Journal of Thermal Analysis, Vol. 32 (1987) 1739–1742

AN INVESTIGATION ON THE EFFECTS OF ADDITIVES DURING THE THERMOCHEMICAL DECOMPOSITION OF PHOSPHOGYPSUM UNDER ISOTHERMAL CONDITIONS

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A study was made of the isothermal kinetics of phosphogypsum in the presence of additives and in a reducing gaseous medium.

Reduction of the energy consumption in the process of thermochemical decomposition of $CaSO_4$ to calcium oxide and sulphur dioxide by the introduction of intensifying additives is the subject of various investigations [1, 2]. The effective action of some additives under dynamic heating conditions in a reducing gaseous medium has been established [3].

Experimental

The investigations were carried out in a high-temperature Shimadzu thermogravimetric system [4] in the temperature range 950–1100°, with a gaseous medium containing 1% H_2 and 99% Ar, a puring gas flow rate of 20 l/h, a sample weight of 15 mg, and a phosphogypsum particle size below 0.1 mm. Calcium chloride and pitch in quantities corresponding to 0.4 and 1 wt.% of the mixture were used as intensifying additives. The pitch was a waste product from the sulphuric acid regeneration of motor oils. The degree of decomposition of samples [2] was determined as a function of time (t) through the equation $\alpha = \Delta G_t/\Delta G_c$, using the recorded thermogravimetric dependences, where ΔG_t = change in mass of the sample after time t, and $\Delta G_c = t$ change in mass of the sample after complete decomposition of phosphogypsum.

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Results and discussion

The thermogravimetric curves presented in Fig. 1 reveal that the change in mass of the phosphogypsum samples with 0.4% $CaCl_2$ and 1% pitch additives (*G*) at 975° has a better linear character, and the time needed for their complete decomposition is much less in comparison with that for phosphogypsum samples without an additive (*PG*).

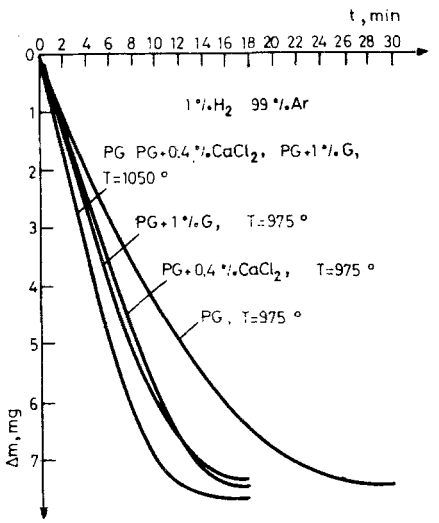

Fig. 1 The change of mass of phosphogypsum samples with and without additives as a function of time at different temperatures

At temperatures above 1025°, the thermogravimetric curves for phosphogypsum samples with and without additives coincide, which shows that $CaCl_2$ and pitch accelerate the process only in the range of lower temperatures, 950–1025°.

The kinetic analysis carried out revealed that the kinetic expression for the process of thermochimical decomposition of phosphogypsum is fitted by the equation of Polany–Wigner. Figure 2 presents the dependences of the rate constant of the process on the temperature for the various samples.

It is seen from the Figure that at a temperature of about 1000° there is a deviation from linearity, as the rate constant changes insignificantly at the higher temperatures. The fact that the additives studied intensify the process only up to 1000° demonstrates that for this range of temperatures the process proceeds under kinetic conditions, as the values obtained for the corresponding apparent energies of activation are 203 kJ/mole for phosphogypsum (PG), 185 kJ/mole for PG with 0.4% $CaCl_2$ added, and 154 kJ/mole for PG with 1% pitch added. At temperatures

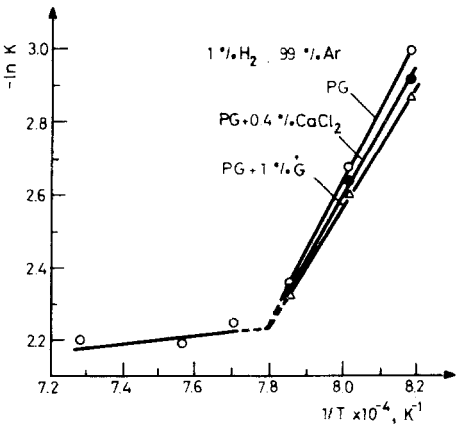

Fig. 2 The rate constant as a function of temperature in Arrhenius coordinates

higher than 1000° a change of mechanism takes place, as the hydrogen diffusion through the layer of the solid product formed, CaCO, becomes rate-determining.

The investigated additives have an effect both on the kinetics of the process and on the content of CaS in the final product of phosphogypsum decomposition. Figure 3 reveals that the effect of the additives is manifested by a decrease of the CaS content in the solid product, which is most markedly exhibited for the range of temperatures 950–1000°.

It should be pointed out as a general regularity that the content of CaS for the samples and conditions investigated decreases when the temperature is raised, but it

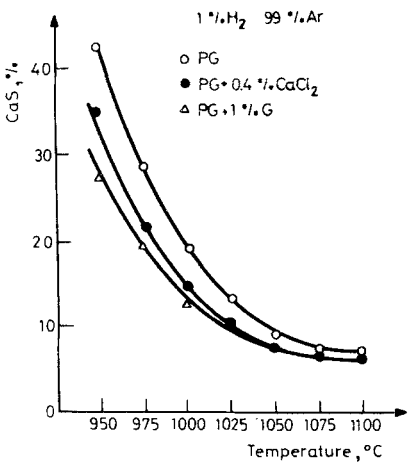

Fig. 3 CaS content in the final product as a function of additives

does not disappear completely even at as high a temperature as 1100°. Consequently, the additives studied accelerate predominantly the reaction of interest in the temperature range 950–1000°.

References

1 A. M. Ginstling and A. D. Volkov, Zh. Prikl. Khim., 33 (1960) 274.
2 L. I. Kiknadze, M. G. Chubiashvili and A. D. Volkov, Soobst. A. N. Georg. SSR, 65 (2) (1972) 369.
3 Iv. Gruncharov, Y. Pelovski, Pl. Kirilov and I. Dombalov, Effect of Some Additives on the Thermochemical Decomposition of Phosphogypsum, Gypsum Lime (in print).
4 Iv. Gruncharov, Y. Pelovski, I. Dombalov and N. Videnov, Scientific Technical Conference with international participation, "Mineral Fertilizers—production and application", Varna, Bulgaria, 11–13, Sept. 1982.

Zusammenfassung — Es wurden ısotherme kinetische Untersuchungen an Phosphogips in Gegenwart von Zusätzen sowie ın reduzierender Atmosphäre durchgeführt.

Резюме — Проведено изучение изотермической кинетики разложения фосфогипса в газообразной восстанавливающей среде и в присутствии добавок.