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Effect of Mechanical Activation on Roasting of Celestite Ore

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Abstract

In this study, effect of mechanical activation in planetary ball mill and disc mill, on carbothermic reduction of celestite ore with coke was investigated. Celestite ore (96% SrSO₄) from Sivas district was blended with excess metallurgical coke and mechanically activated for 1, 5, 15 and 45 min. Mechanically activated blends were analyzed by Particle Size Analyzer, Thermal Gravimetric Analyzer (TGA), Differential Scanning Calorimetric Analyzer (DSC), and X-Ray Diffractometer (XRD). The finest particles were obtained at 45 min disc milling, of which d₅₀ was 1.30 µm. TGA and DSC analyses showed that the reaction temperature was decreasing from 973°C to 892°C, by 1 min disc milling and 45 min planetary ball milling, respectively. XRD peaks broadened and peak intensities decreased by extending the mechanical activation time in both type of milling processes. All of the mechanically activated powders were roasted at 900, 1000, and 1100°C. According to XRD analyses; it is possible to see some peaks of strontium sulphide (SrS) after roasting at 900 and 1000°C, however, at 1100°C carbide formation is obtained.

Keywords: Celestite, Mechanical Activation, Roasting

1. Introduction

Strontium is commonly used for CRT TVs, hard ferrite magnets, phosphorescence materials, color pigments, special glasses and zinc electrolysis (Carrillo, Uribe et al. 1995, Castillejos, de la Cruz del et al. 1996). Until recently, strontium carbonate (SrCO_3) was used for CRT TVs 60-65% of 245,000 tones annual production capacity (Suárez-Orduña, Rendón-Angeles et al. 2007) but it falls flat nowadays (Owusu and Litz 2000).

Although feasible grade of celestite ore is 50-60% SrSO_4 , celestite deposits in Turkey, Spain and Canada have more than 90% SrSO_4 (Martínez-L, Uribe S et al. 2003). Celestite deposits in Sivas, Akkaya district, operated by Barit Maden Türk A.Ş., has excellent quality SrSO_4 reserve. Celestite concentrate reaches 95-96% SrSO_4 after shaking table and jigging with impurities 3% CaSO_4 , 0,5% BaSO_4 , 0,5% SiO_2 and 0,5% Fe_2O_3 (Dogan, Koral et al. 2004).

SrCO_3 is usually produced from celestite although, there is only a few feasible natural SrCO_3 reserve. There are two different methods to produce SrCO_3 from celestite; direct decomposition method and black ash method. Direct decomposition method is sulfate ion change reaction in an carbonating aqueous media (Zhang and Saito 1997) as like sodium carbonate (Na_2CO_3) (Zoraga and Kahruman 2014), ammonium carbonate (NH_4CO_3) (Bingöl, Aydoğan et al. 2012) etc. Black ash method, the common method for producing SrCO_3 , is two-step process; at first strontium sulphide (SrS) is produced by carbothermic reduction of celestite at 1000-1100°C (Halim, Ibrahim et al. 2009), then SrS is leached in water. Second step of the black ash method is the precipitation of SrCO_3 by Na_2CO_3 (Habashi, F.1997), CO_2 (Owusu and Litz 2000), or different carbonating agents (Erdemoğlu and Canbazoğlu 1998).

The present study aims to understand effect of mechanical activation of carbothermic reduction of celestite. For this purpose, black ash properties investigated by mechanically activated blends prepared from Turkish celestite ore.

2. Materials and Method

The starting material celestite ore was supplied from Barit Maden Türk A.Ş. (Sivas). Celestite ore –as received, is -2mm in size with a chemical composition of 95,5% SrSO_4 , 3% CaSO_4 , 0,5% BaSO_4 , 0,5% SiO_2 and 0,5% Fe_2O_3 . The metallurgical coke consists of 88% fixed carbon, 10% ash, 1% volatile compound and 1% sulphur. Two different types of mill were used for mechanical activation; Fritsch Pulversiette 6 planetary ball mill and a universal disc mill. Grinding media are made out of tungsten carbide (WC) and the ratio of grinding medium to solid material blend is 10/1. For planetary ball milling 10 mm diameter balls were used with 17 g celestite and 8 g metallurgical coke blends which have excess carbon. 250 g milling balls and 25 g blend were placed into a 250 ml WC bowl and rotation speed was set to 500 rpm. For disc milling, blends were prepared as the same stoichiometry but approximately 10 times heavier. Milling studies run with for 1, 5, 15, and 45 min as 5 min run and 2 min cooling intervals. Mechanically activated blends were analyzed by Malvern Mastersizer 2000 Particle Size Analyzer, X'pert Pro X-Ray Diffractometer and Linseis STA PT1600 TG-DSC/DTA Simultaneous Thermal Analyzer. 3 g specimens from all blends were tested by roasting in a lab scale muffle furnace at 900, 1000 and 1100°C for 2 hours in an air atmosphere.

3. Results and Discussion

Structural and thermal properties of the milled celestite and coke mixtures were investigated. Mechanically activated blends were roasted at three different temperatures and their structural properties were investigated.

3.1. Mechanical Activation

Effect of the milling time and the type on the particle size changes were investigated by Malvern Mastersizer (Fig.1). 45 min ball-milled blend is defined as the finest particles of which d_{50} is $1.30 \mu\text{m}$ and d_{10} is $0.11 \mu\text{m}$. Considering the d_{50} values disc milling blends are grinded to $156.26 \mu\text{m}$, $7.62 \mu\text{m}$, $1.91 \mu\text{m}$ and $1.30 \mu\text{m}$ for 1min, 5 min, 15 min and 45 min, respectively and ball milled blends are $16.05 \mu\text{m}$, $5.82 \mu\text{m}$, $3.35 \mu\text{m}$ and $2.22 \mu\text{m}$ for 1 min, 5 min, 15 min and 45 min, respectively.

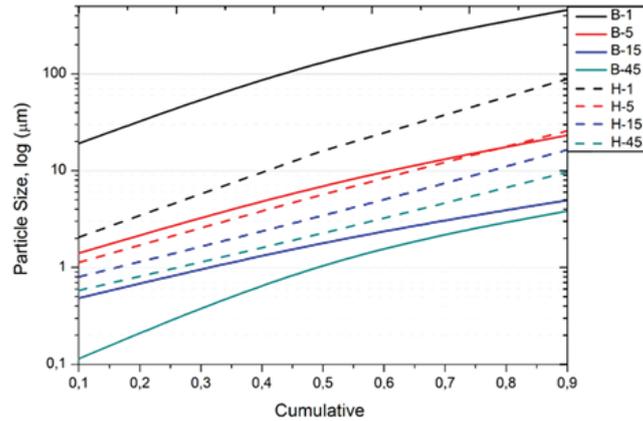


Figure 1. Particle size analyses of mechanically activated blends

X-Ray diffraction patterns of ball milled and disc milled blends and celestite ore as received are gathered for investigation of the structural changes by mechanical activation and shown in Fig.2. As a result of mechanical activation, peaks are broadening and intensities are decreasing by extending the milling time. Broadening and decreasing peak intensities are caused by disordering and thus obtaining partially amorphous structure. The highest peak of 1 min ball-milled blend is on 25.931° belongs to (002) but the other ball-milled (Fig.2.b) and the disc-milled (Fig.2.c) blends the highest peaks on 27.030° belongs to (210).

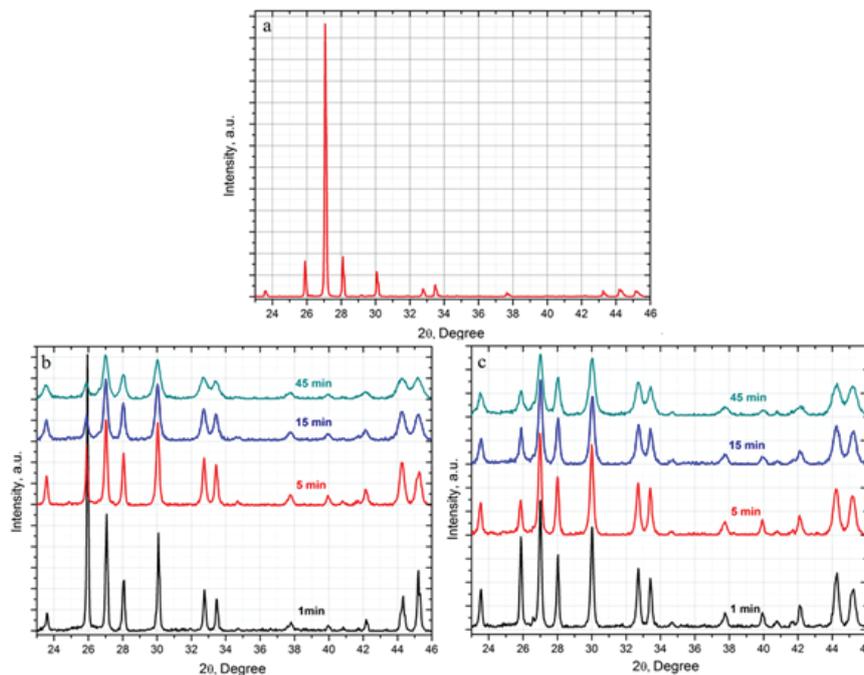


Figure 2. XRD patterns of received celestite (a) and mechanically activated celestite-coke blends; b) ball milled, c) disc milled

Thermal behaviors of mechanically activated celestite and coke mixtures were determined by DSC and TGA analyses, shown in Fig.3. The highest mass losses on the TG lines (Fig.3.b and Fig.3.d) and the pronounced sharp-cut on DSC lines of ball milled (Fig.3.a) and disc milled (Fig.3.c) blends, belong to the following carbothermic reduction reaction;



According to this reaction strontium sulphur (SrS) occurs at the temperatures between 892°C and 973°C depends on the mechanical activation type and period. Reaction temperatures are decreasing from 965°C to 892°C by ball milling, and from 973°C to 915°C by disc milling.

The last and small peak at the DSC analyses means SrC₂ occurrence temperature decrease by mechanical activation about the temperatures from 1100°C to 1050°C. Excessive amounts of carbon can cause the formation of SrC₂ by the reaction with SrS at higher temperatures such as 1180°C (Erdemoğlu 2009). After reduction of celestite if there is some free carbon SrC₂ occurs by the following reaction;



Nevertheless, elemental sulphur was not detected in the roasted blends, by XRD analyses (Fig.4),

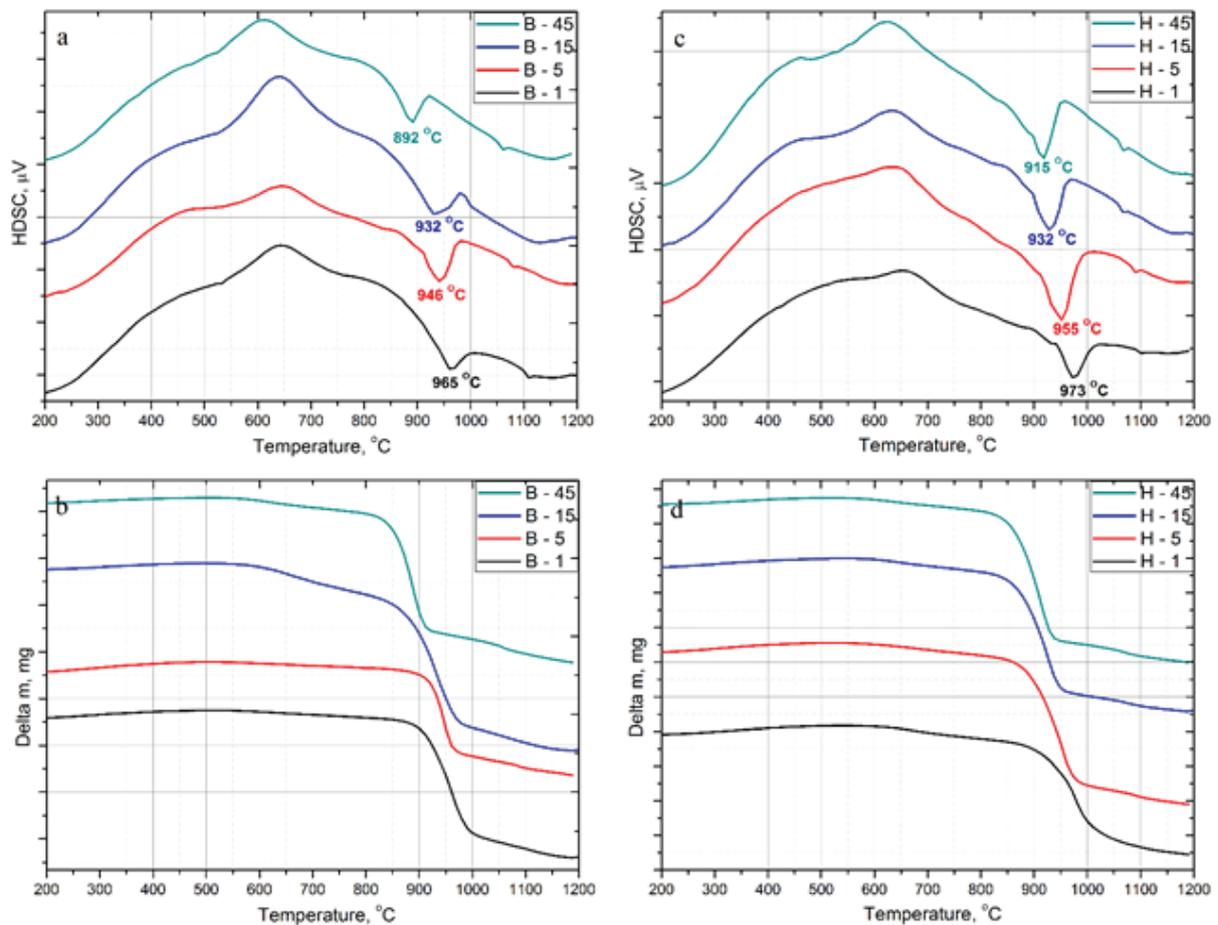


Figure 3. Thermal analyses of mechanically activated blends; a) DSC analyses of ball milled, b) TGA analyses of ball milled, c) DSC analyses of disc milled, d) TGA analyses of disc milled

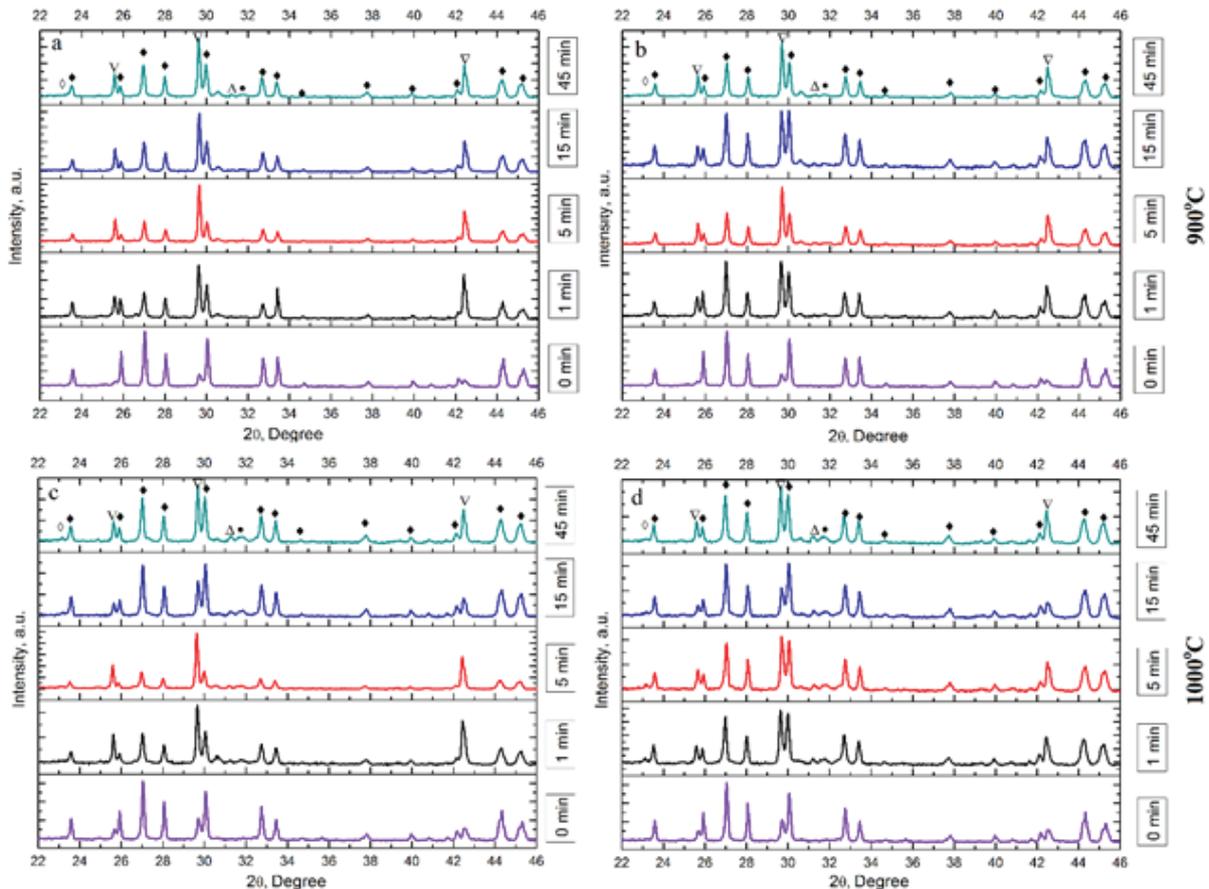
3.2. Roasting

All mechanically activated blends were tested for roasting at different temperatures; 900, 1000, and 1100°C. -45µm celestite ore and coke mixture in the same proportion of the blends was roasted as non-activated (0 min) blend to reference.

X-Ray analyses of activated and non-activated blends roasted at 900°C are given in Fig.4. However, there are no peaks belong to SrS for non-activated blends, peak intensities are increasing instantaneously by extending the mechanical activation period in both ball milling (Fig.4.a) and disc milling (Fig.4.b) processes. Whilst increasing the intensities of SrS peaks at 25.59°, 29.63° and 42.40°, intensities of the peaks belonging to the celestite are decreasing.

Under the light of X-Ray data SrS occur at 1000°C roasting regardless of mechanically activated and non-activated (Fig.4.c and 4.d.) On the other hand, depending on the activation time intensities of SrS peaks are increasing by extending mechanical activation time from 0 to 45 min.

According to XRD results of roasting test at 1100°C, the peaks defining SrS are decreasing by extending milling time and 15 min and 45 min ball milled (Fig.4.e) and 45 min disc milled (Fig.4.f) blends has no SrS peaks, despite non-activated blend has SrS peaks.



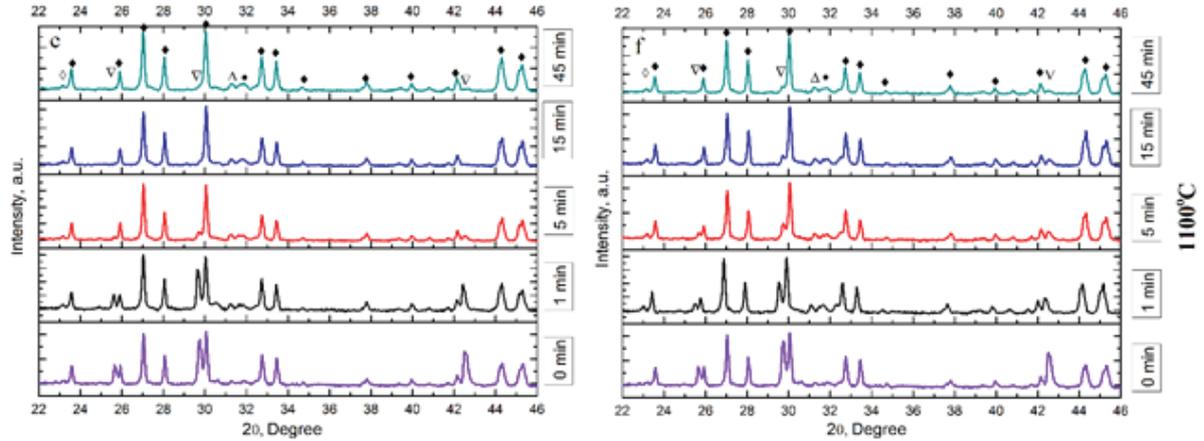


Figure 4. X-Ray analyses of roasted blends. \blacklozenge SrSO₄, Δ SrS, \bullet BaS, \diamond BaC₂, Δ SrC₂

4. Conclusion

Black ash samples prepared from Turkish celestite and metallurgical coke mechanically activated by planetary ball milling and disc milling for short time up to 45 minutes. Particle size after milling processes is related to milling time and decreases by extending milling time. Mechanical activation causes distortions in SrSO₄ crystal structure so that XRD peaks are broadening and intensities decreasing by milling. During high energy milling of black ash blends no chemical reaction occurs to form SrS or any other compound. On the light of thermal analyses such as DSC and TGA, carbothermic reduction temperature decreases from 973°C to 892°C owing to the mechanical activation. The biggest exothermic peaks on DSC analyses and mass losses on TGA analyses point out the SrS occurrence temperature by the carbothermic reduction.

Roasting behavior of mechanically activated blends were tested at 900, 1000, and 1100°C. Mechanically activated blends have SrS at 900 and 1000°C, while non-activated blends have SrS at 1000 and 1100°C. Mechanical activation followed by roasting at 1100°C cause to occur SrC₂ and thus SrS cannot be seen.

As a result, mechanical activation can reduce the energy consumption of a high temperature processes; carbothermic reduction roasting of celestite. On the other hand, different activation systems can be experienced, because there is no remarkable difference between disc milled and ball milled activation.

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