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**INFLUENCE OF PROCESS PARAMETERS ON THE REACTION COURSE  
OF SrSO<sub>4</sub> CONVERSION INTO SrS AND SrS INTO SrSO<sub>4</sub>**

**WPLYW PARAMETRÓW PROCESU NA PRZEBIEG REAKCJI SrSO<sub>4</sub>  
DO SrS I SrS DO SrSO<sub>4</sub>**

The paper presents the results of SrSO<sub>4</sub> reduction and SrS oxidation with the use of gaseous mixture (CO+CO<sub>2</sub>) in 1073–1373 K temperature range. On the base of an assumed equation describing the process in the wide range of reaction stage the dependence of constant reaction rates on CO concentration in the gaseous phase. The value of reaction activation energy and its change depending on the composition of the gaseous phase (CO+CO<sub>2</sub>) has been defined. The boundary value CO concentration in the gaseous phase, above which reductions, and below which oxidation of SrS take place, has been defined.

Celem tej pracy jest sprawdzenie możliwości tworzenia się SrCO<sub>3</sub> w czasie redukcji SrSO<sub>4</sub> za pomocą mieszaniny gazowej (CO+CO<sub>2</sub>). Badania przeprowadzone w zakresie temperatur 1073–1373 K dla SrSO<sub>4</sub> i SrS przy zmiennej zawartości CO w fazie gazowej (CO+CO<sub>2</sub>) od 0–100% pozwoliły określić zakres temperatur oraz skład fazy gazowej, przy których redukcja SrSO<sub>4</sub> zachodzi do SrS względnie następuje utlenianie SrS do SrSO<sub>4</sub>. Nie stwierdzono tworzenia się węgla strontu w zakresie stosowanych temperatur procesu oraz składu fazy gazowej.

## 1. Introduction

Strontium belongs to very active metals, being placed between calcium and barium in the group of alkaline metals. It reacts with oxygen, nitrogen, hydrogen and sulphur, creating SrO, SrN<sub>2</sub>, SrH<sub>2</sub>, SrS stable compounds. The initial raw material for obtaining strontium salt in the form of SrCO<sub>3</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> as well as metallic strontium is a sulphate mineral called celestite. Strontium compounds are obtained from this mineral

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with the use of carbon reduction or leaching in soda solution. The  $\text{SrSO}_4$  reduction leads to  $\text{SrS}$  formation, which is used to obtain other strontium salts. Therefore, strontium sulphate is a subject to many research works.

Panek and Fitzner [1] determined phase stability in Sr-S-O system and defined Gibbs energy of  $\text{SrSO}_4$  decomposition. The results of  $\text{SrSO}_4$  reduction with the use of hydrogen, as shown in 1073–1273 K temperature range in this paper, indicate the formation of  $\text{SrS}$  only. Pedak et al. [2], presented the results of  $\text{SrSO}_4$  reduction with the use of hydrogen in 1073–1273 K temperature range, which revealed, beside  $\text{SrS}$ , the presence of  $\text{SrSO}_3$  and  $\text{SrS}_2\text{O}_3$  at the levels of ca 1% and 0.1%, respectively; it did not depend on  $\text{SrSO}_4$  reduction rate. Sukiennik et al. [3] defined the enthalpy and the temperature of  $\text{SrSO}_4$  polymorphous change. Plewa et al. [4] suggested that  $\text{SrCO}_3$  phase appears beside  $\text{SrS}$  when conducting research on  $\text{SrSO}_4$  reduction with the use of gaseous mixture ( $\text{CO} + \text{CO}_2$ ) containing 10 vol. % of  $\text{CO}$  in 1280–1400 K temperature range. Moreover, they suggested that when there is 5 vol. % of  $\text{CO}$  in the gas only  $\text{SrCO}_3$  is formed. In turn, Sukiennik et al. [5] determined the influence of temperature and  $\text{CO}$  concentration of the gaseous phase ( $\text{CO} + \text{CO}_2$ ) on  $\text{SrSO}_4$  reduction rate. In this paper, the formation of  $\text{SrCO}_3$  phase in 1073–1273 K temperature range, even with low concentration of  $\text{CO}$ , have not been observed. Sonavane et al. [6] presented the results of  $\text{SrSO}_4$  reduction with the use of charcoal in 1073–1148 K temperature range. They have also investigated the influence of catalysts on reaction rate and defined the reaction activation energy. Finally, Erdemoglu et al. [7] shown the results of  $\text{SrSO}_4$  reduction in a rotary furnace in the temperature range from 923–1073 K up to 1473–1573 K.

The purpose of this paper is to define the influence of  $\text{CO}$  concentration in the gaseous phase on  $\text{SrSO}_4$  reduction as well as oxidation of  $\text{SrS}$  to  $\text{SrSO}_4$ .

## 2. Experiments

### 2.1. Characteristics of material and the experimental technique

Investigations of  $\text{SrSO}_4$  reduction kinetics with the use of the gaseous phase ( $\text{CO} + \text{CO}_2$ ) have been conducted on pure samples with changing temperature and  $\text{CO}$  concentration in gaseous phase. Investigations of  $\text{SrS}$  oxidation rate with the use of gaseous mixture ( $\text{CO} + \text{CO}_2$ ) have been conducted on  $\text{SrS}$  which was obtained from  $\text{SrSO}_4$  reduction with the use of hydrogen.

The measurements have been made in a vertical, electric furnace with temperature being controlled with a thermocouple Pt-PtRh which was introduced from the bottom of the furnace directly under the investigated sample. The sample in the form of powder has been placed on the pan made of  $\text{Al}_2\text{O}_3$ , suspended to the scales. This made continuous recording of mass changes during the process with the accuracy of  $1 \cdot 10^{-3}$  g.

The gaseous phase, in the amount of 60 dm<sup>3</sup>/h and with a specified composition, which was controlled by rotameters, was flowing from the bottom of the furnace towards its top. The measurements were made in the following way. A specified amount of the sample was introduced into a pre-heated furnace, through which the gas, having the specified composition, was flowing. Since the sample was introduced into the furnace, the changes of the mass as a function of time were recorded. After a specified time, the experiments were interrupted and the samples were tested with an X-ray phase analysis.

## 2.2. Experimental results

The first of experiments covered SrSO<sub>4</sub> reduction in the temperature range from 1073 to 1373 K with the use of gaseous mixtures (CO+CO<sub>2</sub>), where CO content changed from 100 to 7.5 vol. % The total recorded loss of mass, especially in higher temperatures or at higher CO contents in the gaseous phase corresponded to the course of SrSO<sub>4</sub>+CO = SrS+CO<sub>2</sub> reaction. At small CO contents in the gaseous phase, because of a small reaction rate and a limited time of the experiment, the loss of mass corresponding to the theoretical oxygen contents in SrSO<sub>4</sub> was not achieved. Taking into consideration suggestions [4] about the possibility of SrCO<sub>3</sub> formations, samples of a specified loss of mass, especially obtained at lower CO concentration in the gaseous phase, were tested with an X-ray phase analysis. The results of such an analysis, which was made with the use of CoK<sub>α</sub> radiation and an Fe filter in the angular range 2θ from 10 to 80° indicate the presence of SrSO<sub>4</sub> and SrS phases only, irrespective of temperature and composition of the gaseous phase. It enabled to calculate the rate of reduction, expressed by the ratio

$$\alpha = \frac{\Delta m_{\text{prakt}}}{\Delta m_{\text{teoret}}} \cdot 100\%, \quad (1)$$

where:  $\Delta m_{\text{prakt}}$  — recorded change of the sample mass after time  $t$ ,  
 $\Delta m_{\text{teoret}}$  — theoretical maximum change of mass calculated from oxygen amount in sample mass.

Fig. 1 and 2 show exemplary results in temperatures of 1173 and 1248 K.

When analysing the obtained dependences attention should be paid to a significant decrease of reaction rate at CO contents of 7.5 vol. % in the gaseous phase in relation to 15 vol. % of CO. Probably, it may be connected with the approach of the system to dynamic equilibrium, where the reversible oxidation reaction of SrS with the use of CO<sub>2</sub> is possible. In order to answer that question, oxidation of SrS with the use of CO<sub>2</sub> and (CO+CO<sub>2</sub>) mixture was also conducted at several temperatures. Also, in that case the samples were tested with an X-ray phase analysis after a specified increase of mass. It revealed the presence of SrS<sub>3</sub>O<sub>10</sub> and SrSO<sub>4</sub> phases beside SrS phase. The presence of SrS<sub>3</sub>O<sub>10</sub> phase means gradual embodying of oxygen into the sulphate

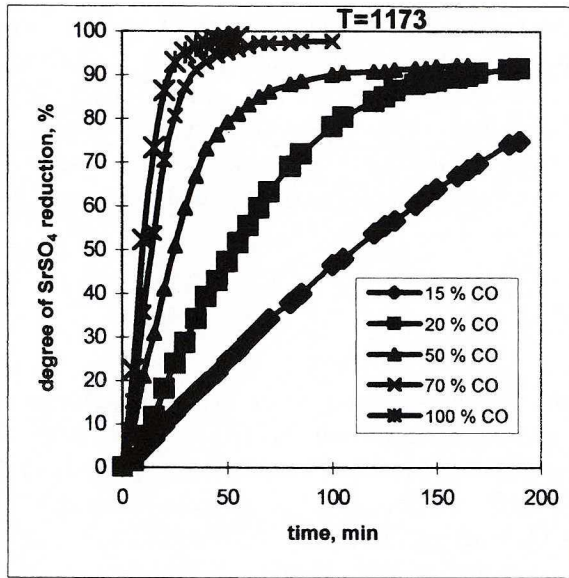


Fig. 1. Time dependence of a degree of  $\text{SrSO}_4$  reduction on CO concentration in gaseous phase at temperature 1173 K

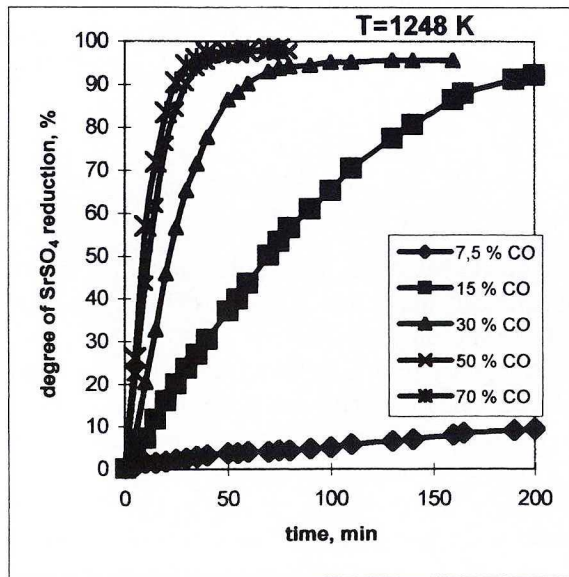


Fig. 2. Time dependence of a degree of  $\text{SrSO}_4$  reduction on CO concentration in gaseous phase at temperature 1248 K

phase and forming oxysulphide compounds which, as a result of oxygen chemisorption are converted into  $\text{SrSO}_4$ . The increase of  $\text{SrSO}_4$  specific volume in relation to  $\text{SrS}$  makes oxygen diffusion process to  $\text{SrS-SrSO}_4$  phase boundary more difficult, thus slowing down  $\text{SrS}$  oxidation rate.

$\text{SrS}$  oxidation number was calculated using experimental data and equation (1). This number is shown in Fig. 3 and 4.

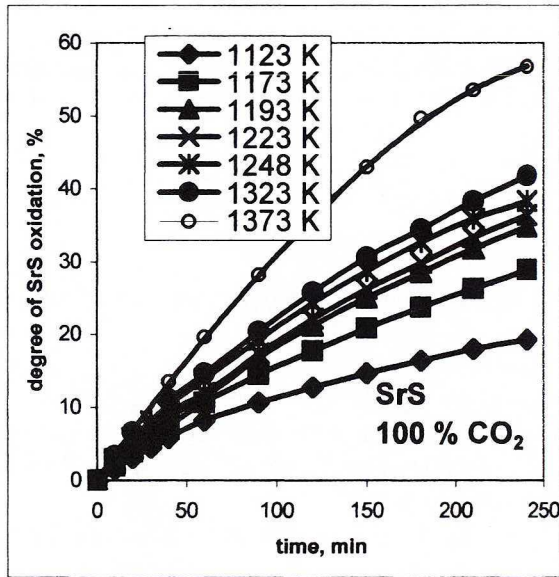


Fig. 3. Degree of  $\text{SrS}$  oxidation in pure  $\text{CO}_2$  at different temperatures with time

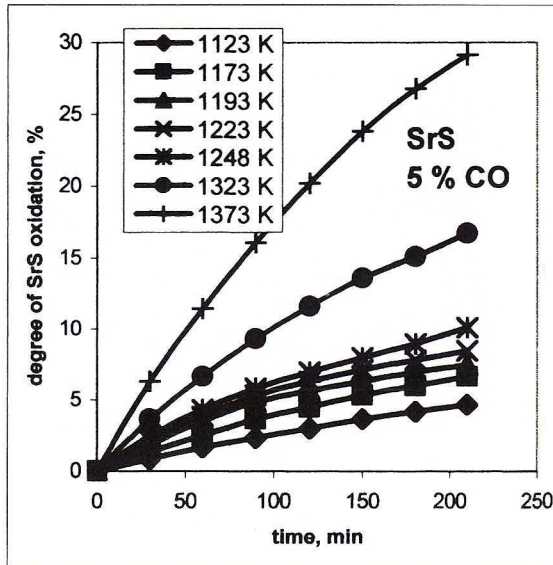


Fig. 4. Degree of  $\text{SrS}$  oxidation in  $(\text{CO} + \text{CO}_2)$  gaseous mixture at different temperatures with time

The comparison of respective curves shown in Fig. 3 and 4 demonstrate that the introduction of 5 vol. % CO into gaseous phase ( $\text{CO} + \text{CO}_2$ ) slows down SrS oxidation rate nearly twice.

### 3. Results

To describe the process in a wide range of reaction degree, calculations of the obtained experimental data with different models found in literature [8, 9] were done for different conditions. The best fit of experimental points was obtained with equation [10]:

$$1 - (1 - \alpha)^{\frac{2}{3}} = k \cdot t \quad (2)$$

where:  $\alpha$  — conversion rate

$k$  — constant, proportional to reaction rate dependent on temperature and % CO

$t$  — process time

Calculations showed a good agreement of experimental data with the model equation in the wide range of conversion, which was proved by a high correlation coefficient above 0.99, whereas the diversion of the initial ordinate which for  $t = 0$  should be 0 was found to be between  $-0.0192$  to  $0.0133$ .

Fig. 5 shows results of calculations compared with experimental points obtained in the temperature 1223 K, in general, it can be said, that the range of application of the assumed equation with reference to conversion rate  $\alpha$  increases with temperature and CO concentration in the gas phase.

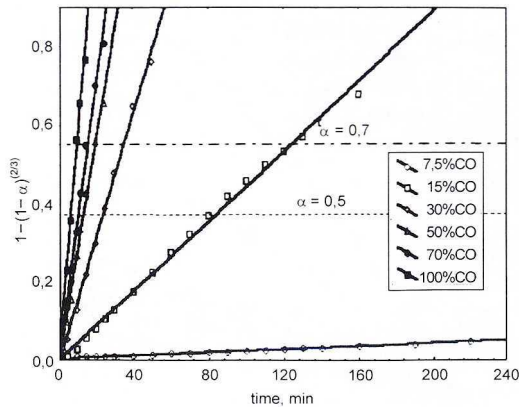


Fig. 5. Fit of eq. (2) to experimental points obtained for  $\text{SrSO}_4$  reduction by means of mixtures of gases ( $\text{CO} + \text{CO}_2$ ) at temperature 1223 K

The obtained experimental data showed that  $\text{SrSO}_4$  reduction rate decreases with the decrease of CO concentration in the gaseous ( $\text{CO} + \text{CO}_2$ ) phase, while SrS oxidation rate increases. Here comes the question: is there such a CO concentration in the gaseous mixture, that the rates of both reactions are equal? To solve this problem, the dependence between  $k$  values and CO concentration in the gaseous phase has been determined for an assumed temperature. Obtained values for the temperature 1223 K are shown in Fig. 6. The character of the obtained linear dependences shows that reaction rate constants reach the same values at the specific CO concentration in the gaseous phase.

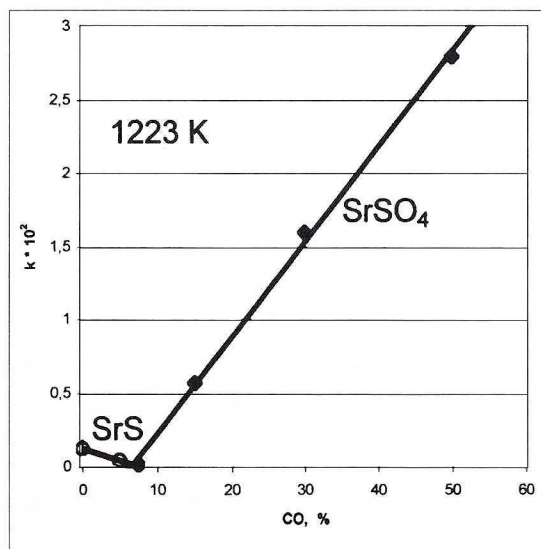


Fig. 6. Dependence of regression coefficients  $k$  for  $\text{SrSO}_4$  reduction and for SrS oxidation on CO concentration at temperature 1223 K

Assuming the linear change of constant  $k$  value along with CO concentration regression lines for both reactions have been obtained, and their mutual solution has given the value of CO concentration in the gaseous phase for which both reactions achieve the same rates. Fig. 7 shows an example of these calculations. It shows that CO boundary concentration in the gaseous phase for reduction of  $\text{SrSO}_4$  to SrS slightly decreases with the temperature increase.  $\text{SrSO}_4$  reduction takes place at CO concentrations above this curve, whereas SrS oxidation with the use of  $\text{CO}_2$  takes place at CO concentrations below this curve.

Using calculated  $k$  values from equation (2), activation energy of  $\text{SrSO}_4$  reduction and SrS oxidation reactions have been calculated. The highest activation energy value has been found for  $\text{SrSO}_4$  reduction with the use of pure CO in the temperature range 1073–1148 K. It is equal to 300 kJ/mol. In the range of temperatures 1148–1223 K this value decreases to 72 kJ/mol, which may mean the transition of the reaction from the

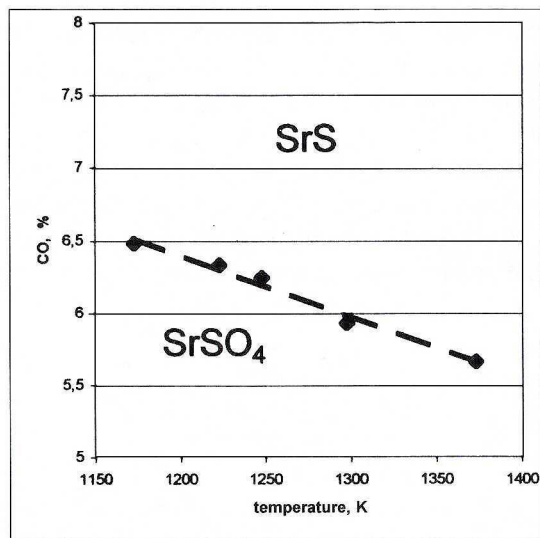


Fig. 7. Influence of CO concentration in gaseous phase and of temperature on phase stability in  $\text{SrSO}_4$ - $\text{SrS}$ - $\text{CO}$ - $\text{CO}_2$  system

kinetic to the diffusion controll. When the CO contents in the gaseous phase was 15%, activation energy value was found to be 85 kJ/mol in the temperature range 1173–1371 K. For  $\text{SrS}$  oxidation with the use of the gaseous ( $\text{CO} + \text{CO}_2$ ) mixture activation energy value in the temperature range 1123–1371 K is 36 kJ/mol when oxidation in pure  $\text{CO}_2$  takes place and 100 kJ/mol for oxidation reaction with the use of gas ( $\text{CO} + \text{CO}_2$ ) mixture containing 5% CO.

#### 4. Summary

On the base of the obtained results from  $\text{SrSO}_4$  reduction and  $\text{SrS}$  oxidation with the use of the gaseous mixture ( $\text{CO} + \text{CO}_2$ ) it can be stated that:

1.  $\text{SrSO}_4$  reduction and  $\text{SrS}$  oxidation can be described in the wide range of conversion by the equation  $1 - (1 - a)^{\frac{2}{3}} = k \cdot t$ .
2. Along with the CO concentration increase in the ( $\text{CO} + \text{CO}_2$ ) gaseous phase the constant  $k$  for  $\text{SrSO}_4$  reduction increases, while its value for  $\text{SrS}$  oxidation decreases.
3. CO boundary concentration in the ( $\text{CO} + \text{CO}_2$ ) gaseous phase above which  $\text{SrSO}_4$  reduction takes place, and below which  $\text{SrS}$  oxidation takes place, has been defined as a function of temperature.
4. Energy activation value for  $\text{SrSO}_4$  reduction and  $\text{SrS}$  oxidation for different compositions of the gaseous phase ( $\text{CO} + \text{CO}_2$ ) have been found.
5. The formation of  $\text{SrCO}_3$  has not been confirmed in both  $\text{SrSO}_4$  reduction and  $\text{SrS}$  oxidation even with low CO concentrations in the gaseous ( $\text{CO} + \text{CO}_2$ ) phase.



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