

## Interaction of Celestine Concentrate and Reagent Grade SrSO<sub>4</sub> with Oxalate Solutions

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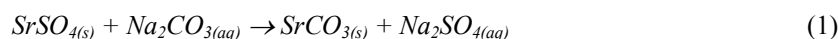
*The interaction of reagent grade strontium sulphate and celestine concentrate with aqueous solutions of oxalic acid, sodium oxalate and ammonium oxalate for the production of strontium carbonate were investigated for different oxalate compound:SrSO<sub>4</sub> mole ratios and reaction times using x-ray diffraction analysis and dissolution tests. Under the same experimental conditions, it was found that aqueous oxalic acid and sodium oxalate solutions had no or little effect on reagent grade strontium sulphate or celestine concentrate, but aqueous ammonium oxalate solution converted them into strontium oxalate hydrate. Strontium carbonate was obtained at conversion ratios of 74.7% for the celestine concentrate and 84.6 % for the reagent grade strontium sulphate by the decomposition of the obtained strontium oxalate hydrate at 600 °C under air atmosphere.*

**Keywords:** Ammonium oxalate, Strontium carbonate, Strontium sulphate.

### Introduction

Celestine (SrSO<sub>4</sub>) and strontianite (SrCO<sub>3</sub>) are the two important strontium minerals, but only celestine is mined commercially and used mainly for the production of strontium carbonate (Hong, 1993). Strontium carbonate is used especially as an additive in the production of glass for colour TV and computer monitors, as a constituent of magnetic ferrites, in pyrotechnics and in the manufacture of Sr and Sr compounds (Griffiths, 1985; Castillejos-Escobar et al., 1996).

The black ash and the double decomposition are the two commercial processes for the production strontium carbonate from celestine concentrates. In the black ash process, celestine is interacted with coke at about 1100°C to obtain SrS. The obtained SrS is dissolved in hot water and strontium is precipitated using sodium carbonate and/or carbon dioxide as SrCO<sub>3</sub>. In the double decomposition method, celestine is reacted with hot aqueous sodium carbonate solution to obtain directly SrCO<sub>3</sub> (Equation 1). The conversion reaction goes to completion due to the difference between the solubility products of SrSO<sub>4</sub> ( $K_{sp}=7.6 \cdot 10^{-7}$ ) and SrCO<sub>3</sub> ( $K_{sp}=7 \cdot 10^{-10}$ ) (Snell and Ettore, 1973; Castillejos-Escobar et al., 1996). Other than these two commercially employed methods, strontium carbonate can be obtained from celestine by hydrothermal synthesis (Suárez-Orduña et al., 2004) and directly or indirectly by mechanochemical synthesis methods (Zhang and Saito, 1997; Obut et al., 2006). Erdemoğlu et al. (2006) also produced strontium carbonate by sodium carbonate precipitation from strontium loaded solution obtained by HCl leaching of solid residue resulted from the interaction of celestine and Na<sub>2</sub>S aqueous solution.



Strontium oxalate hydrates are generally prepared by precipitation in an aqueous medium using water soluble strontium and oxalate salts and according to the preparation procedure they can contain different amounts of water between 1 to 2.5 moles (Gardner and Nancollas, 1976; Yu et al., 2005). If oxalic acid is used, SrC<sub>2</sub>O<sub>4</sub>·1/2H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O can also precipitate (Knaepen et al., 1996). Anhydrous strontium oxalate single crystals can also be prepared by hydrothermal syntheses methods (Price et al., 1999).

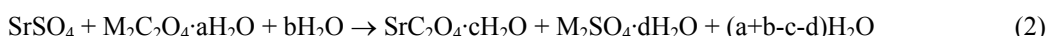
The thermal dehydration and decomposition reactions of strontium oxalates under different experimental conditions have been extensively investigated (Walter-Lévy and Laniepce, 1965; Gérard and Watelle-Marion, 1969; Derouane et al., 1975; Nagase et al., 1975; Selim et al., 1978; Dollimore, 1985; Christensen and Hazell, 1998; Bacce et al., 2001; Celis et al., 2001). Although different temperature values were found by TG/DTA analyses in the literature due to the application of different heating rates and atmospheres, the dehydration of strontium oxalate hydrates complete mainly around 200-210 °C and anhydrous SrC<sub>2</sub>O<sub>4</sub> forms (Peltier and Duval, 1947; Walter-Lévy and Laniepce, 1965; Derouane et al., 1975; Knaepen et al., 1996,1998; Bacce et al., 2001). In some TG/DTA studies, small peaks related to dehydration at about 270°C were also observed (Selim et al., 1978; Al-Newaiser et al., 2007). The anhydrous strontium oxalate starts to decompose at about 400°C and the decomposition is completed at 600°C forming SrCO<sub>3</sub>.

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In this study, the interaction between reagent grade strontium sulphate and celestine concentrate with the aqueous solutions of oxalic acid, sodium oxalate and ammonium oxalate were investigated at different oxalate compound: SrSO<sub>4</sub> mole ratios and reaction times using x-ray diffraction analysis and dissolution tests. The thermal decomposition products of strontium oxalate hydrate obtained by interacting oxalate solutions with strontium containing solids were also investigated considering the production of strontium carbonate.

### Experimental

In the experimental studies, reagent grade strontium sulphate (>99 % SrSO<sub>4</sub>), Turkish celestine concentrate (>92 % SrSO<sub>4</sub>), oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), disodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) and diammonium oxalate monohydrate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O) were used. In a typical experiment, 25 g SrSO<sub>4</sub> and calculated amounts of oxalate reagent (theoretical or 2 times theoretical according to Equation 2) were added into 100 ml distilled water at 95 °C and mixed for 30, 60, 120 and 240 minutes. After mixing, the solids were vacuum filtered and washed over filter paper with equal amounts of water. Then, the obtained solids were dried at 200 °C to obtain anhydrous Sr oxalate. In some experiments, the effects of drying temperature were also investigated by drying solids at 25 °C, 100°C and 300 °C.



After drying, the samples were heated at 600 °C for 2 hours in a muffle furnace under air atmosphere to convert strontium oxalate or its hydrate into SrCO<sub>3</sub>. The x-ray diffraction patterns of dried or dried-heated solids were determined by a Rigaku x-ray (CuKα) diffractometer to observe the changes in the solids. Also, leaching tests were done in an aqueous HCl solution on heated solids to determine the extent of SrCO<sub>3</sub> conversion. Other than reagent grade strontium sulphate, some experiments were also performed on a celestine concentrate for comparison purposes.

### Results and Discussions

#### Interaction of reagent grade strontium sulphate by sodium oxalate or oxalic acid

The x-ray diffraction patterns of the dried (D) or dried-heated (H) solids obtained by leaching (L) of strontium sulphate with sodium oxalate (Na-Ox) or oxalic acid (H-Ox) solutions at the oxalate compound: SrSO<sub>4</sub> mole ratio of 1 for different reaction times were given in Fig. 1. Although hot oxalic acid solution has no or unobservable effect on reagent grade SrSO<sub>4</sub> for a leaching time of 240 minutes (H-Ox, L240min, D200°C in Fig. 1), hot sodium oxalate solution has some effect and converts part of SrSO<sub>4</sub> (JCPDF 5-593) into SrC<sub>2</sub>O<sub>4</sub> (JCPDF 22-1437) (Na-Ox, L240min, D200°C in Fig. 1).

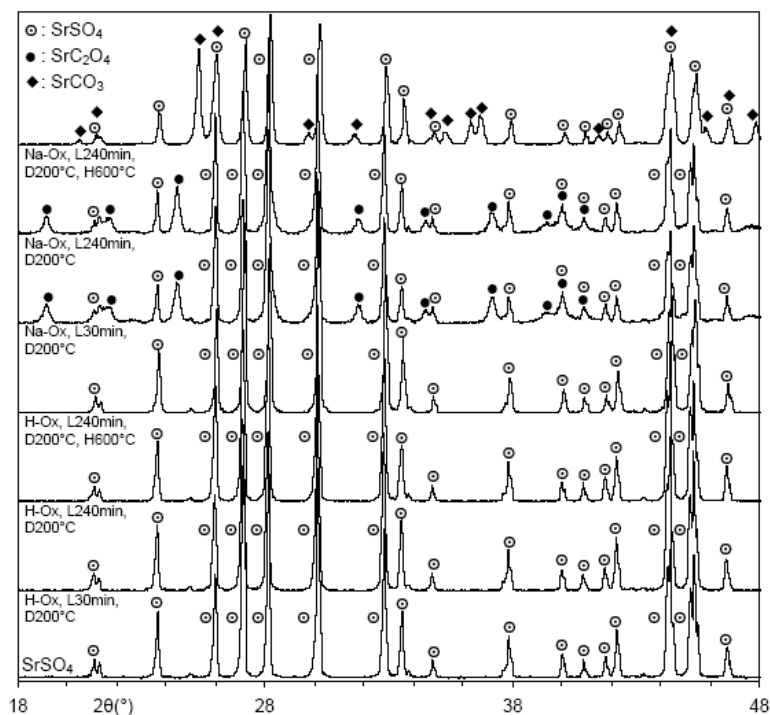


Fig. 1. The x-ray diffraction patterns of dried or dried-heated solids obtained by oxalic acid or sodium oxalate leaching of reagent grade strontium sulphate.

After heating of the dried solids at 600 °C, no peaks related to SrCO<sub>3</sub> (JCPDF 5-418) was observed in the xrd pattern of the oxalic acid treated SrSO<sub>4</sub> (H-Ox, L240min, D200 °C, H600 °C in Fig. 1) conforming again no or unobservable conversion, but characteristic peaks at about 2θ values of 25.2°, 31.5°, 36.2°, 36.6° and 47.7° for SrCO<sub>3</sub> were observed in the xrd pattern of the sodium oxalate treated SrSO<sub>4</sub> (Na-Ox, L240min, D200 °C, H600 °C in Fig. 1) due to the decomposition of SrC<sub>2</sub>O<sub>4</sub> into SrCO<sub>3</sub>. The conversion ratio of reagent grade SrSO<sub>4</sub> into SrCO<sub>3</sub> using sodium oxalate solution was found as 30.8 %, average of three experiments.

#### Interaction of reagent grade strontium sulphate by ammonium oxalate

Because of the low conversion ratios obtained with oxalic acid or sodium oxalate, ammonium oxalate was also tested as an alternative oxalate source and a conversion agent. The x-ray diffraction patterns of the dried or dried and heated solids obtained by leaching of reagent grade SrSO<sub>4</sub> with ammonium oxalate at oxalate compound:SrSO<sub>4</sub> mole ratios of 1 and 2 (doubled) for different reaction times were given in Fig. 2. Although theoretical or 2 times theoretical amount of ammonium oxalate reagent gave better conversion results than either oxalic acid or sodium oxalate, 2 times theoretical amount of ammonium oxalate reagent gave the highest conversion ratios of SrSO<sub>4</sub> into SrCO<sub>3</sub> after heating of the dried solids at 600 °C (NH<sub>4</sub>-Ox doubled, L240min, D200 °C, H600 °C in Fig. 2). The average conversion ratios obtained in the presence of theoretical and 2 times theoretical ammonium oxalate are 47.3 % and 84.6 %, respectively.

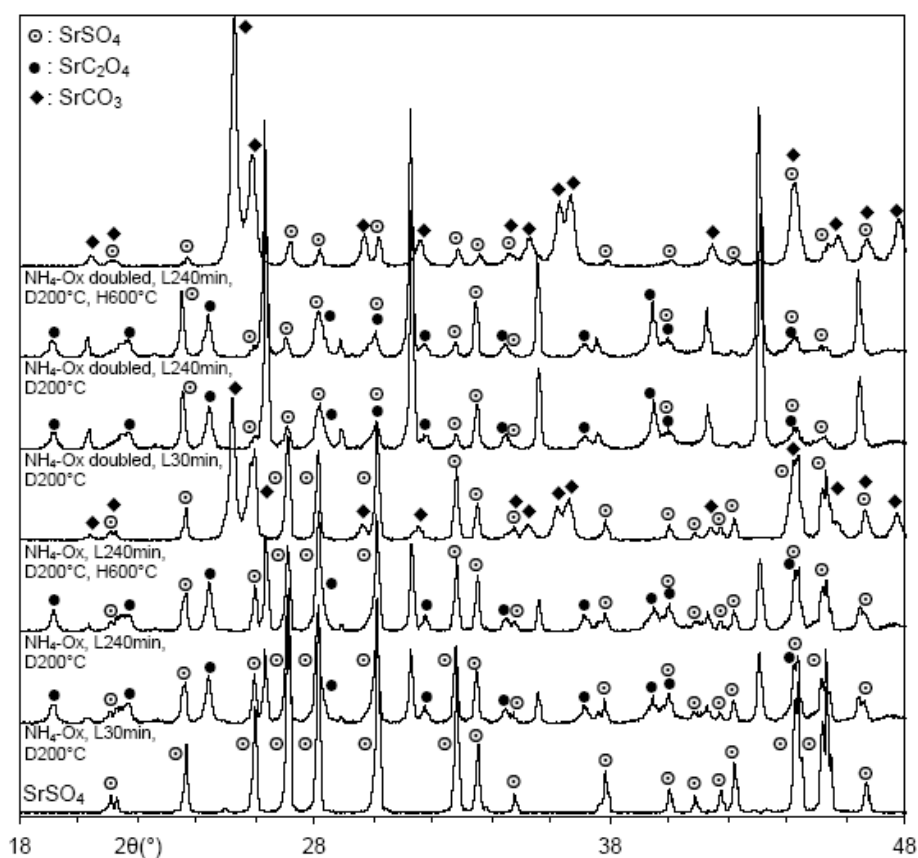


Fig. 2. The x-ray diffraction patterns of dried or dried-heated solids obtained by ammonium oxalate leaching of reagent grade strontium sulphate.

In some experiments, the heating temperature was increased to 800 °C to be sure for complete removal of residual carbon impurities left after heating at 600 °C in the sample, since the colour of heated solids obtained at 600 °C are light gray and at 800 °C are white. The conversion ratio obtained at 800 °C was 86.0 %, indicating small amounts of carbon impurities left in the sample.

The effect of drying temperature following leaching was investigated for 240 minute-ammonium oxalate leaching at the oxalate compound:SrSO<sub>4</sub> mole ratio of 2, because the best conversion ratios were obtained under these conditions. The solids obtained after leaching and filtering were dried separately at 25 °C, 100 °C, 200 °C and 300 °C, and their corresponding xrd patterns were given in Fig. 3. Figure 3 showed that by drying at temperatures lower than 200 °C, the solids obtained also contain strontium oxalate hydrate

together with the anhydrous form. By the increase of the drying temperature to 300 °C, the solids only contain anhydrous strontium oxalate and unreacted  $\text{SrSO}_4$  (D300 °C in Fig. 3).

Although the samples were washed by water during vacuum filtering, some impurities remained in the samples and can be shown as unidentified peaks especially in the xrd patterns of solids dried at 25 °C and 100 °C. Some of these unidentified peaks were partially matched with peaks of  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $(\text{NH}_4)_2\text{Sr}(\text{SO}_4)_2$  compounds. On the other hand, all the unidentified peaks and peaks belonging to strontium oxalate hydrate disappear by drying at 300 °C and irrespective of the drying temperature, all the solids gave the similar xrd pattern after heating at 600 °C, showing conversion into strontium carbonate.

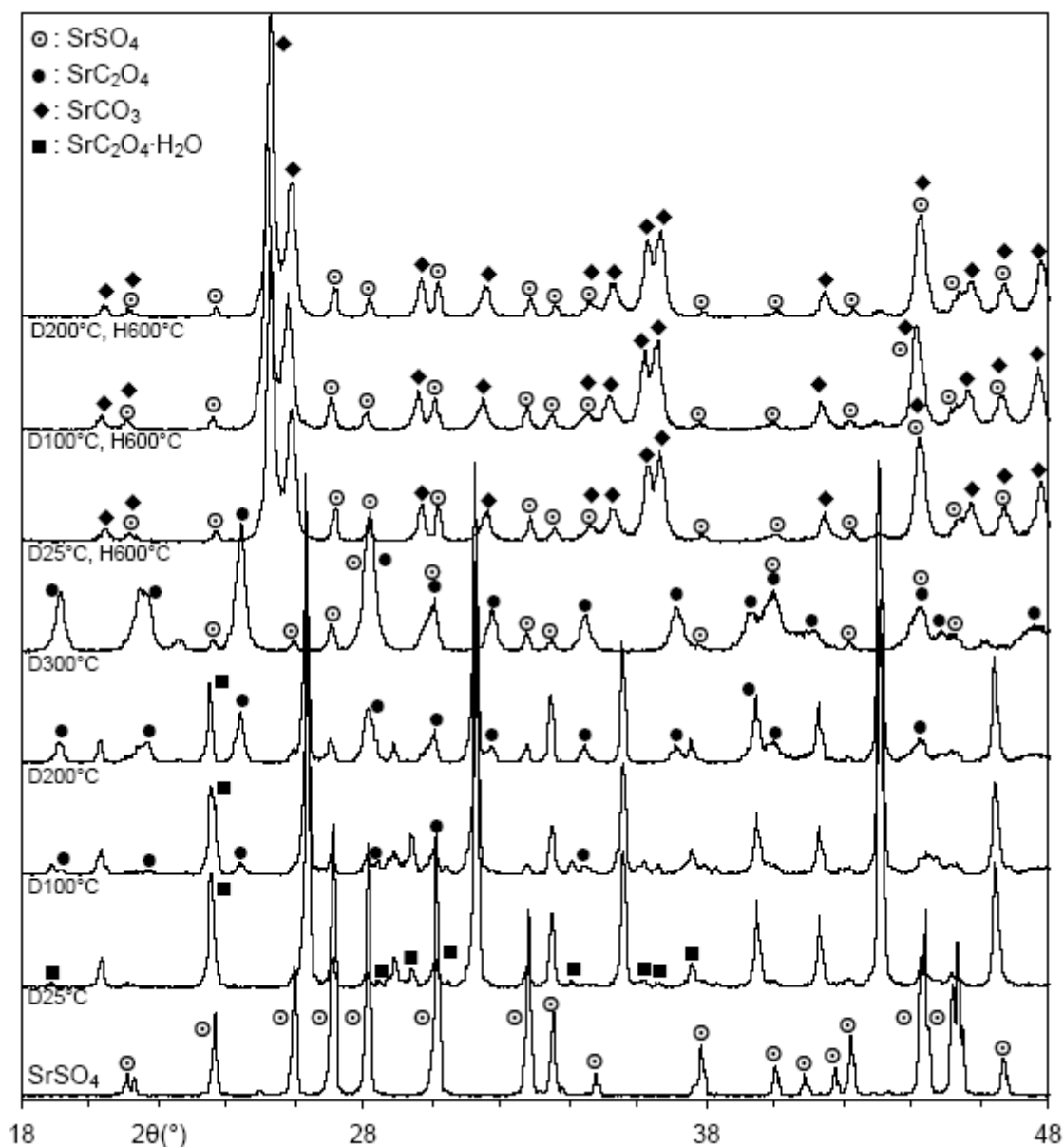


Fig. 3. The x-ray diffraction patterns of dried or dried-heated solids obtained by ammonium oxalate leaching of reagent grade strontium sulphate at oxalate compound: $\text{SrSO}_4$  mole ratio of 2 for 240 minutes.

#### Interaction of celestine concentrate by ammonium oxalate

Since the best conversion ratios were obtained with reagent grade strontium sulphate for 240 minute-ammonium oxalate leaching at the oxalate compound: $\text{SrSO}_4$  mole ratio of 2, celestine concentrate was interacted with hot ammonium oxalate solution under these conditions. The xrd patterns of the obtained solids after drying or drying-heating were given in Fig. 4. As can be seen from Fig. 3 and 4, it can be said that similar type of conversions were occurred, namely Sr oxalate hydrate was formed and it was transformed into strontium carbonate by heating. The average conversion ratio obtained for celestine concentrate

is 74.7 %. This value is lower than the conversion value obtained for the reagent grade SrSO<sub>4</sub>. This may arise because of the finer size distribution of the reagent grade SrSO<sub>4</sub> (80 %, 50 % and 20 % of the reagent is finer than 13.3, 9.3 and 6.2 μm, respectively) than the celestine concentrate (80 %, 50 % and 20 % of the concentrate is finer than 56.9, 25.4 and 7.1 μm, respectively).

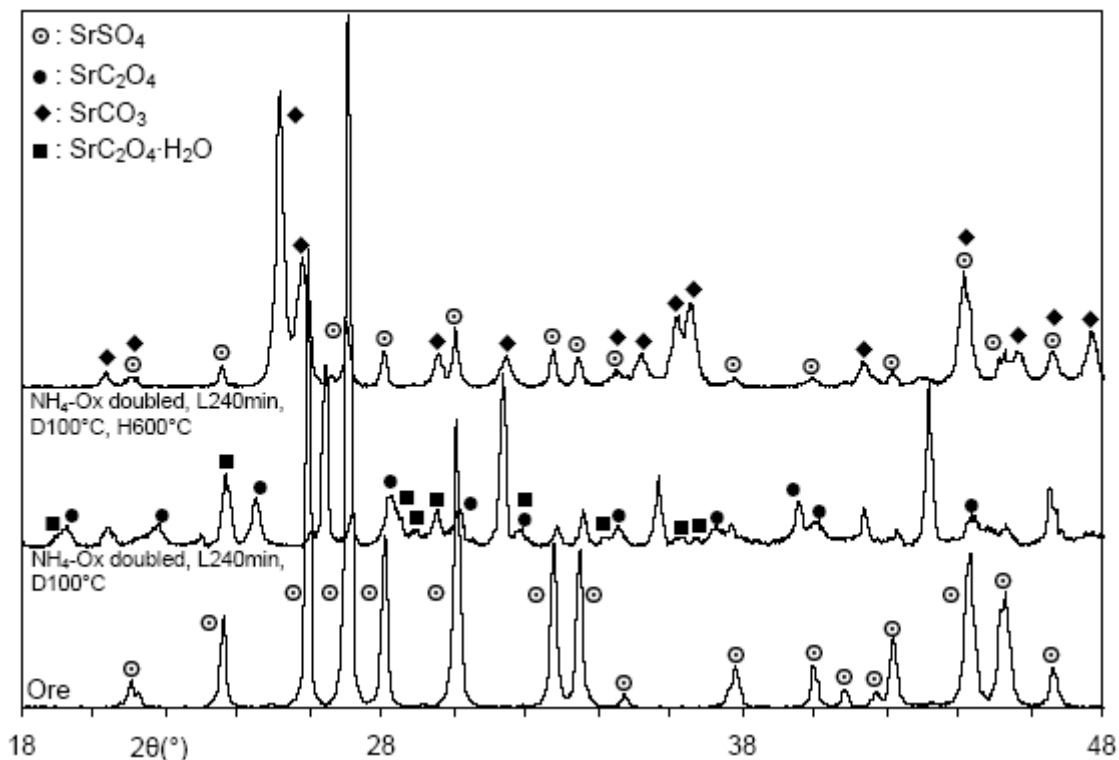


Fig. 4. X-ray diffraction patterns of dried or dried-heated solids obtained by ammonium oxalate leaching of celestine concentrate at the oxalate compound:SrSO<sub>4</sub> mole ratio of 2 for 240 minutes.

In all of the conversion tests, either pure SrSO<sub>4</sub> or celestine concentrate used as initial compound, maximum conversion ratio of initial Sr from SrSO<sub>4</sub> to SrCO<sub>3</sub> obtained was ~85 % for long reaction times. This conversion value is lower than the conversion ratios (over 90 %) obtained in shorter reaction times when Na<sub>2</sub>CO<sub>3</sub> is used as a converting agent (Iwai and Toguri, 1989; Castillejos-Escobar et al., 1996). This is caused by the higher difference in solubility product constants between SrSO<sub>4</sub> ( $K_{sp}=7.6 \cdot 10^{-7}$ ) and SrCO<sub>3</sub> ( $K_{sp}=7 \cdot 10^{-10}$ ) couple than SrSO<sub>4</sub> and SrC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O ( $K_{sp}=5.6 \cdot 10^{-8}$ ) couple (Snell and Etre, 1973).

### Conclusions

The effects of different oxalate solutions (oxalic acid, sodium oxalate and ammonium oxalate) on the reagent grade SrSO<sub>4</sub> and celestine concentrate were investigated using mainly x-ray diffraction analyses for different oxalate compound:SrSO<sub>4</sub> mole ratios and reaction times, considering the production of strontium carbonate. Although hydrogen and sodium forms of oxalate solutions had no or little effect on the reagent grade SrSO<sub>4</sub> or the celestine concentrate, ammonium oxalate solutions converts these solids into different strontium oxalate hydrate under the same experimental conditions. By the decomposition of the obtained strontium oxalate hydrate at 600 °C under air atmosphere, SrCO<sub>3</sub> was obtained at conversion ratios of 84.6 % and 74.7 % for reagent grade SrSO<sub>4</sub> and celestine concentrate, respectively.

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### References

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