

THE CONVERSION OF CELESTITE TO SrCO_3 IN AMMONIACAL SOLUTION CONTAINING AMMONIUM CARBONATE/BICARBONATE

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Abstract

In this study, high-grade concentrate celestite (SrSO_4) has been converted to strontium carbonate in ammoniacal solution containing ammonium carbonate/bicarbonate (AC). The effect of stirring speed, concentration, particle size and temperature on the dissolution rate was investigated. It was found that the fractional conversion was increased by increasing temperature and decreasing particle size. On the other hand, it was decreased with increasing ammoniacal solution containing ammonium carbonate/bicarbonate concentration. It was also determined that stirring speed had no effect on the fractional conversion. The quantitative analysis of solution taken in a specified period of experiments was performed by ICP-OES. The SEM-EDS and XRD analysis were used for material characterization.

Keywords: Non-ferrous metallic ores, sulphide ores, extractive metallurgy and hydrometallurgy

1. INTRODUCTION

Celestite ore is the most important strontium source with its 56.4 % SrO content. Turkey has one of the leading ore reserves in the world with approximately 2 million tons of high graded reserves (Demirkaya, 1996). Strontium metal and its compounds are utilized in a wide range of areas which vary from colored television tubes to pyrotechnics, from hard ferrite ceramic magnet production to zinc refining. The conversion process from sulphate to carbonate is carried out by two methods. The first one is the black ash method which is based on pyrometallurgical principles. The ore that is mixed with coal is converted under the temperatures of 1000 – 1200 °C and rendered as water-soluble. The second one is the leaching through soda ash method which is a hydrometallurgical process. In this method, the conversion of celestite to SrCO_3 is maintained through the use of Na_2CO_3 solution (Demirkaya, 1996).

Alternative methods are developed because the process steps are complex and, accordingly, the costs are high. De Buda (1987) has applied a two-staged purification process by making use of HCl solution in the ore for the purpose of obtaining SrCO_3 . Celestite ore that contained less than 80 % of SrSO_4 was extracted to 99 % purity by solving the extracted-concentration with ammonium carbonate solution. Castillejos et al (1996) worked with an ore that contained 76.43% SrSO_3 and treated with HNO_3 solution to obtain 97.85% SrSO_4 by use of Na_2CO_3 . They came to the conclusion that at the beginning the reaction took place on the surface of the celestite which fitted the shrinking core model (topochemical reaction). The step which controlled the rate was the diffusion of carbonate ions from product layer and the activation energy was $70.05 \text{ kJ.mol}^{-1}$. In their studies, Erdemoğlu and Canbazoğlu (1998) leached strontium sulphide by black ash method in water to produce SrCO_3 and also

compared the effects of Na_2CO_3 and CO_2 concentrations on SrCO_3 . They managed to extract SrCO_3 that is 97.7 % pure when Na_2CO_3 is used. 98.67 % purity was obtained when CO_2 was solved in water; however, they concluded that when Na_2CO_3 solution was utilized, SrCO_3 precipitation rate increased. Regrettably, the high sodium content was undesirable by the ferrite industry. Owusu and Litz (2000) studied with SrCO_3 which was obtained through the solution of CO_2 out of strontium sulphide in the water and came up with 99 % leach efficiency as a result of the process carried through two stages. Aydoğan et al (2006) worked on SrCl_2 that was utilized as SrCO_3 source in the HCl solution containing BaCl_2 from celestite. During this study, they studied the effects of BaCl_2 concentration, HCl concentration, temperature and particle size on the leach process. They determined that as BaCl_2 and HCl concentration increased, the solubility also increased. They particularly determined that $[\text{H}^+]$ concentration had catalytic effect and as particle size decreased, the rate of reaction increased; and as the temperature increased, the solubility increased. Suarez – Orduna et al (2007) carried out experiments under alkaline hydrothermal conditions without any kind of pretreatment on celestite ore containing 96.8 SrSO_4 . They discovered that the conversion was completed at the end of 96 hours where $(\text{CO}_3)^{2-}$ to $(\text{SO}_4)^{2-}$ ratio was 10. Erdemoğlu et al (2007) concluded that the reaction was completed in 45 minutes when the ratio of solid/liquid was 1/10. In the first stage of his study, Demirkaya (1996) analyzed the effects of concentration, temperature and particle size on the SrCO_3 outcome. The solution of celestite ore was firstly treated with H_2SO_4 and then placed into HCl solutions to be processed with Na_2CO_3 solution. Demirkaya (1996) concluded that the kinetic model fit the shrinking core model and the reaction was controlled by the diffusion.

In this study, ammoniac solutions were used and the effects of ammonium carbonate/bicarbonate (AC) concentration, stirring speed, temperature and particle size on the production of SrCO_3 from high graded celestite concentration is determined.

2. MATERIALS AND METHODS

The concentrated celestite used in this study was provided from Barit Maden Türk A.Ş.. The chemical analysis of celestite is given in Table 1.

Table 1. Chemical analysis of celestite

	SrSO_4	CaSO_4	CaSO_3	BaSO_4	SiO_2	Fe_2O_3
Weight %	96.79	1.55	0.34	0.48	0.44	0.12

Celestite concentration is subjected to particle size classification through the use of standard test sieves on the sieve apparatus (Octagon 200). In the leach experiments, ammoniacal solution (AC) containing ammonium carbonate/bicarbonate symbolized by $\text{CH}_6\text{N}_2\text{O}_2.\text{CH}_5\text{NO}_3$ (1:1) chemical formula and Merck 1.59504.1000 coded in the purity of chemical analysis was utilized. Leach experiments were carried out within the mechanism illustrated in Figure 1. For the determination of fractional conversion, a definite volume of solution was taken from the reactor in selected time intervals. The same amount of fresh AC solution (which was at the reactor temperature) was added to the reactor after each sampling. In this way, the AC concentrations and the total volume of the reaction mixture were kept constant during the experiments. The analysis of obtained liquid samples was carried in the ICP – OES (Spectro Ciros Vision) apparatus. In the characterization of the strontium carbonate product obtained at the end of leaching of celestite ore in different temperature and

different AC concentrations, XRD (Rigaku D/Max – 2200/PC, Cu - K $_{\alpha}$ ($\lambda=1,5406$)) and SEM – EDS (Jeol JSM 5600 – i-XRF 500i) techniques were used.

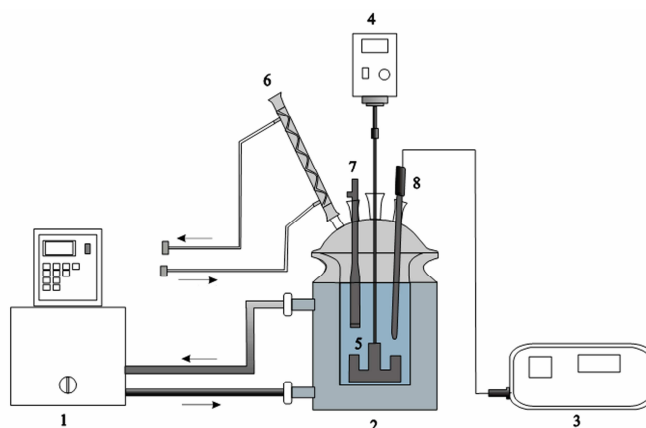
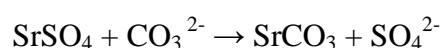


Fig. 1. Experimental set up (1- Thermostat 2- Glass Reactor 3- PT 100 probe 4-Stirrer
5-Propeller coated teflon 6-Condenser 7-Sampler 8-Temperature sensor)

3. RESULTS AND DISCUSSIONS

According to the experimental findings (Figs 2-14), the conversion of celestite (SrSO $_4$) into SrCO $_3$ in the ammoniacal solutions (AC) containing ammonium carbonate / bicarbonate takes place according to the following reaction:



XRD and SEM-EDS analysis of the celestite concentrate and products obtained in the experiments are given in Figs 2 and 3.

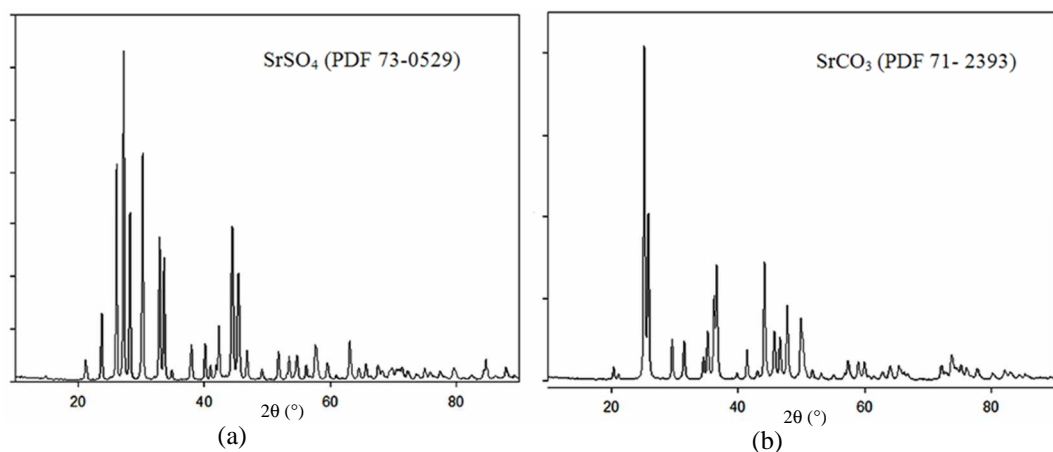


Fig. 2. XRD diagrams (a- Celestite Concentrate, b- Solid Reaction Product)

The conversion of celestite into strontium carbonate is seen in XRD diagrams in Figure 2 and in the EDS analysis indicated in Figure 3.

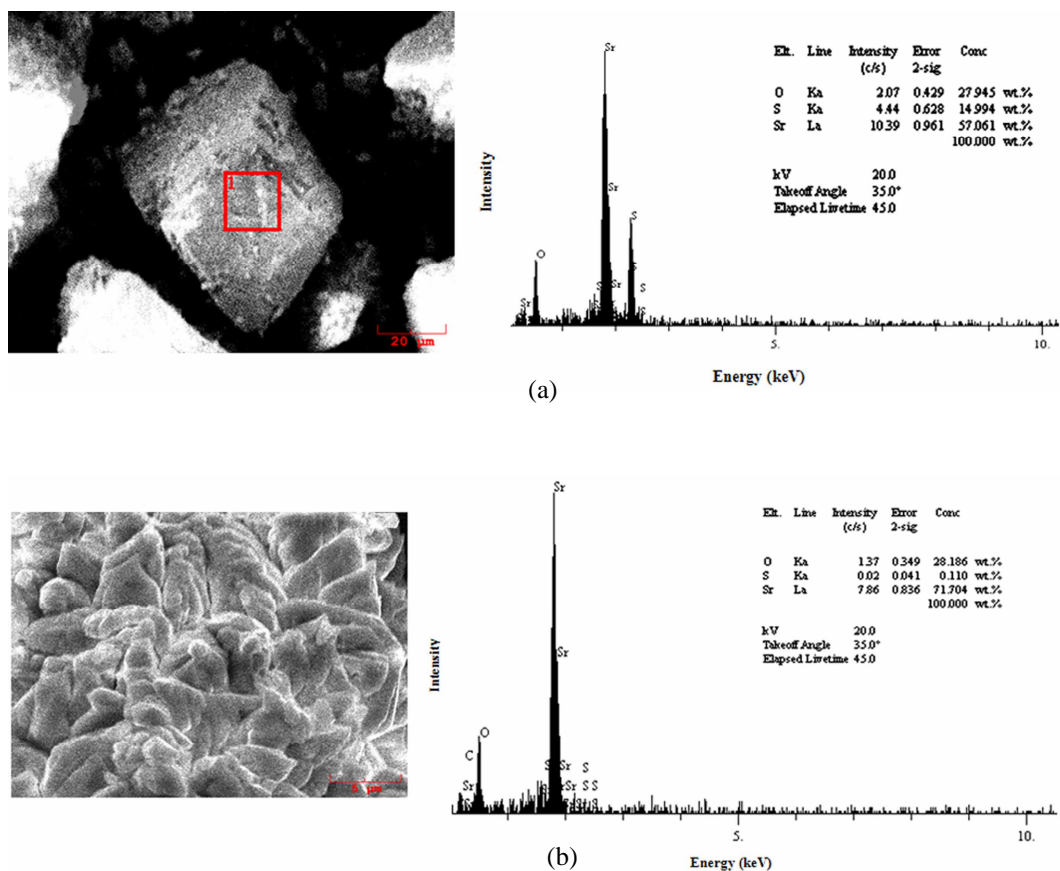


Fig. 3. SEM - EDS analyses (a- Celestite Concentrate, b- Solid Reaction Product)

3.1. Effects of stirring speed

3 g celestite concentration with 53 – 75 μm particle size was subjected to leach experiments with 200, 250, 300 min^{-1} stirring rate, 50°C temperature and 1.5 M AC concentration. The fractional conversion – time obtained for the stirring speed is illustrated in Figure 4.

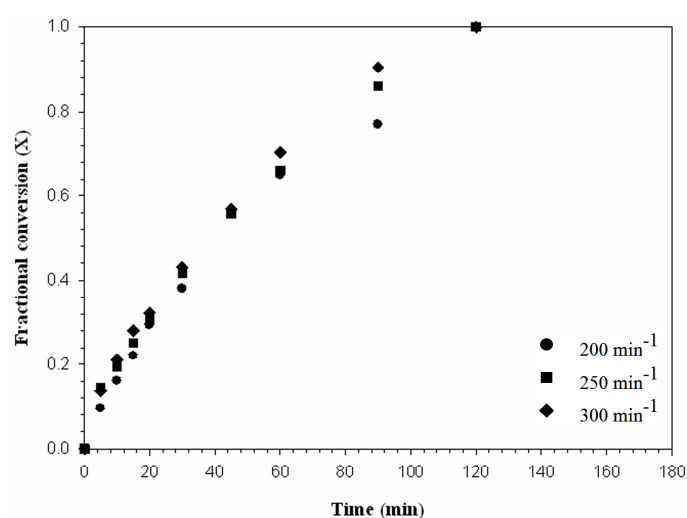


Fig. 4. The effect of stirring speed on fractional conversion

It can be seen in Figure 4 that the stirring speed has no affect on reaction rate in the AC solutions. This case proved that 300 min^{-1} stirring speed does not affect the reaction rate of the resistance of liquid layer of film surrounding the particles.

3.2. Effects of temperature

3 g celestite concentration with particle sizes of 53 – 75 μm was subjected to leach experiments with the following conditions: 0.5, 0.75, 1, 1.25, 1.5 M AC concentration, 20, 30, 40, 50 °C temperature and 300 min^{-1} stirring speed. The fractional conversion – time figures for each AC concentration is given in Figs 5-9.

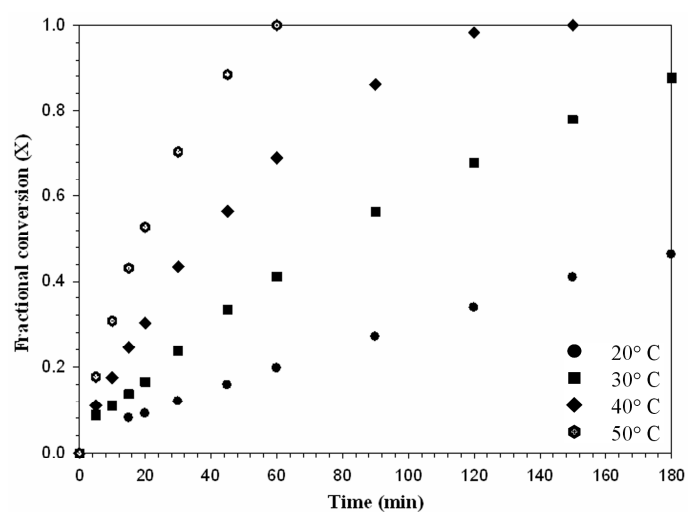


Fig. 5. The fractional conversion for 0.5 M AC concentration

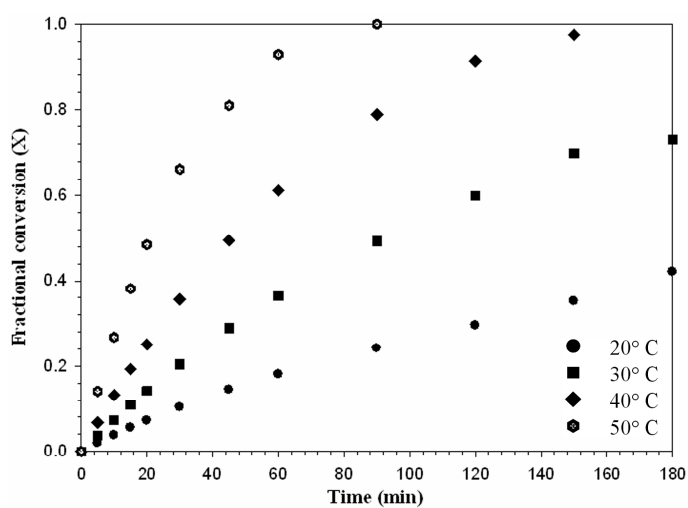


Fig. 6. The fractional conversion for 0.75 M AC concentration

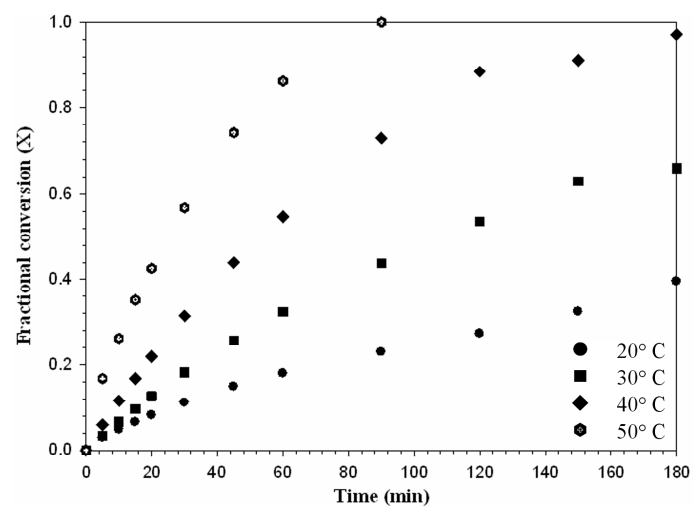


Fig. 7. The fractional conversion for 1 M AC concentration

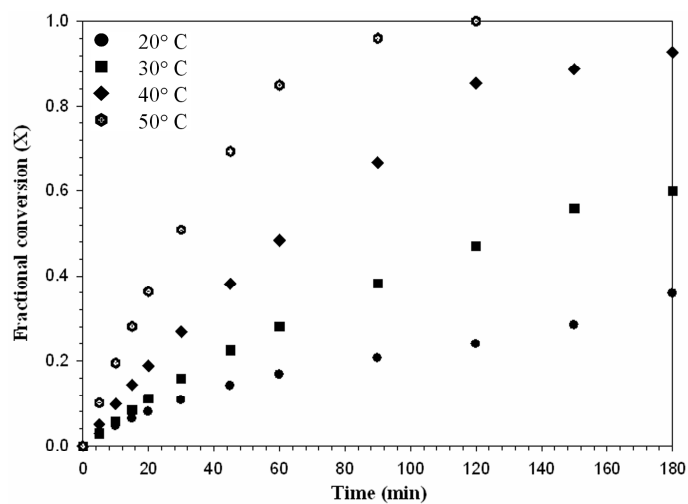


Fig. 8. The fractional conversion for 1.25 M AC concentration

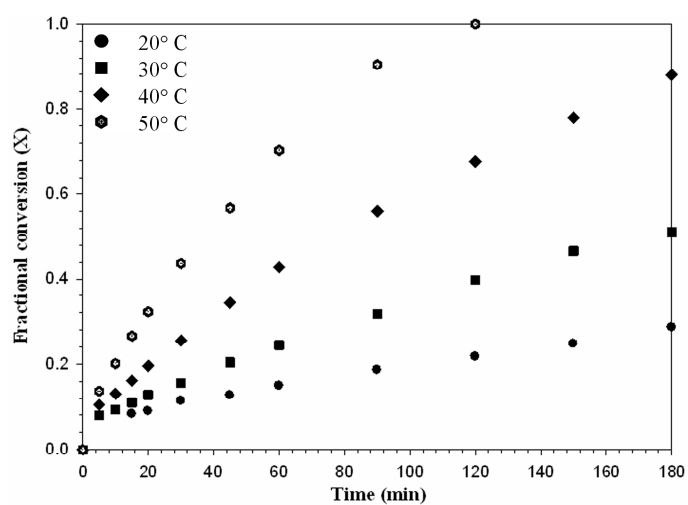


Fig. 9. The fractional conversion for 1.5 M AC concentration

The cycling with the heating up in the fixed AC concentration (Figure 5-9) has increased according to the Arrhenius equation, while in Figure 10-13, the fractional conversion with the AC concentration increasing in fixed temperature is seen to decrease. The balance taking place among NH_3 , NH_4^+ , CO_3^{2-} and HCO_3^- which exists in ammonical solutions including ammonium carbonate/bicarbonate giving such a result and so that with the increased AC concentration it is seen that the fractional conversion have decreased.

3.3. Effects of AC concentration

The effect of temperature over the fractional conversion for 300 min^{-1} stirring speed is given in Figs 10-13.

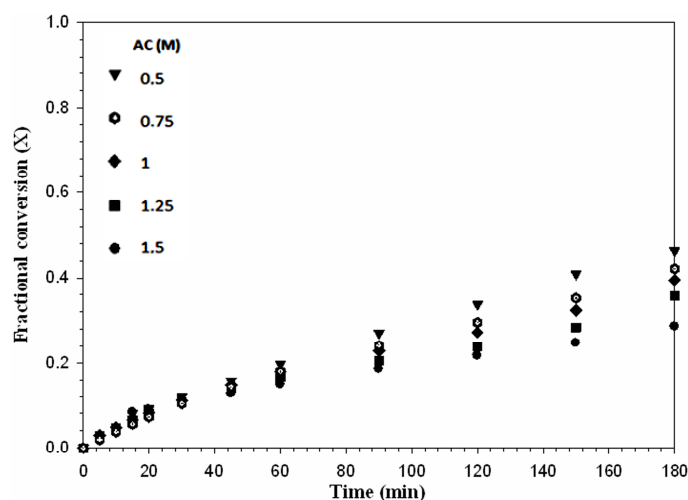


Fig. 10. The fractional conversion for 20°C

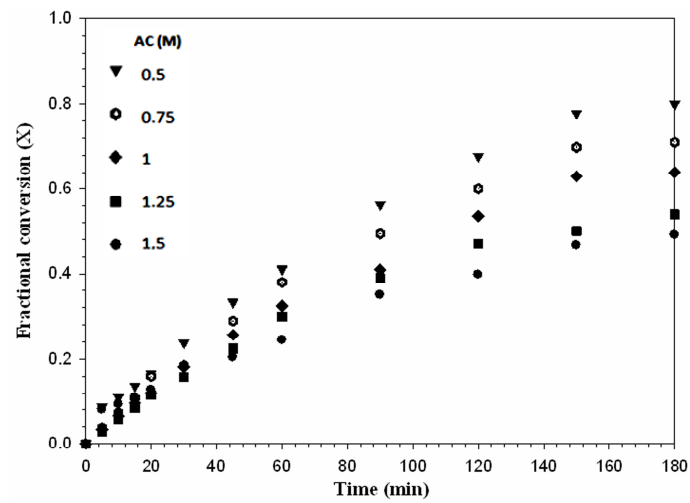


Fig. 11. The fractional conversion for 30° C

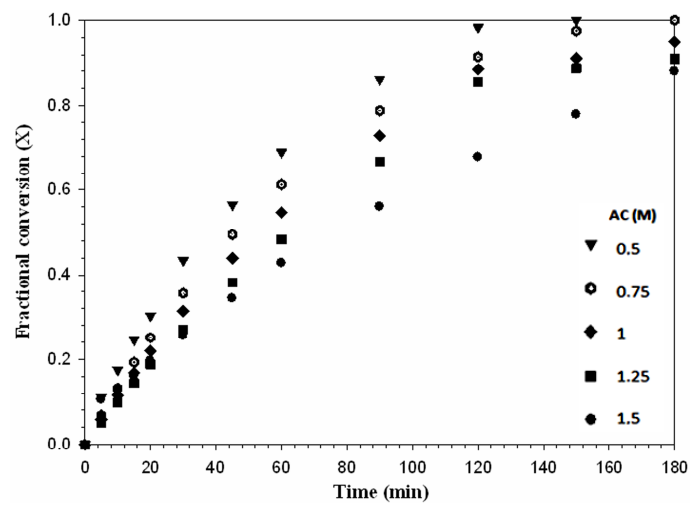


Fig. 12. The fractional conversion for 40° C

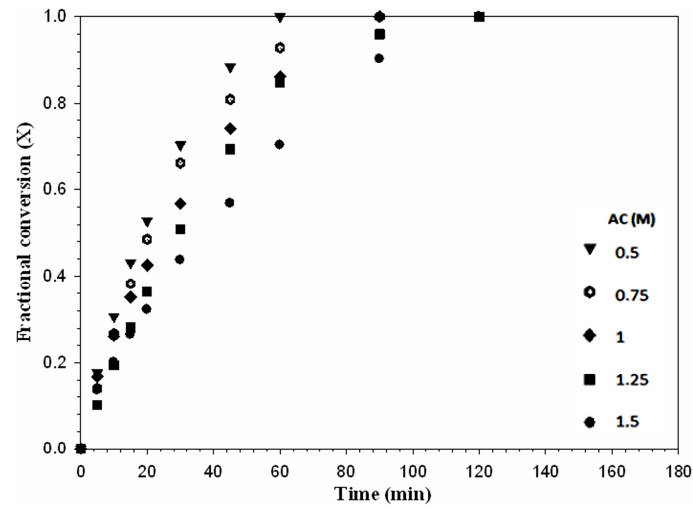


Fig. 13. The fractional conversion for 50° C

3.4. Effects of particle size

The effect of particle size ($-125 +90$, $-75 +53$, $-45 +38 \mu\text{m}$) over the fractional conversion in 1 M AC concentration, 300 min^{-1} stirring rate at 50°C temperature is given in Fig 14.

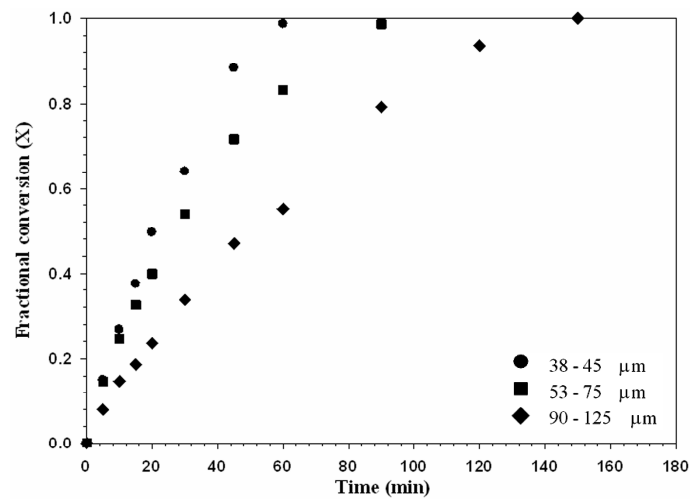


Fig. 14. The effect of particle size on fractional conversion

It is seen in the Figure 14 that as the particle size gets smaller the fractional conversion increases.

4. CONCLUSIONS

The conclusions, derived from the conversion between celestite and strontium carbonate in AC solution, are summarized below.

1. The highest conversion rates were obtained at 50 °C, 0.5 M AC concentration with 300 min⁻¹ stirring speed.
2. The conversion rate increased with increasing temperature and decreasing particle size, stirring speed did not effect on the conversion rate.
3. With the increasing ammoniac concentration, the conversion rate decreased due to the balance in AC solution (NH₃, NH₄⁺, CO₃²⁻ and HCO₃⁻).
4. More experimental work is needed in future to develop the results presented in this study.

Acknowledgements

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