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ISOTHERMAL GRAVIMETRICAL KINETIC STUDY OF THE DECOMPOSITION OF PHOSPHOGYPSUM UNDER $CO-CO_2$-Ar ATMOSPHERE

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ABSTRACT

Thermochemical decomposition of phosphogypsum was studied in the temperature range 1000-1100°C.Carrier gas contains 4%CO,5-20% CO_2 and Ar.The kinetics study of decomposition enable to calculate activation energy derived from the Arrhenius equation.The results are compared with our earlier work in CO-Ar atmosphere.

INTRODUCTION

Phosphogypsum is a by-product from manifacturing of phosphates to phosphoric acid by wet process.Degree of substitution of different impurities and phosphates in the calcium sulfate depends on the technological conditions and raw materials origin.The influence of temperature and external gases on the reaction rate of the decomposition of gypsum and phosphogypsum has been studied by few authers [1,2,3] but the experimental conditions have varied so widely,that the corelation between the results of different workers is seldom possible.At the same time there are not complete kinetics investigations yet.The present work is to continue our early study on the influence of gas atmosphere [4,5] on the thermochemical decomposition of phosphogypsum.

MEASURING METHODS

Decomposition of phosphogypsum was studied by means of Shimadzu Thermoanalyzer using up-hold thermoprogramme mode and coupled with gas-mixing system.This system enable us to flow through the balance balloon continuously 85cc min^{-1} argon and after getting the isothermal level to flow through the reactor mixer additionally 250cc min^{-1} of the other gas components.Sample weight is 15mg. The diameter of platinum sample pan is 10mm with 1mm height.The weight change and chemical analysis data give the possibillity to calculate the rate of decomposition to CaO and CaS.Phosphogypsum contains:38.6%CaO;54.7%SO_3;0.7%P_2O_5;0.2%F;1.5%SiO_2;0.7%Fe_2O_3;

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0.4% Al_2O_3;0.2%MgO.The unsoluble compounds are 2.1% and particles are under 0.1mm.All the gases are reagent grade.

RESULTS AND DISCUSSION

Thermogravimetric curves describing the thermochemical decomposition of phosphogypsum are shown in Fig.1 and Fig.2.The curves were obtained in the temperature range:1000-1100°C.The carrier gas contains 4%CO,5-20% CO_2 and the rest Ar.The flow rate is 355cc min^{-1} It is seen that the decomposition rate depends on both temperature and partial pressure of CO_2 (P_{CO_2}).The temperature has higher positive effect to 1050-1075°C and at the same time it is obvious that CO_2 inhibits the process in the whole temperature range.The results of chemical analysis of solid product showed the absence of $CaSO_4$.The ratio of CaO/CaS is controled by the temperature and P_{CO_2}.At 1100°C (Fig.3) when carrier gas contains 20% CO_2,only the reaction to CaO proceeds.The influence of CO_2 and temperature on formation of CaS is higher at higher temperatures.Additional experiments and chemical analyses were made to check a step reaction but we did not find any conformation about it.Therefore we suppose the reactions 1 and 2 proceed in parallel:

$$CaSO_4 + CO = CaO + CO_2 + SO_2 \quad (1)$$

$$CaSO_4 + 4CO = CaS + 4CO_2 \quad (2)$$

The increasing of P_{CO_2} depress the second reaction stronger.The relationships of initial (r_o) and maximum (r_{max}) process rate from the temperature (Fig.4) show a straight line for r_o and maximum at 1075°C for r_{max}.Wheelock and Boylan [3] found the same character for natural gypsum but the maximum is at 1200°C.This difference of 125°C can be due to the specific impurities and different crystal origin of gypsum and phosphogypsum.The experimental results can be best represented,over the temperature range 1000-1075°C by the Avrami equation: $[-\ln(1-\mathcal{L})]^{1/3} = k.t$,where $\mathcal{L}$ is a fraction of decomposition,t-time and k-rate constant.The appirant activation energy (E) deduced for the process is 27.2kcal/mol when the flow gas contains 4%CO,10% CO_2 and 86%Ar,and 21.2kcal/mol in gas atmosphere 4%CO,20% CO_2 and 76%Ar.Thus the diffusion becomes rate determination at higher temperatures in comparison with CO-Ar gas atmosphere.

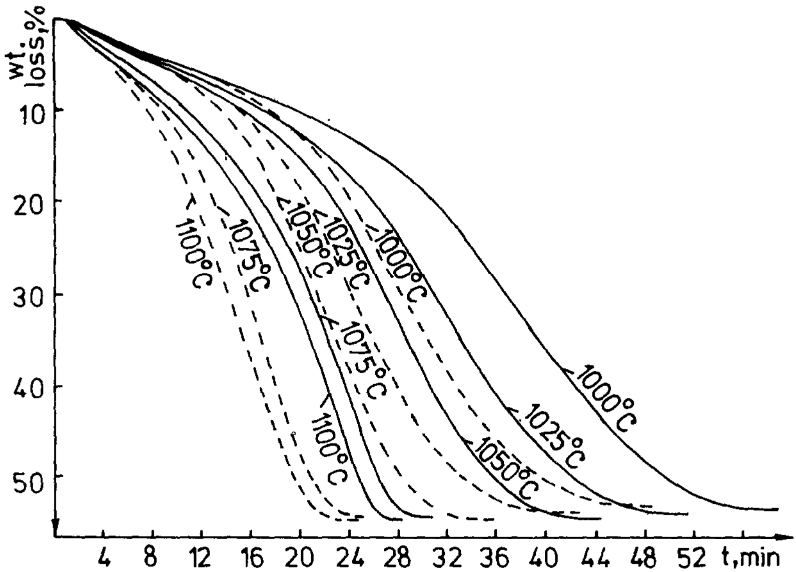

Fig. 1. TG curves of phosphogypsum at various temperatures and gas atmosphere: ---4%CO, 5%CO_2, 91%Ar;—4%CO, 15%CO_2, 81%Ar.

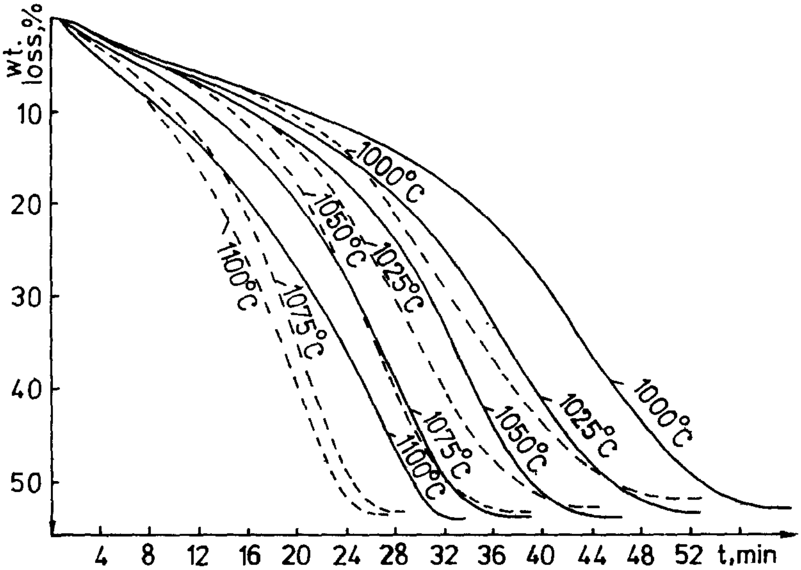

Fig. 2. TG curves of phosphogypsum at various temperatures and gas atmosphere: ---4%CO, 10%CO_2, 86%Ar;—4%CO, 20%CO_2, 76%Ar.

CONCLUSIONS

The present study has shown that the rate of phosphogypsum decomposition and activation energy vary considerably with temperature and P_{CO_2}.Carbon dioxide inhibits the process,but mainly it affects the reaction to CaS.At 1100°C under gas atmosphere 4%CO, 20%CO_2 and 76%Ar proceeds only the reaction to CaO.Dependence of r_{max} on temperature at different partial pressures of CO_2 shows a maximum at 1075°C which is 125°C lower than for natural gypsum, due to the difference of impurities and crystal origin.In comparison with our previous studies in gas phase CO-Ar the diffusion becomes rate determining in the presence of CO_2 at higher temperatures.

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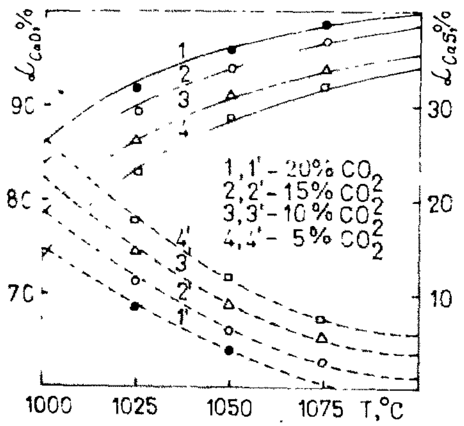

Fig. 3.Degree of decomposition to CaO(——) and CaS(---) in gas atmosphere: 4%CO,5-20%CO_2 and Ar

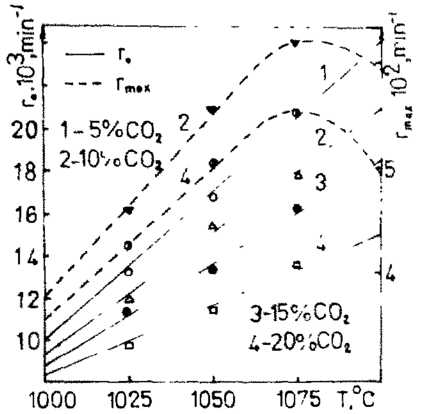

Fig. 4.Dependence of $r_{•}$ and r_{max} on the temperature and gas atmosphere: 4%CO,5-20%CO_2 and Ar