

BEHAVIOUR OF SrSO₄ AT HIGH TEMPERATURE.

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ABSTRACT

The conversion pyrometallurgical process of SrSO₄ transformation to SrCO₃ take place by reduction of SrSO₄ to SrS in a gaseous mixture of CO-CO₂, H₂ or CO; and a second stage to obtain SrCO₃ from SrS, with reaction with gaseous phase CO₂. The process is highly dependent on temperature and composition of the gaseous mixture. In the first reaction between SrSO₄ and CO-CO₂ several important physical and chemical phenomena occurs. In this work an analysis of the behavior of SrSO₄ at high temperature was carried out. During heating a structural change occurs at 1413 K. The transformation enthalpy of the structural change of the SrSO₄ not reported in the literature was determined, using a procedure based a Differential Thermal Analysis technique. The structural transformation also was confirmed by X-Ray diffraction technique. Also decomposition of SrSO₄ was observed before its fusion occurs contrarily as reported in the literature. Using the Thermogravimetric Analysis technique was determine that its decomposition begin at 1500 K.

INTRODUCTION

Mexico is the leading producer of celestite. The most common strontium ore. About 95% of all U.S.A. strontium imports came from Mexico [Ober-2000]. Nowadays, the main strontium ore is the celestite (SrSO₄), which is used as raw material to obtain other compounds that have applications in different industries [Kirk-1962, Ferrel-1981]. The most important strontium compounds is SrCO₃, which has two main applications: (1) as an additive in the manufacture of glass cathode-ray colour for television and computers monitors, and (2) in the magnetic ceramic ferrites, in some high technology ceramics.

Furthermore, it is also used as raw material to obtain other chemical compounds that have applications on a smaller scale in different industries [Griffiths-

1985].

The SrCO₃ can be obtained by two methods: hydrometallurgical or direct conversion [Castillejos et. al- 1985] and pyro-hydrometallurgical [Iwai-1989]. Another alternative, is the pyrometallurgical process [Méndez-1993] which consist on the reduction of celestite (SrSO₄) to SrS with gases such as H₂ [Habashi-1976], CO or CO-CO₂ mixtures [Méndez-1993, Pérez-1995, Plewa-1989], to finally obtain SrCO₃.

The stability of the strontium compounds in atmospheres of CO-CO₂ have been studied in several research works [Sukiennik et. al.-1992, Méndez et. al.-1995, Sukiennik-1995, Méndez et. al.-1996]. These works show that the pyrometallurgical process mainly depends on temperature and gas composition. The main conclusions found in those works are: the most important reaction in the pyrometallurgical process is the reduction of SrSO₄ with CO to produce SrS. This reaction takes place when the CO concentration in the gas phase is higher than 10%. The chemical mechanism changes when the CO concentration is lower than 10% and SrO is formed at temperatures higher than 1600 K. The SrO reacts with CO₂ and then SrCO₃ is formed. The SrS reacts with CO₂ and a reaction opposite to the main reaction takes place at lower temperature [Torres-1999]. When the temperature reaches approximately 1540 K, the chemical mechanism change and then SrO is formed.

The condensed phases presents during the reduction process of celestite (SrSO₄) in gaseous phase CO-CO₂ are as SrS, SrO, SrCO₃ and SrSO₄. Compounds such as SrS and SrO, does not undergo structural changes or fusion at temperatures as high as 1773 K. Compounds such as SrCO₃ and SrSO₄ undergo structural changes and decomposition as temperature increases.

According to the literature [Arvanitidis-1996, Morgan-1982], the SrCO₃ shows a structural transition at 1204 K. The thermal decomposition of SrCO₃ takes place at a temperature of about 1433 K when the partial pressure of CO₂ reaches the value of one atmosphere [Austin-1982].

The SrSO₄ is very stable and its decomposition is not registered even at 1600 K. At the process pyrometallurgical, a structural transformation is shown, whose transformation enthalpy has not been reported on the literature. This phenomena has effect on the chemical [Habashi-1970] and kinetic [Méndez-1993] characteristics of the pyrometallurgical process.

For all the above reasons an study of the behavior of SrSO₄ at the temperature range of 1000 K to 1750 K is suggested to be important. Using DTA, TGA and, X-ray diffractometry techniques was carried out this study.

The SrSO₄ is a very stable compound and its thermal decomposition temperature has been studied previously [Méndez-1993], but unfortunately, widely discrepant values have been reported, making impossible any dependable correlation. Even at the temperature of 1650 K no decomposition is observed. The temperature of decomposition of SrSO₄ is 1966 K. However, in an atmosphere with argon flow, the decomposition process of the SrSO₄ to SrO begins at temperatures near to 1500 K. To explain decomposition of the SrSO₄, it was necessary to consider the isothermal phase equilibrium Sr-S-O ternary system, as a function of the partial pressures of SO₂ and O₂; this can be represented conveniently by diagrams of predominance areas, in addition of the TGA analysis.

EXPERIMENTAL PROCEDURE

Materials

SrSO₄ powder (99.99%) from FLUKA CHEMICAL was used. Argon gas ultra high purity was used, during thermogravimetric and differential analysis and X-Ray diffraction tests.

Experimentals techniques

Differential Thermal Analysis and Thermogravimetric Analysis techniques were used to determine thermal and weight changes in the samples. The structural changes were analyzed by X-ray diffraction technique.

The transformation enthalpy of SrSO₄ was determined using a high temperature Differential Thermal Analyzer (DTA) model 1700 trade mark Perkin Elmer.

Samples of 100 mg in form of powder were placed in platinum crucibles. Alumina powdered was used as a reference. After placing the samples in the

platinum crucibles from DTA, a 1.66X10⁻⁴m³-min⁻¹ flow of argon was passed through the chamber of the analyzer in order to establish an inert atmosphere. This argon flow was maintained throughout the experiment. The sample was heated at a constant rate of 10 K-min⁻¹ up to achieve a temperature higher than that of melting. The thermal evolution was registered on graphical paper.

The X ray patterns of the structural transformation of SrSO₄, were carried out in a diffractometer trade mark PHILLIPS model TW 3040 with copper-ceramic anode, vertical goniometer and, high temperature chamber with platinum filament.

X ray diffraction patterns of SrSO₄ were obtained at temperatures lower and higher to the transformation temperature (1413 K). The samples of SrSO₄ were placed on the platinum filament in the high temperature chamber of the diffractometer and an argon flow of 1.66X10⁻⁴m³-min⁻¹ was passed through the chamber in order to achieve an inert atmosphere. This argon flow was maintained throughout the experiment. The sample was heated at constant rate of 10 K-min⁻¹ up to achieve the temperature of tests. The conditions used during the experiments was heating up to 1373 K followed by a holding time of 30 minutes for carried out the respective diffraction pattern. Once obtained the diffraction pattern the sample was heating up to 1473 K followed by holding time of 30 minutes for carried out another diffraction pattern.

SrSO₄ at higher temperatures in argon atmosphere shows that its decomposition takes place before fusion occurs. Tests in Thermogravimetric Analyzer model TGA 7 trade mark Perkin Elmer was carried out. Samples of 100 mg in form of powder were placed in platinum crucibles. After placing the samples in the platinum crucibles from TGA, a 1.66X10⁻⁴m³-min⁻¹ flow of argon was passed through the chamber of the analyzer in order to achieve an inert atmosphere. This argon flow was maintained throughout the experiment. The sample was heated at a constant rate of 10 K-min⁻¹ up to 1773 K.

The thermal evolution was registered on a computer.

RESULTS AND DISCUSION

The DTA analysis allows to determine the transformation temperature and the value of the calorific effect of the transformation temperatures as high as 1773 K. Compounds such as SrCO₃ and SrSO₄ undergo structural changes and decomposition as temperature increases.

The SrSO_4 pure undergoes a phase transformation at the temperature of 1413 K approximately, whose enthalpy transformation is not reported in the literature.

In Figure 1 the calorific effect registered in the DTA shows that the structural transformation is reversible and it is repeated in the sample during heating and cooling.

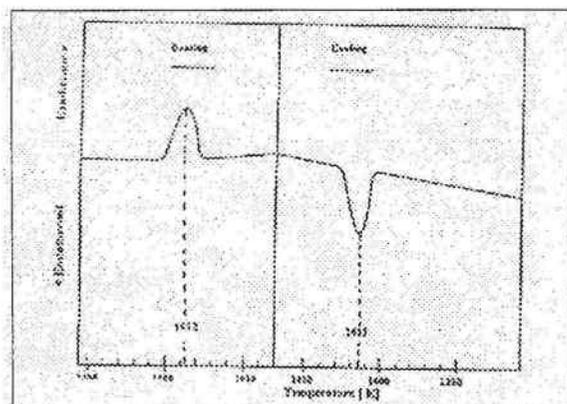


Figure 1. DTA chart for the transformation of SrSO_4 .

Due to the lack of heat of transformation values of SrSO_4 , the differential thermal analysis technique was used to determine this value [Torres et. al. 1999]. The heat of transformation value to obtained was $52.22 \text{ kJ}\cdot\text{mol}^{-1}$.

The X ray diffraction experiments shows that the structural transformation occurs at 1413 K, since there are change in the respective diffraction pattern. A difference between both diffraction patterns is establish.

The structural transformation was also evident by X-Ray Diffraction analysis. In Figure 2 the change of crystal structure of SrSO_4 is showed [Torres et. al. 1999].

The X ray diffraction experiments were carried out at three different temperatures: room temperature (298 K), 1373 K and 1473 K. The diffraction patterns show that the transformation occurs at temperatures between 1373 and 1473. The difference between diffraction patterns is clearly established. Literature data [Méndez-1993] show that the

SrSO_4 has a rhombohedral structure which breaks down the crystalline order, and another structure is obtained, when the temperature of 1573 K is reached.

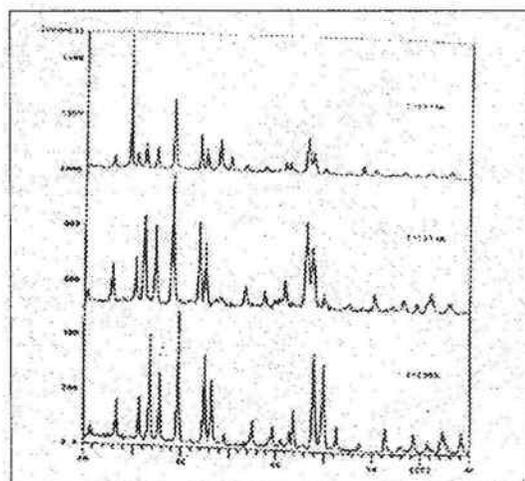
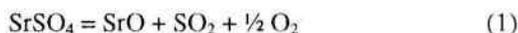


Figure 2. X-ray diffraction patterns of SrSO_4 .

Literature data show that the SrSO_4 is a very stable compound with melting point at 1873 K [Knake-1991, Turkdogan-1980] or 2273 K [Kubaschewski-1979]. The thermal decomposition temperature has been studied previously. In this compound at temperature of 1650 K no decomposition is observed. The decomposition process of SrSO_4 takes place according to the equation:



In an atmosphere with argon flow, the decomposition process of the SrSO_4 to SrO begins near to temperatures of 1500 K as shown the Figure 3. By decreasing the partial pressure of oxygen, the reaction (1) will go to the right to form SrO .

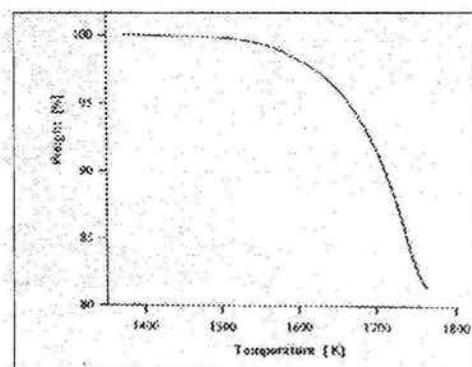


Figure 3. Decomposition of SrSO_4

To explain decomposition of the SrSO_4 , it was necessary considered the isothermal phase equilibrium Sr-S-O ternary system, as function of the partial pressures of SO_2 and O_2 , and the data represent conveniently by diagrams. The isothermal bivariant

equilibria defining the phase stability regions, are the so called phase predominance areas [Turkdogan-1980, Rosenqvist-1987, Young-1986].

The diagram of phase predominance areas for Sr-S-O ternary system at 1523 K is show in Figure 4.

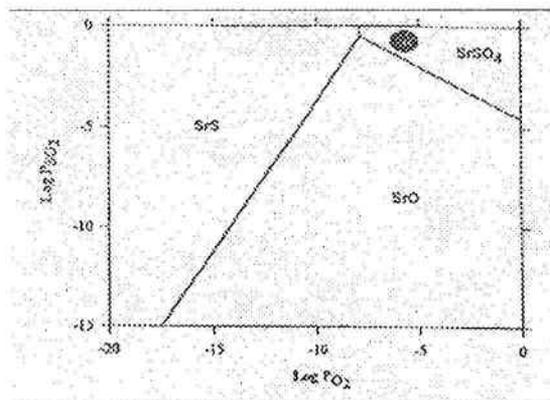


Figure 4. Diagram of predominance areas at 1523 K.

This diagram was development in agreement with equations from Table 1.

Table 1. Equations for diagram of predominance areas.

Reaction	$\Delta G^\circ / \text{mol}^{-1}$	Equation
$\text{SrSO}_4 \rightarrow \text{SrO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	136478.21	$\log P_{\text{SO}_2} + 0.5 \log P_{\text{O}_2} = -8.4787$
$\text{SrS} + \frac{1}{2}\text{O}_2 \rightarrow \text{SrO} + \text{SO}_2$	-329373.68	$\log P_{\text{SO}_2} - 1.5 \log P_{\text{O}_2} = 11.3959$
$3\text{SrSO}_4 + \text{SrS} \rightarrow 4\text{SrO} + 4\text{SO}_2$	61944.12	$\log P_{\text{SO}_2} = -9.3310$
$2\text{SrSO}_4 \rightarrow \text{SrS} + 2\text{O}_2$	459232.6	$\log P_{\text{O}_2} = -7.8456$

As the temperature increase, the phase stability regions move to higher pressure of SO_2 and O_2 . If the sulphate is the desired end product, the decomposition do not take place at lower temperature; but at high temperature, the SrSO_4 is unstable and its decomposition begins, to obtain SrO as end product.

Special attention should be put in this fact, due to the possible interactions among the resulting compounds during the reduction reaction of SrSO_4 . The SrO formed during the decomposition process can react with the unreacted SrSO_4 in order to form complex compounds very stable termically according to the following reactions:



Hence, the phenomena of phase transformation and formation of complex compounds between SrSO_4 and SrO should strongly affect the chemical and kinetic properties of the transformation process of SrSO_4 to SrCO_3 .

CONCLUSIONS

A structural transformation of SrSO_4 was found. The transformation enthalpy of the change has not been reported in the literature. The Differential Thermal Analysis (DTA) shows that the structural transformation of SrSO_4 takes place at 1413 K.

This structural transformation also occurs during cooling. So, the original condition of the compound is reestablished during cooling. The transformation enthalpy of this change was determined. The structural transformation of SrSO_4 was also found by X-Ray Diffractometry Analysis.

Decomposition of SrSO_4 was registred at 1500K insted of melting.

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