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ISOTHERMAL REDUCTION OF BARITE WITH HYDROGEN

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The reduction of barite concentrate with hydrogen was studied by using a Shimadzu 31 H Thermoanalyser coupled with a gas-feeding system and a Uras 7 N infrared SO_2 gasanalyser made by Hartman Brown Co. The kinetic parameters were determined by means of a computer program on the basis of the thermogravimetric curves in the temperature range 1098-1223 K. The experimental data obey the contracting volume kinetic equation $kt = 1-(1-\alpha)^{1/3}$.

The process of reduction of pure barium sulphate with hydrogen was studied by Gulver and Hamdorf [1, 2], who proposed the following equation for the equilibrium constant: $\log K_p = 5.447 + 697.5\ T$ in the temperature range 1073-1373 K.

For the same temperature range at a partial pressure of hydrogen of 1 atm, they obtained an activation energy of 246 kJ/mol. It was shown that the rate of reduction was a function of the temperature and that it was relatively independent of the composition of the gaseous phase, i.e. the process was controlled by the chemical reactions. The kinetics of reduction of the barite concentrate with carbon [3] differed considerably from that for pure barium sulphate. The impurities in the natural barite and the structure of the barite concentrates significantly influenced the kinetics of reduction with carbon. The effects of the impurities could be ascribed to the formation of some intermediate compounds and to the intensity of gasification of carbon too.

The aims of the present work were to extend the range of the investigations to the reduction of pure barium sulphate and barite concentrate obtained during exploration of the complex Kremikovtzi ferrous ore deposit; on this basis, to characterize in more detail the properties and the reactivity of the Bulgarian barite concentrate; and as a result to attain a better understanding of the mechanism of action of the impurities.

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Experimental

The investigations on the reduction of barium sulphate and barite were carried out on a Shimadzu 31 H thermogravimetric analyser equipped with a gas-feeding system for operation with a flowing gaseous mixture of different compositions. The experiments were performed in the temperature range 1098-1223 K. The weight of the sample was 10 mg, and it was disposed in a monolayer in a platinum crucible with a diameter of 10 mm and a height of 2 mm. The argon mixture flow rate was 6.94 $cm^3 \cdot sec^{-1}$ and the hydrogen content was about 1-5 vol.%. The size of the barium sulphate particles was below 100 μm.

The pure barium sulphate was of p.a. quality, as supplied by Reachim, USSR. The barite concentrate contained 93.2% $BaSO_4$, 0.789% Fe_2O_3, 0.68% CaO, 0.73% SiO_2, 0.23% MgO, etc.

Results and discussion

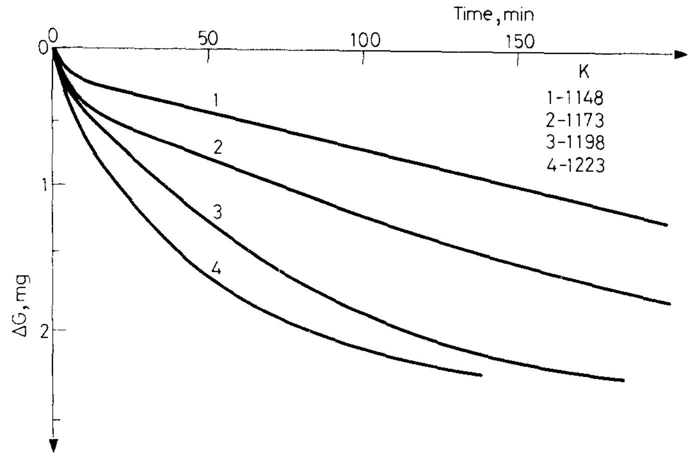

Fig. 1 Isothermal TG curves of the reduction of $BaSO_4$ with 3% H_2 + Ar at various temperatures

The thermogravimetric curves in Figs 1 and 2 characterize the kinetics of reduction of $BaSO_4$ in gaseous media containing 3 or 5 vol.% of H_2 at different temperatures from 1148 to 1123 K. At 1148 K, a degree of reduction of 69.3% was achieved in 280 min at 3 vol.% of H_2, and in 202 min at

5 vol.%. With increase of the temperature up to 1223 K, almost complete reduction (97-98.5%) was achieved in 190 min and 147 min, respectively. At the same time, the barium sulphide content in the solid end-product increased from 47-48% to 85.2-98.3 weight % BaS. The rate of the process at the same degree of reduction appeared to be an exponential function of the partial pressure of hydrogen (Figs 3 and 7) in the gaseous phase in the investigated temperature range. For the examined conditions at $p_H = 0.01$ kg cm^{-2}, the rate of decomposition of the barite concentrate was in the range 0.01-0.05 mg$\cdot$min^{-1}, while at $p_{H_2} = 0.05$ kg$\cdot$cm^{-1} it ranged from 0.12 to 0.34 mg$\cdot$min^{-1} 1148 K. For pure barium sulphate, the rate of decomposition varied from 0.2 to 0.34 mg$\cdot$min^{-1} 1223 K.

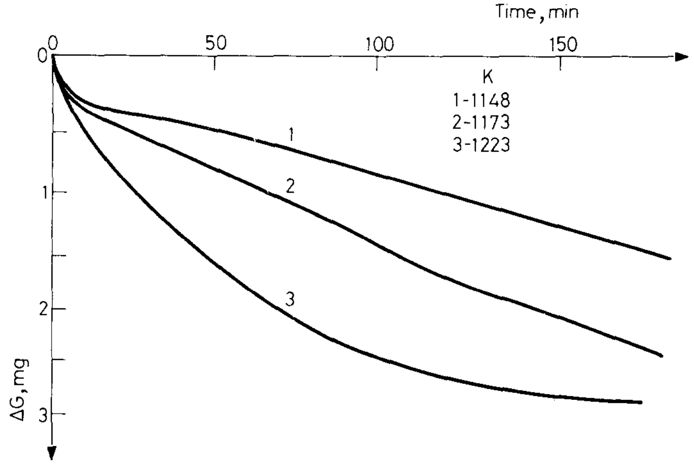

Fig. 2 Isothermal TG curves of the reduction of BaSO$_4$ with 5% H$_2$ + Ar at various temperatures

Considerable differences were found in the thermogravimetric curves characteristic of the barium concentrate (Figs. 4-6) and those for pure barium sulphate. The reduction of the barium concentrate still took place with a high rate at 1098 K and, depending on the hydrogen partial pressure, the time required to achieve α = 74-86% was 58-85 min. At a higher partial pressure of hydrogen in the interval 1098-1223 K, after the starting stage, a period of delay in the rate of reduction was observed, which was ascribed to the formation of the denser structure of the solid products. The diminished effect of the partial pressure of hydrogen at a degree of reduction above 50% confirmed the determinative role of the rate of mass transport of hydrogen to the reaction surface. The diffusion delay in the process of reduction with hydrogen was characteristic for a degree of reduction above 70%, independently of the partial pressure of hydrogen. The complete coincidence of the thermogravimetric curves at temperatures above 1173 K (Figs 5 and 6) also confirmed the limiting role of diffusion. The mass losses were found in some cases to exceed the maximum loss for the reduction of $BaSO_4$ to BaS, which was an indication of secondary reactions with the participation of some of the impurities.

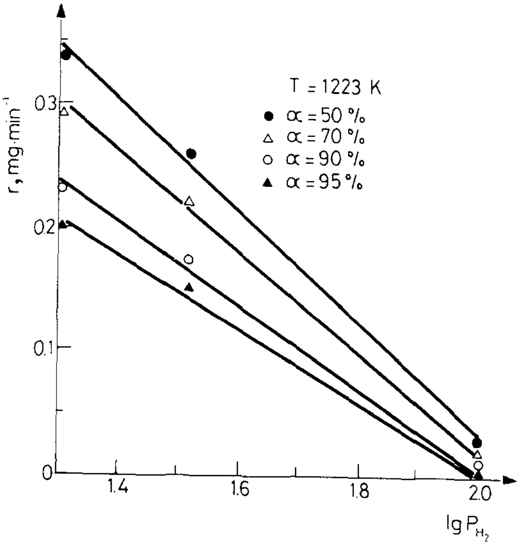

Fig. 3 Dependence of the rate of reduction of $BaSO_4$ on the partial pressure of hydrogen at 1223 K

It was plausible to assign the increased reactivity of the barite concentrate to these reactions. The higher rate of reduction was most probably connected with the activation due to the impurities of ferrous oxides and SiO_2, which was confirmed during the examination of the reduction of $BaSO_4$ with carbon.

The experimental data were described by a kinetic equation of a model for a compressible sphere: $kt = 1 - \sqrt[3]{1-\alpha}$. The results obtained for the rate constants of the reduction of pure barium sulphate in the temperature range 1148-1223 K lay in the range $1.58\text{-}7.10 \cdot 10^{-3}$ min^{-1}, and the temperature coefficient did not exceed 1.53.

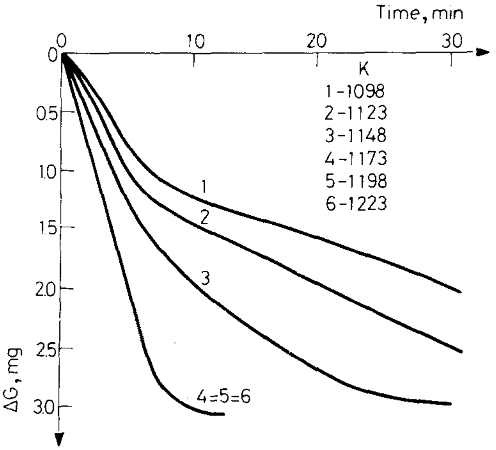

Fig. 4 Isothermal TG curves of the reduction of barite concentrate from the Kremikovitzi ore deposit with 1% H_2 + Ar at various temperatures

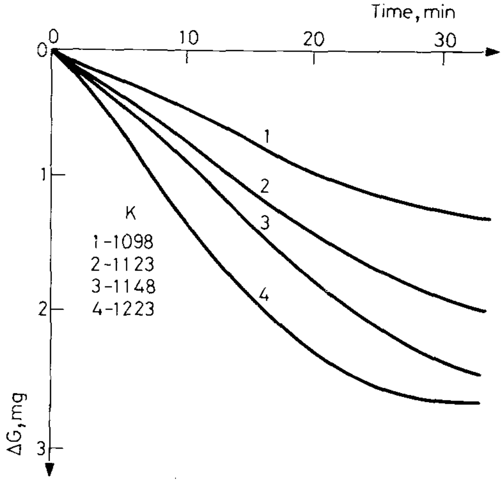

Fig. 5 Isothermal TG curves of the reduction of barite concentrate from the Kremikovitzi ore deposit with 3% H_2 + Ar at various temperatures

The apparent activation energy of the process for $p_{H_2} = 0.03$ kg·cm^{-2} was about 108.2 kJ/mol, and that for $p_{H_2} = 0.05$ kg·cm^{-2} was 101.5 kJ/mol.

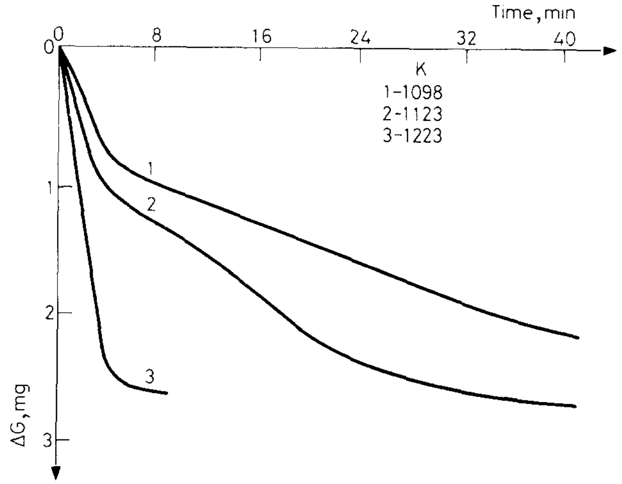

Fig. 6 Isothermal TG curves of the reduction of barite concentrate from the Kremikovitzi ore deposit with 5% H_2 + Ar at various temperatures

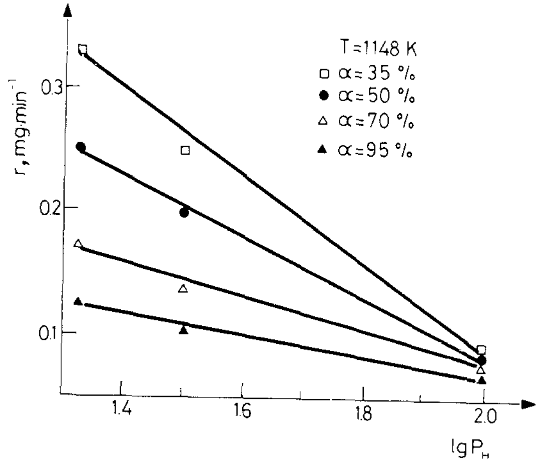

Fig. 7 Dependence of the rate of reduction of barite concentrate from the Kremikovitzi ore deposit on the partial pressure of hydrogen at 1148 K

The rate constants for the reduction of barite concentrate at 1098 K were $5.5\cdot10^{-3}$ min^{-1} for p_{H_2} = 0.01 and $16.5\cdot10^{-3}$ min^{-1} for p_{H_2} = 0.05 kg/cm^{-2}.

For the same partial pressures of hydrogen, the activation energy of the process was 72.5 and 112.3 kJ/mol, respectively.

Conclusion

The results of the investigations on the kinetics of reduction of pure barium sulphate and barite concentrate confirmed the findings concerning the multifactorial monitoring of the process of solid-gas type. Under the investigated experimental conditions, the main parameters were the temperature and the partial pressure of hydrogen. The essential differences in the kinetics of reduction of pure barium sulphate and of barite concentrate under similar experimental conditions confirmed the effects of the structure and the composition of the solid phase on the optimal parameters for the realization of the process in practice.

References

1 R. V. Gulver and C. J. Hamdorf, J. Appl. Chem., 5 (1955) 383-389.
2 R. V. Gulver, C. J. Hamdorf, and E. C. Spooner, J. Appl. Chem., 8 (1958) 810-819.
3 Y. Pelovski and M. Taniguchi, J. Thermal Anal., 33 (1988) 603-608.

Zusammenfassung — Mittels eines Shimadzu 31 H Thermoanalysators, ausgerüstet mit einem Gasspeisungssystem und einem von Hartman Brown Co hergestellten Uras 7 N Infrarot-SO_2-Gasanalysator, wurde die Reduktion von Bariumkonzentrat mit Wasserstoff untersucht. Auf der Basis der TG-Daten im Bereich 1098-1223 K wurden unter Zuhilfenahme eines Computerprogrammes die kinetischen Parameter ermittelt. Die experimentellen Daten folgen einer kinetischen Gleichung der Form $kt = 1 - (1 - \alpha)^{1/3}$.