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EFFECTS OF SOME ADMIXTURES ON THE DECOMPOSITION OF CALCIUM SULPHATE

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The by-product phosphogypsum contains $CaHPO_4$, H_3PO_4, $Ca_5(PO_4)_3F$, Al_2O_3, Fe_2O_3, SiO_2 etc. besides the main product $CaSO_4$. By means of TG–DTA the thermochemical decomposition of pure phosphogypsum and phosphogypsum containing CaO, Al_2O_3, Fe_2O_3 and SiO_2 in a reductive atmosphere was studied. The solid phase was examined by high-temperature thermomicroscopy, scanning electronmicroscopy, X-ray diffraction and other methods. It could be confirmed, that most of the admixtures undergo secondary reactions with CaO and CaS, modifying the decomposition rate of $CaSO_4$.

The reductive thermochemical decomposition of $CaSO_4$ leads to a solid product containing three separate phases: calcium sulphate, calcium oxide and calcium sulphide. Both natural gypsum and phosphogypsum (PHG), a waste product in the production of phosphoric acid, contain various admixtures: SiO_2, Fe_2O_3 and Al_2O_3. PHG is also characterized by some specific admixtures of phosphoric and fluorine compounds [1, 2]. It has been established (1–4] that the admixtures exert considerable effects on the kinetics and mechanism of the thermochemical decomposition of $CaSO_4$, as well as on its thermal stability. While some of the admixtures have a promoting action, others inhibit the process [4]. At the same time, a decreased thermal stability was found in many cases, associated with changes in the phase state of the system [2, 4], which influences the process engineering requirements.

The present paper reports a study of the changes in structure of some two-, three- and four-component systems formed during the thermochemical decomposition of natural gypsum or PHG, by the method of high-temperature optical microscopy.

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Experimental

Various mixtures of pure $CaSO_4$ or PHG with CaO, Fe_2O_3, Al_2O_3, kaolin and natural phosphates were studied by differential thermal analysis with a Q-1500 D derivatograph (MOM), coupled with an automatic Uras 7N SO_2 gas analyser (Hartmann-Braun). The sample weight was 180 mg and the purging gas consisted of 4% H_2 +96% Ar with a flow rate of 500 cm^3 min^{-1}. The CaO, CaS, Fe_2O_3, SiO_2 and Al_2O_3 were reagent grade chemicals, and the PHG used was from an industrial installation for the production of phosphoric acid from North-African phosphorites. The PHG was subjected to preliminary heating at 500°. It was characterized by the following composition: 38.6% CaO, 54.7% SO_3, 1.5% SiO_2, 0.7% P_2O_5, 0.7% Fe_2O_3, 0.4% Al_2O_3, 0.2% F and 0.2% MgO. The same mixtures were also studied with a high-temperature optical microscope (Leitz) equipped with a photosystem. The purging gas flow rate was 83 cm^3 min^{-1} and the sample weight was 10 mg. All experiments were carried out at least in the temperature range 20-1200°, and for some samples up to 1350°. The state of the system was photographed at 20, 500, 900, 1000, 1050, 1100, 1150 and 1200° during the processes of heating and cooling. At 1000, 1100 and 1200°, an isothermal regime was maintained for a period of 30 min.

Some of the solid end-products obtained were subjected to electronic, X-ray diffraction and chemical analysis.

Results and discussion

Heating of PHG at a rate of 7.5 deg min^{-1} in a reducing gaseous medium containing 4% H_2 (Fig. 1) causes a 52.5% decrease of the mass, which verifies that the main component of PHG ($CaSO_4$) decomposes almost completely to CaO and CaS. This process takes place in the temperature range 930-1135°, with the maximum rate at 1060°. The considerable endothermic effect and the increased SO_2 concentration in this temperature range confirm this mechanism. In the temperature range 600-930°, the initial mass loss and the thermal effects are associated with the partial reduction of $CaSO_4$ to $CaSO_3$ and CaS.

The addition of Fe_2O_3, Al_2O_3 and SiO_2 to PHG results in changes in both the thermogravimetric and the DTA curves. Figure 2 shows a clearly expressed two-stage process, partial $CaSO_4$ reduction to CaS (T = 702-810°) and the subsequent complete conversion of $CaSO_4$ to CaO and SO_2, in the DTA curves relating to added CaO, Al_2O_3, Fe_2O_3 and SiO_2. The end-product contained only traces of CaS, which shows that it interacts with $CaSO_4$ in the temperature range 908-1085° to yield CaO and SO_2. As pointed out recently [4, 5], CaO reacts with the added

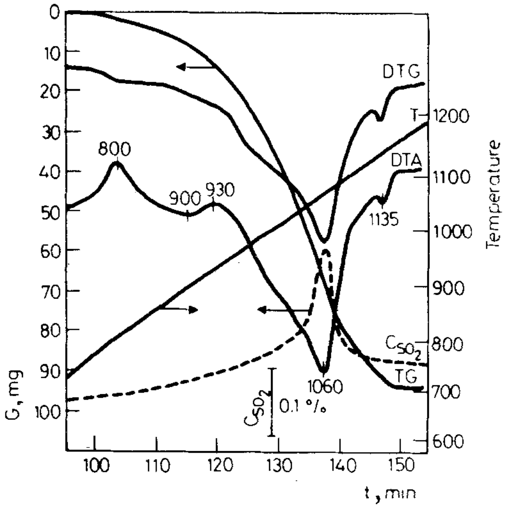

Fig. 1 DTA and C_{SO_2} curves of PHG

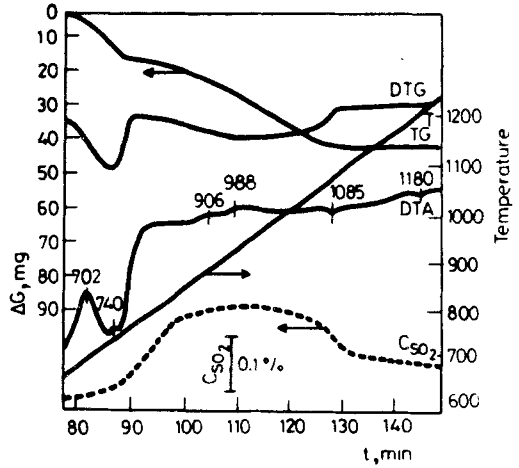

Fig. 2 DTA and C_{SO_2} curves of mixture (28% PHG + 42% CaO + 10% Al_2O_3 + 10% Fe_2O_3 + 10% SiO_2

oxides to form ferrites, aluminates and aluminosilicates. In the present studies this was proved by the X-ray phase and electron microscopic analysis of the solid end-products (Fig. 3). The changes proceeding in the solid phase of various mixtures of $CaSO_4$ or PHG in the temperatures range 20–1200° and in an inert or reducing atmosphere, recorded by high-temperature microscopy, are shown in part in Fig. 4. At 950–1000°, the appearance of small rounded crystals typical of CaO was

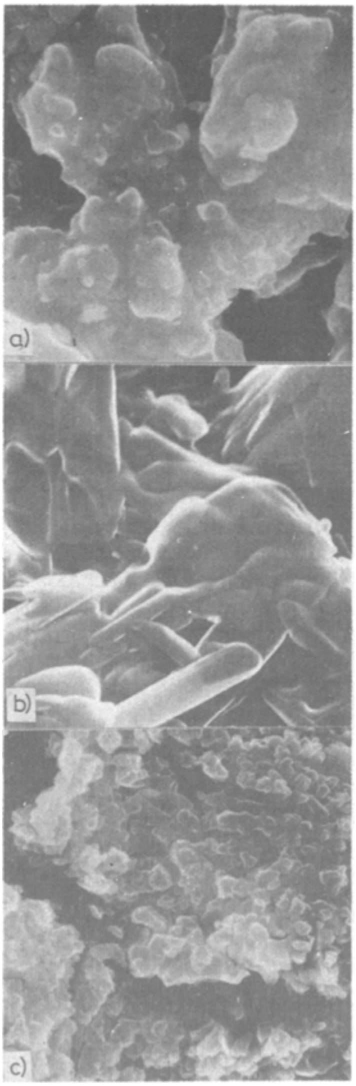

Fig. 3 SEM-photos of solid product after decomposition of × 650:
a) 28% PHG + 42% CaO + 10% Fe_2O_3 + 10% Al_2O_3 + 10% SiO_2, b) PHG + 5% kaolin, c) PHG + 10% Phosphorite

observed for the system $CaSO_4$–CaS in an inert atmosphere. At the same time, the crystal aggregates were destroyed to give a set of smaller crystals. A similar phenomenon was characteristic for all systems in Fig. 4 in a reducing medium or at a higher content of CaS in the initial mixture. At lower $CaSO_4$ and CaS contents

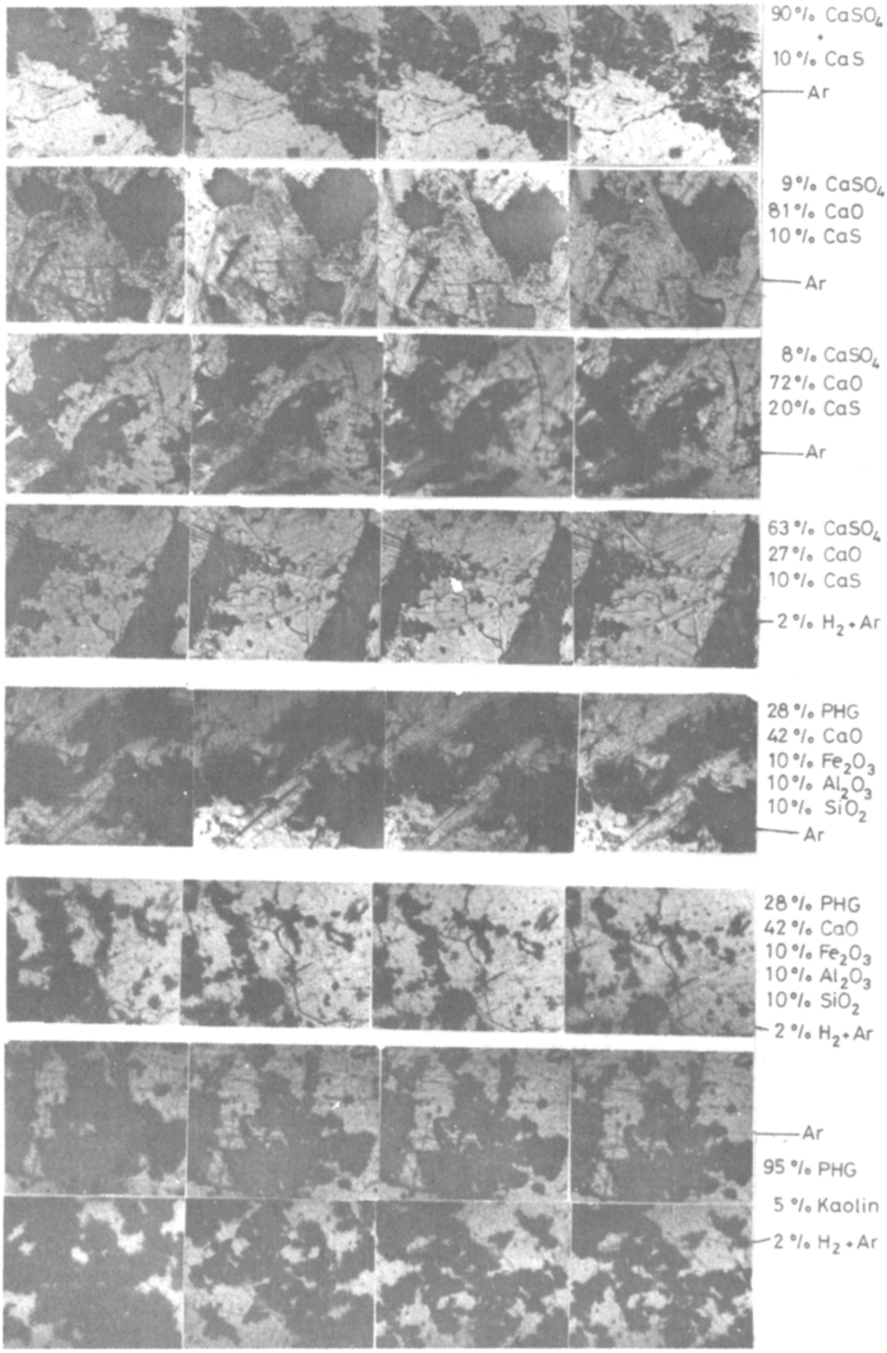

Fig. 4 HTM photos at temperatures 20, 1000, 1100 and 1200 °C of mixtures in Ar or 2% H_2 + Ar atmosphere

(9–10%) in the system $CaSO_4$–CaO–CaS, a lower thermal stability was established, with an onset of eutectic zone formation starting at 1000° (Fig. 4). Similar melting was observed for PHG mixtures containing 42% CaO, 10% Fe_2O_3, 10% Al_2O_3 and 10% SiO_2 in an Ar medium.

Conclusion

The investigations confirmed the strong effects of admixtures of Fe_2O_3, SiO_2 and Al_2O_3 on the kinetics of decomposition of $CaSO_4$ and PHG. Heating to 950–1000 °C results in the formation of eutectic zones depending on the composition of the gas phase. In the system $CaSO_4$–CaO–CaS, similar eutectic compositions exist when the contents of $CaSO_4$ and CaS are about 10%. The additives considerably change the crystal structure and the phase composition of the end-product.

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Zusammenfassung — Das Abfallprodukt Phosphatgips enthält neben dem Hauptbestandteil $CaSO_4$ noch $CaHPO_4$, H_3PO_4, $Ca_5(PO_4)_3F$, Al_2O_3, Fe_2O_3, SiO_2 und anderes. Die thermochemische Zersetzung von Phosphatgips bzw. Phosphatgips mit Zusätzen von CaO, Al_2O_3, Fe_2O_3 und SiO_2 wurde in reduzierender Atmosphäre mittels TG–DTA untersucht. Die feste Phase wurde durch Hochtemperatur-Thermomikroskopie, Rasterelektronenmikroskopie, Röntgenbeugung und andere Methoden untersucht. Dabei wurde bestätigt, dass die meisten Beimengungen mit dem Calciumoxid bzw. -sulfid Sekundärreaktionen eingehen, wodurch auch die Zersetzungsgeschwindigkeit des $CaSO_4$ beeinflusst wird.

Резюме — Фосфогипс, кроме основной компоненты сульфатш кальция, содержит побочные продукты $CaHPO_4$, $Ca_5(PO_4)_3F$, Al_2O_3, Fe_2O_3, SiO_2 и другие. С помощью ТГ—ДТА изучено термохимическое разложение в восстановительной газовой атмосфере чистого фосфогипса и фосфогипса, содержащего оксиды кальция, железа, алюминия и двуокись кремния. Твердые фазы жыли исследованы методом высокотемпературной микроскопии, сканирующей электронной микроскопии, рентгенофазовым анализом и другими методами. Подтверждено, что большинство примесей подвергается вторичным реакциям с окисью и сульфидом кальция, изменяя тем самым скорость разложения сульфата кальция.