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**INFLUENCE OF PROCESS PARAMETERS ON THE REACTION COURSE
OF SrSO₄ CONVERSION INTO SrS AND SrS INTO SrSO₄**

**WPLYW PARAMETRÓW PROCESU NA PRZEBIEG REAKCJI SrSO₄
DO SrS I SrS DO SrSO₄**

The paper presents the results of SrSO₄ reduction and SrS oxidation with the use of gaseous mixture (CO+CO₂) 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+CO₂) 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 SrCO₃ w czasie redukcji SrSO₄ za pomocą mieszaniny gazowej (CO+CO₂). Badania przeprowadzone w zakresie temperatur 1073–1373 K dla SrSO₄ i SrS przy zmiennej zawartości CO w fazie gazowej (CO+CO₂) od 0–100% pozwoliły określić zakres temperatur oraz skład fazy gazowej, przy których redukcja SrSO₄ zachodzi do SrS względnie następuje utlenianie SrS do SrSO₄. 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, SrN₂, SrH₂, SrS stable compounds. The initial raw material for obtaining strontium salt in the form of SrCO₃ and Sr(NO₃)₂ 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 SrSO_4 reduction leads to 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 SrSO_4 decomposition. The results of SrSO_4 reduction with the use of hydrogen, as shown in 1073–1273 K temperature range in this paper, indicate the formation of SrS only. Pedak et al. [2], presented the results of SrSO_4 reduction with the use of hydrogen in 1073–1273 K temperature range, which revealed, beside SrS , the presence of SrSO_3 and SrS_2O_3 at the levels of ca 1% and 0.1%, respectively; it did not depend on SrSO_4 reduction rate. Sukiennik et al. [3] defined the enthalpy and the temperature of SrSO_4 polymorphous change. Plewa et al. [4] suggested that SrCO_3 phase appears beside SrS when conducting research on SrSO_4 reduction with the use of gaseous mixture ($\text{CO} + \text{CO}_2$) containing 10 vol. % of CO in 1280–1400 K temperature range. Moreover, they suggested that when there is 5 vol. % of CO in the gas only SrCO_3 is formed. In turn, Sukiennik et al. [5] determined the influence of temperature and CO concentration of the gaseous phase ($\text{CO} + \text{CO}_2$) on SrSO_4 reduction rate. In this paper, the formation of SrCO_3 phase in 1073–1273 K temperature range, even with low concentration of CO , have not been observed. Sonavane et al. [6] presented the results of 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 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 CO concentration in the gaseous phase on SrSO_4 reduction as well as oxidation of SrS to SrSO_4 .

2. Experiments

2.1. Characteristics of material and the experimental technique

Investigations of 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 CO concentration in gaseous phase. Investigations of SrS oxidation rate with the use of gaseous mixture ($\text{CO} + \text{CO}_2$) have been conducted on SrS which was obtained from 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 Al_2O_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 dm³/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 SrSO₄ reduction in the temperature range from 1073 to 1373 K with the use of gaseous mixtures (CO+CO₂), 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 SrSO₄+CO = SrS+CO₂ 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 SrSO₄ was not achieved. Taking into consideration suggestions [4] about the possibility of SrCO₃ 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_α radiation and an Fe filter in the angular range 2θ from 10 to 80° indicate the presence of SrSO₄ 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: Δm_{prakt} — recorded change of the sample mass after time t ,
 Δm_{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 CO₂ is possible. In order to answer that question, oxidation of SrS with the use of CO₂ and (CO+CO₂) 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 SrS₃O₁₀ and SrSO₄ phases beside SrS phase. The presence of SrS₃O₁₀ phase means gradual embodying of oxygen into the sulphate

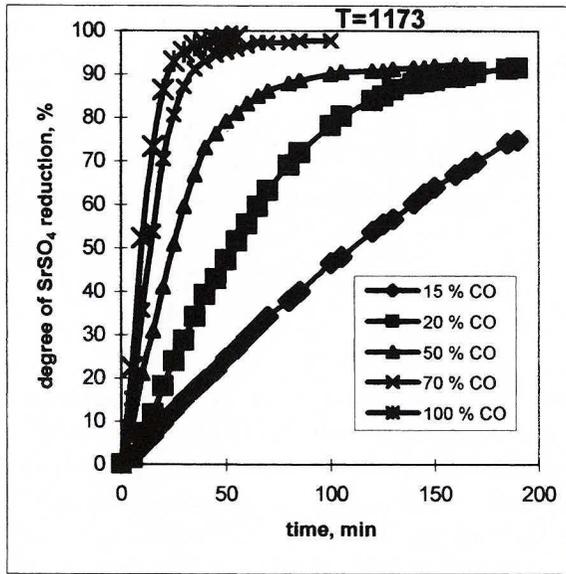


Fig. 1. Time dependence of a degree of SrSO_4 reduction on CO concentration in gaseous phase at temperature 1173 K

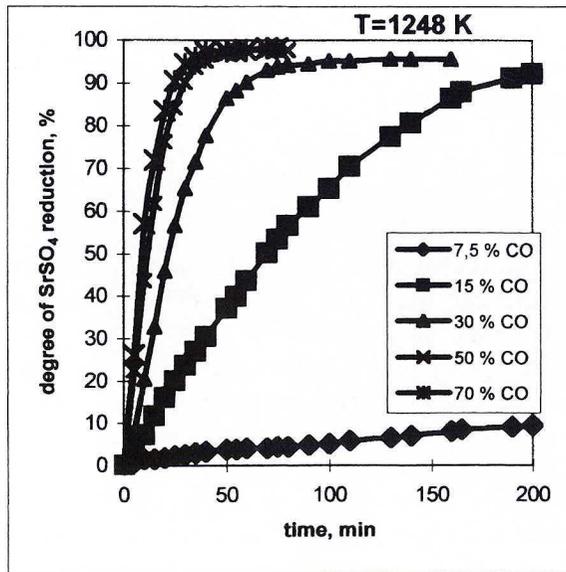


Fig. 2. Time dependence of a degree of SrSO_4 reduction on CO concentration in gaseous phase at temperature 1248 K

phase and forming oxysulphide compounds which, as a result of oxygen chemisorption are converted into SrSO_4 . The increase of SrSO_4 specific volume in relation to SrS makes oxygen diffusion process to SrS-SrSO_4 phase boundary more difficult, thus slowing down SrS oxidation rate.

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

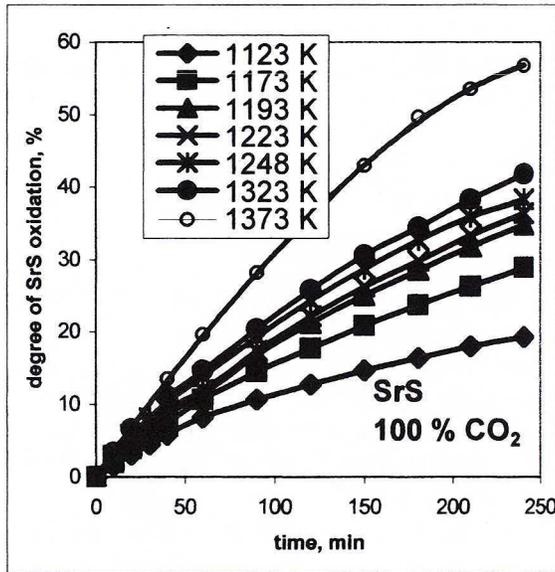


Fig. 3. Degree of SrS oxidation in pure CO_2 at different temperatures with time

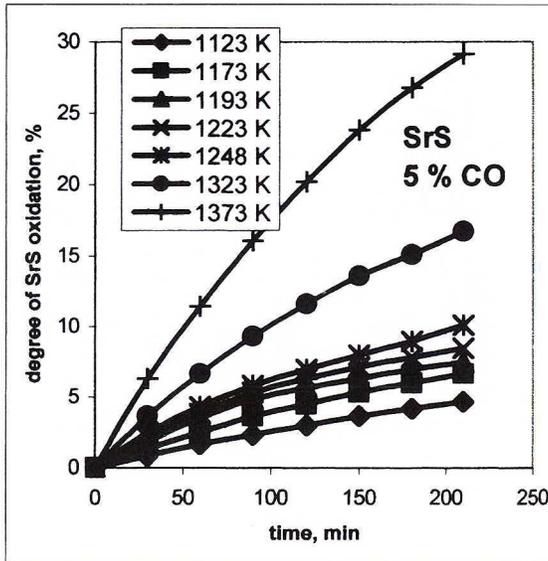


Fig. 4. Degree of SrS oxidation in $(\text{CO} + \text{CO}_2)$ gaseous mixture at different temperatures with time

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: α — 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 α increases with temperature and CO concentration in the gas phase.

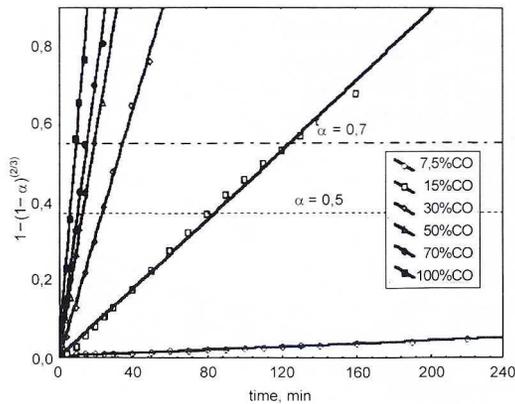


Fig. 5. Fit of eq. (2) to experimental points obtained for SrSO_4 reduction by means of mixtures of gases ($\text{CO} + \text{CO}_2$) at temperature 1223 K

The obtained experimental data showed that 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.

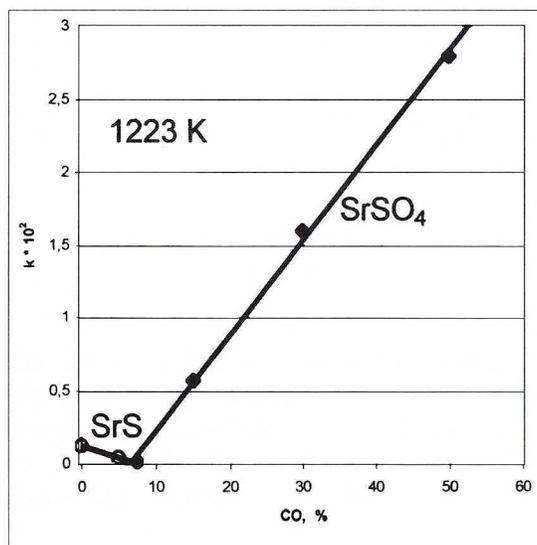


Fig. 6. Dependence of regression coefficients k for SrSO_4 reduction and for SrS oxidation on CO concentration at temperature 1223 K

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 SrSO_4 to SrS slightly decreases with the temperature increase. SrSO_4 reduction takes place at CO concentrations above this curve, whereas SrS oxidation with the use of CO_2 takes place at CO concentrations below this curve.

Using calculated k values from equation (2), activation energy of SrSO_4 reduction and SrS oxidation reactions have been calculated. The highest activation energy value has been found for 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

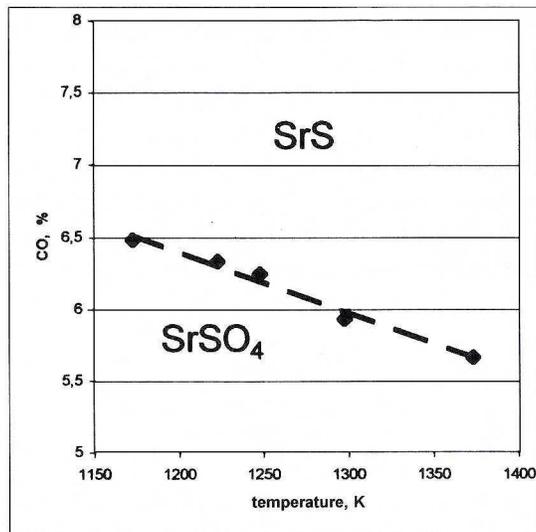


Fig. 7. Influence of CO concentration in gaseous phase and of temperature on phase stability in SrSO_4 - SrS - CO - CO_2 system

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 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 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 SrSO_4 reduction and SrS oxidation with the use of the gaseous mixture ($\text{CO} + \text{CO}_2$) it can be stated that:

1. SrSO_4 reduction and 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 SrSO_4 reduction increases, while its value for SrS oxidation decreases.
3. CO boundary concentration in the ($\text{CO} + \text{CO}_2$) gaseous phase above which SrSO_4 reduction takes place, and below which SrS oxidation takes place, has been defined as a function of temperature.
4. Energy activation value for SrSO_4 reduction and SrS oxidation for different compositions of the gaseous phase ($\text{CO} + \text{CO}_2$) have been found.
5. The formation of SrCO_3 has not been confirmed in both SrSO_4 reduction and SrS oxidation even with low CO concentrations in the gaseous ($\text{CO} + \text{CO}_2$) phase.

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