place readily, CO is the principal reducing agent. Thus, the solid-state reaction between SrSO_4 and C is of little importance. Thermodynamic calculation reveals that the net free energy change of reaction (1) is $\Delta G = -6.6 \text{ kJ mol}^{-1}$ at 500°C [14], which shows the reaction (1) is only just favorable.

The rate of carbothermic reduction reactions can be greatly increased by pre-milling the mineral and carbon together when compared to with powders milled separately and then mixed [15-19]. Erdemoglu [13] studied the carbothermic reduction of mechanically activated celestite-coke mixtures for the first time. Milled and un-milled samples were heated isothermally at 500-1200°C for 2 hours in air and the products examined using XRD analyses. The results showed that mechanical activation of celestite-coke mixture intensified the carbothermic reduction.

The present work is intended to study the effects of mechanical activation on the carbothermic reduction of purified celestite concentrate with activated carbon. In this research the carbothermic reduction of celestite studied in the tube furnace without holding the samples in the desired temperatures for long times. Therefore, the structural changes of the reactant and product phases study in nearly non-isothermally condition. The mechanically activated mixtures of celestite and carbon heated to desired temperature in an argon atmosphere and then cooled immediately in order to study the reduction stages in milled and samples. For this

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purpose, fundamental characteristics of the intensively milled celestite-activated carbon mixtures and their black ashes were examined by XRD analyses.

II. EXPERIMENTAL PROCEDURE

Celestite concentrate was collected from the Likak celestite mine near Yasouj, southwest Iran. The samples were first crushed by a hammer and then ground in a laboratory type tumbling mill. The ground samples were washed with dilute HCl (1 N) solution in order to remove any carbonate impurity present. After acid washing and filtration, the solid residues were washed several times with distilled water then dried at 110°C for 2 hours. The purified celestite concentrate was milled in a laboratory type tumbling mill for 5 minutes, and then the fine powders screened to give a starting particle size range of $d_{0.9} = 66 \mu\text{m}$ and a specific surface area of $1.22 \text{ m}^2/\text{g}$. The initial morphology of the purified celestite was nearly round. X-ray fluorescence analysis of the purified celestite concentrate showed that it comprised 98% SrSO_4 and 2% gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The activated carbon was 99% C, $d_{0.9} = 58 \mu\text{m}$ and specific surface area: $0.613 \text{ m}^2/\text{g}$.

A planetary type ball mill (Farapazhouhesh, Iran, FP2 model) was used in all milling experiments. Preliminary experiments indicated the following conditions were appropriate: 600 rpm, five 20 mm diameter high Cr-steel balls in a high Cr-steel milling chamber gave a ball-to-sample weight ratio of 40:1. The milling runs were undertaken in argon (high purity, 99.99%) atmosphere for 1 and 24 hours. For inserting argon atmosphere in the vial, it is first evacuated by a vacuum pump up to $\sim 10^{-2}$ kPa then backfilled with high purity argon. The reactants were prepared in accordance with the stoichiometry given by reaction (1).

After finishing each milling run, the vial was opened and the samples thermogravimetrically analysed using a Netzsch STA 409 PC/PG. Samples of 69 mg were loaded into an alumina crucible which was then heated from room temperature to 1400°C at 10°C/min in dry argon gas (purity 99.99%) flowing at 30 ml/min. Isothermal experiments were conducted in a tube furnace. About one gram of the as-milled mixtures was put in an alumina crucible and heated up from 25°C to the desired temperature at 10°C/min under a flowing dry argon gas (purity 99.99%). The samples were held at the desired temperature for 5 minutes in the hot zone of the tube furnace, the power was turned off. After cooling, the samples were removed and examined using XRD. The temperatures investigated were selected from the TGA data.

Powder X-ray diffraction (XRD) patterns were recorded using a Philips diffractometer (Model: PHILIPS-X Pert, APD software) under following condition : radiation - Cu K α , tube current and voltage – 30 mA, 40 kV; scanning range (2 θ)- 20-100°, step size- 0.05°, count time per step – 3s. Peak identification was undertaken manually using the JCPDS card files for possible phases. For studying the carbothermic reduction in un-milled powder, a physical mixture of raw

materials was prepared in accordance with the stoichiometry given by reaction (1).

III. RESULT AND DISCUSSION

Fig. 1 shows the mass loss of the celestite concentrate-activated carbon mixtures during the TGA/DTA analysis in the milled and un-milled samples. The mass loss of un-milled and one hour milled samples begin approximately at above 400°C and continues beyond 1200°C whilst in 24 hours milled sample, the decreasing in mass loss begins at about 150°C. There is an increased mass loss at about 730°C in the un-milled sample whilst in the 1-h and 24 hours of milling samples, an increased mass loss begin at about 630°C and 550°C respectively. The final mass loss in the un-milled sample is about 47.8% which is more than the one hour and 24 hours milled samples. The theoretical mass loss for the reaction (1) is about 48.4%. Therefore, it seems that the reaction between celestite concentrate and activated carbon has been completed in both milled and un-milled runs after heating in dry argon atmosphere up to 1400°C.

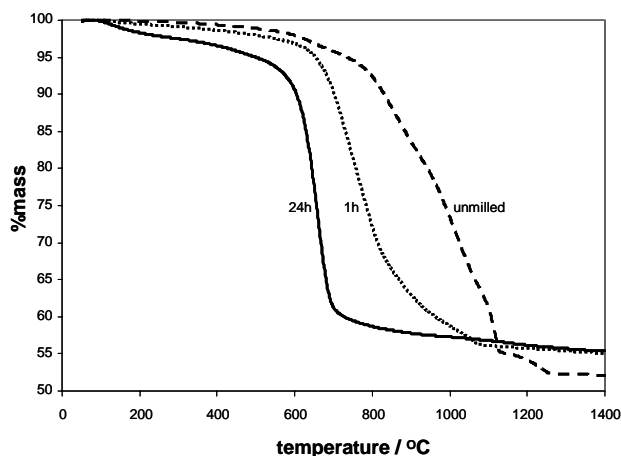


Fig.1 TGA traces of the milled and un-milled celestite-carbon mixtures heated to 1400°C in argon with 10°C/min

Fig.2 shows the rates of mass losses were derived from Fig.1 by differentiating the curves mathematically and these exhibit the reaction regions clearly. In the un-milled sample, five peaks are observed in the DTG graph (Fig. 2). The first peak in the un-milled sample appeared around 660°C and the second observed around 850°C. In the 1-h milling sample, there are only two peaks which the first one appeared nearly at 650°C. In the 24-hours-milled sample only one large peak observed which around 550°C appeared. According to the Erdemoglu [13] works just two peaks observed in the range of temperature 600-1200°C in the un-milled sample. The largest peak which was observed at 958°C, attributed to the formation of strontium sulphide as a result of carbothermic reduction of celestite. Erdemoglu [13] observed that the formation temperature of strontium sulfide decreased to 900°C and nearly 700°C in samples milled for 1 and 24 hours. This work shows that the intensive milling in the planetary ball mill

decreased the formation temperature of strontium sulfide to as low as 500°C.

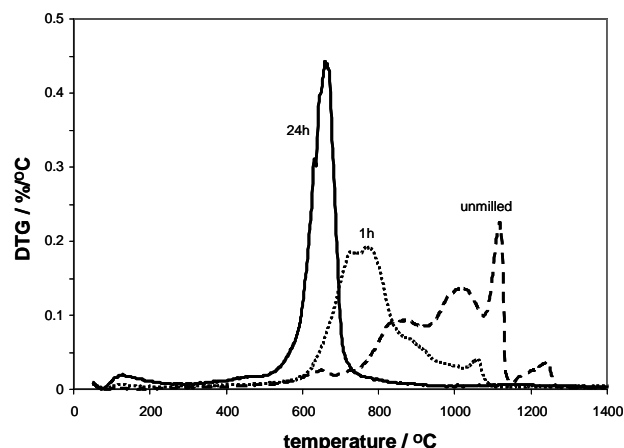


Fig. 2 DTG traces of the milled and un-milled celestite-carbon mixtures derived from Fig. 1

Erdemoglu [13] showed that when an excess of carbon was used, SrC_2 formed according to reaction (4). In the un-milled sample SrC_2 formed at 1180°C, 1 h milling decreased the formation temperature to 990°C and to 850°C after 24 hours milling.



It should be notified that the boiling temperature of elemental sulfur is 445°C (718 K). Thermodynamic calculation reveals the net free energy change of reaction (4) is $\Delta G = 305 \text{ kJ}$ at 1400°C [14], clearly this reaction is not favorable under the conditions claimed by Erdemoglu. Further doubt is provided by the lack of any indication by Erdemoglu that elemental sulfur was present after reaction. During this work, neither elemental sulfur nor SrC_2 were identified in any sample.

In order to study the reactions occurring during each peak in Fig 2 samples from the un-milled run were heated to 500, 720, 945, 1083 and 1150°C, for the 1 h milled sample, runs were at 600°C and 1000°C; after 24 h milling the samples were heated to 530°C and 820°C. Holding the samples at the desired temperature allow a high extent of the desired reaction without significant subsequent reaction.

Fig. 3 shows the XRD traces of the un-milled samples and clearly shows the main celestite peaks weaken as the heating temperature is increased. Clearly, the celestite is being increasingly converted to another phase as the temperature increased. Strontium sulfide peaks began to appear at 720°C in the un-milled sample. After heating to 945°C there are few traces of the celestite in sample. By increasing the temperature, the remaining celestite peaks vanished and only SrS peaks are present in the samples heated at 1083°C and 1150°C.

Fig. 4 shows the XRD traces of the one hour milled samples before and after heating at 600°C and 1000°C. In the as-milled sample, the intensities of the main peaks of celestite became

weaker and broader than those for the unmilled powder due to disordering of the celestite crystal structure. The activated carbon was amorphous. The main peaks of strontium sulfide appeared only after heating at 600°C. Clearly, 1 h of milling reduced the formation temperature of SrS by about 100°C. After heating the mixture up to 1000°C, only intense and narrow peaks for crystalline SrS are present implying complete conversion of SrSO_4 to SrS.

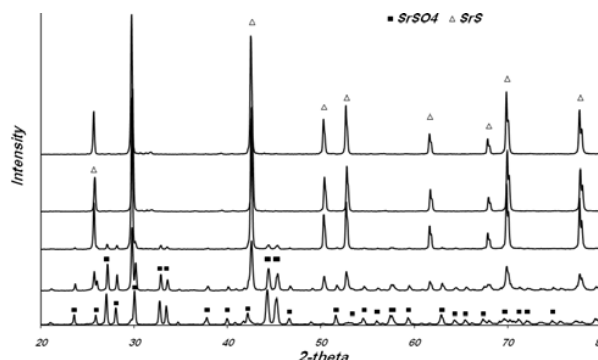


Fig. 3 XRD traces of the un-milled celestite-carbon mixtures heated at 500°C (below), 720°C, 945°C, 1083°C and 1150°C (top)

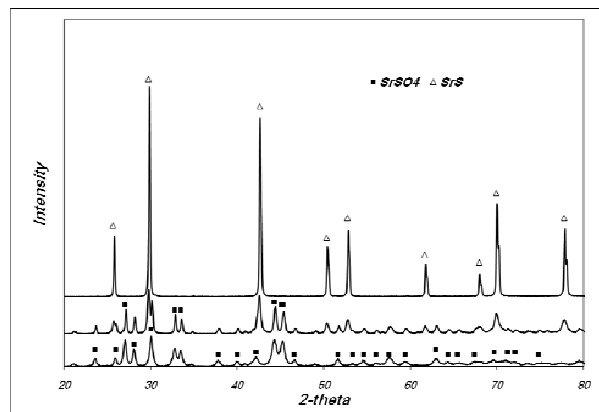


Fig.4 XRD traces of the one hour as-milled celestite-carbon mixtures (below) and after heating at 600°C and 1000°C (top)

In Fig. 5, the XRD traces the 24 h milled sample are shown. As expected, the celestite peaks were weaker and broader than after 1 h indicating further refinement of the crystallite size. After heating at 530°C, most celestite peaks were absent whilst the main SrS peaks are very clear and sharp. The conversion temperature of mixtures of celestite and activated carbon has been reduced to about 530°C after 24 h milling. At 820°C only SrS peaks are present in the XRD traces. The decreasing reduction temperature with increasing milling time is consistent with thermogravimetric analyses (Fig.1).

IV. CONCLUSION

The stages of carbothermic reduction of purified celestite concentrate and activated carbon was studied by using the non-isothermally condition under flowing high purity Argon atmosphere. The TGA graphs and the XRD analyses of the mixtures showed that the carbothermic reduction of celestite was improved by extended of milling. The mass losses and the reductions in milled samples initiated at lower temperature than in the un-milled sample. The formation of strontium sulfide as a result of carbothermic reduction of celestite occurred at about temperature of 720°C in the un-milled sample whilst in the 24 hours milled samples reached to about 530°C. It was concluded that the mechanical activation of celestite-carbon active mixtures intensified the carbothermic reduction of celestite. The future tasks are to study the kinetic of the carbothermic reduction in the both un-milled and milled samples.

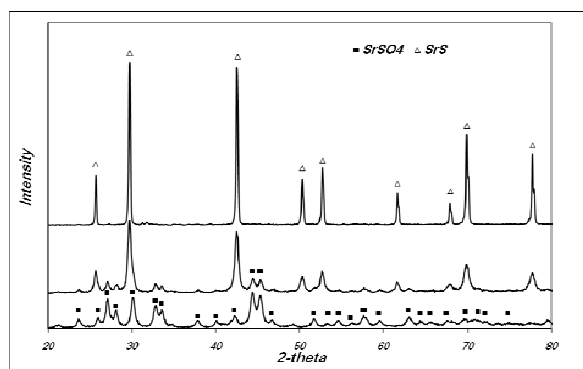


Fig.5 XRD traces of the 24 hours as-milled celestite-carbon mixtures (below) and after heating at 530 C and 820 C (top)

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