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THE INFLUENCE OF GUDRON ADDITIVE ON THE STRUCTURE OF THE SOLID PHASE FROM THE THERMAL DECOMPOSITION OF PHOSPHOGYPSUM

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ABSTRACT

The thermochemical decomposition of phosphorite phosphogypsum in the presence of Gudron additive, was investigated by TG, electron microscopy (TEM and SEM), X-ray diffraction and chemical analysis.

INTRODUCTION

The influence of the additives of 0,4% $CaCl_2$, 5% $(NH_4)_2SO_4$ and 5% $CO(NH_2)_2$ on the microstructure of the solid phase products from the thermochemical decomposition of phosphorite phosphogypsum /PPG/ in a reducing atmosphere and in the atmosphere of argon was established in our previous investigations /1,2/. The results obtained by a transmission and a scanning electron microscopy correlated with the data of the X-ray phase analysis, the chemical analysis and the values of the specific surfaces. In this way, the enhanced effectivity of the process of thermochemical decomposition of PPG in the presence of some of the mentioned additives-activators regarding the microstructure of the initial and of the final products was explained.

The present work is a part of this cycle of investigations. It aims to explain the mechanism of action of the gudron additive on the thermochemical decomposition of phosphorite phosphogypsum.

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EXPERIMENTAL

The object of this investigation as in our previous works /3-6/, is phosphogypsum obtained from the processing of North-African phosphorites to phosphorus acid. The thermochemical decomposition is carried out on a thermogravimetric installation /4/ in a reducing atmosphere (2-5% H_2 + 98-95% Ar) or in an inert atmosphere of argon where the flowing gas is saturated with vapour. The electron-microscopy (TEM and SEM), the X-ray phase analysis and the chemical analysis have been the basic methods for investigation and analysis of the solid phase. The specific surface of the intermediate products and the final solid products were determined.

The apparatus and the methods applied were discussed in earlier work /1 and 2/

RESULTS AND DISCUSSION

Gudron essentially differs from the additives-activators used up to now. It is an industrial waste from the regeneration of white oil, thus, it contains 60% heavy organic fractions, 20-28% sulphuric acid and inorganic residuals, etc.

Fig.1 gives data about the specific surface depending on the temperature and the thermal treatment of PPG without additive as well as of PPG with additive of 5% of gudron in an inert and in a reducing atmosphere. The values of the specific surface for gudron and more of the additives /1,2/ have high maximum which is at $\sim$ 400°C in a reducing atmosphere, at $\sim$ 500°C in the atmosphere of argon. Both maximal values: 10,38 m^2/g and 14,40 m^2/g are by 1,4 - 1,9 times higher than the maximal values of the specific surfaces obtained for the other activators /1,2/. A sharp decrease of the specific surfaces appears at

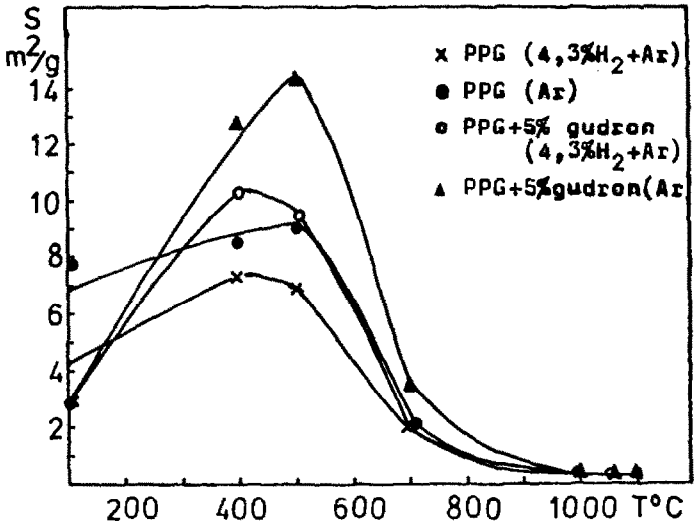

Fig.1. Change of the specific surface of PPG without additives and PPG + 5% of gudron treated thermally in inert and in a reducing atmosphere

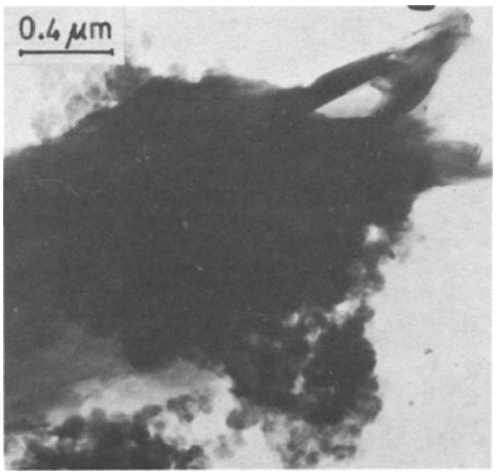

Fig.2. TEM-view (transmission electron microphotography, direct observation) oa sample of PPG + 5% of gudron without thermal treatment; x 37 500

1000°C. The specific surface does not change practically in the temperature range of 1000 - 1100°C.

Evident changes of the colour and the volume of the solid phase at the thermochemical decomposition of PPG with 5% of gudron which the other activators do not exhibit, are observed here. Mixtures are grey before the thermal treatment under the influence of gudron. The binding action of gudron is weak and the granules have low mechanical strength up to the treatment temperature of 1000°C. The granules become solid and stable to destruction after this temperature; their volume decreases and the colour turns brown depending on the content of a reductor in the reducing atmosphere.

The X-ray phase analysis of PPG with gudron activator treated at 500°C in a reducing atmosphere shows the presence of the anhydride form of calcium sulphate - anhydrite II. Diffraction maximums of anhydrite II, CaO and $Ca(OH)_2$ at 1100°C in a reducing atmosphere are observed. Decomposition of PPG at 1100°C in the atmosphere of argon is not observed.

The electron-microscope analysis of solid products from the thermal treatment of PPG with gudron activator shows the presence of some structures more different from those of the other activators. Surfaces and fragments of gudron, powder samples obtained after grinding of the granules were observed as well.

Fig. 2 represents a microphotograph of a PPG sample with 5% of gudron without thermal treatment. The observations are directly over powder prepared after grinding of the granules. Gudron is completely safe and forms a layer where the powder particles are kept.

The structure of the gudron granules is very complicated at low temperature, e.g. 100°C: they are conglomerates of crystals and dehydrate, semi-hydrate and anhydrite III pertaining to the monoclinical,

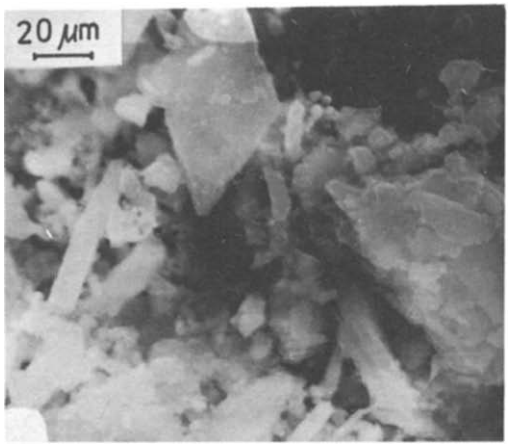

Fig.3.SEM-view (scanning electron microphotograph) of a sample of PPG+5%gudron treated thermally at 100°C in an inert reducing atmosphere; x 500

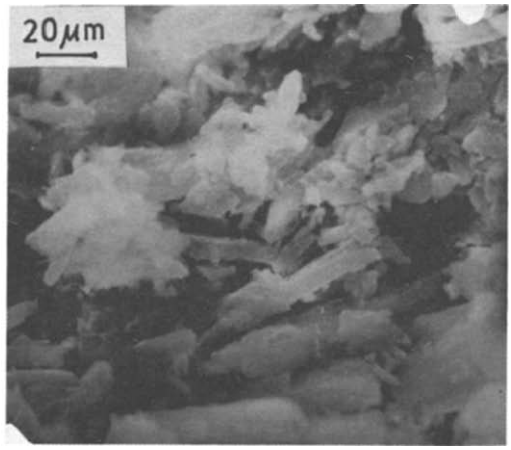

Fig.4.SEM-view of a sample of PPG+5% of gudron treated thermally at 500°C in an inert reducing atmosphere; x 500

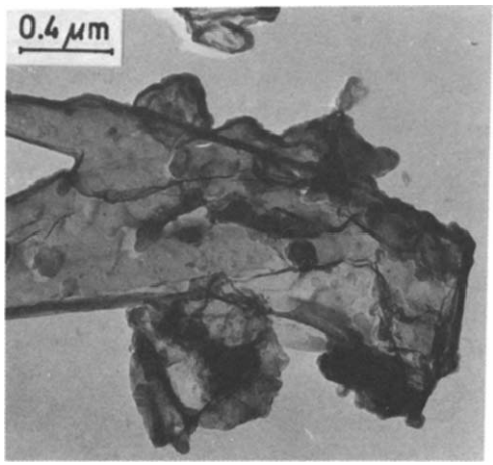

Fig.5. TEM-view (replic) of a sample of PPG + 5% of gudron treated thermally at 1050°C in a reducing atmosphere; x 37 500

hexagonal and the triclinic syngonia. Some of these crystals have irregular forms /Fig.3/ due to pressing. The irresolved gudron is to be found in some areas on the surface in the form of dark, formless spots.

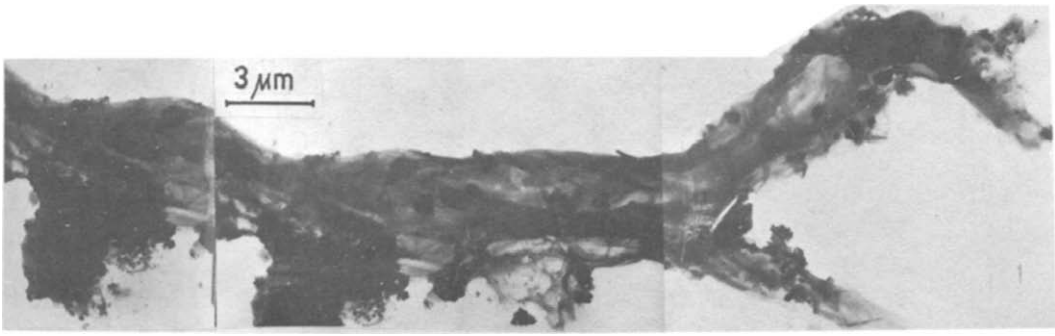

Fig.6. TEM-view (direct observation) of a sample of PPG + 5% of gudron treated thermally at 1100°C in a reducing atmosphere; x 4 500

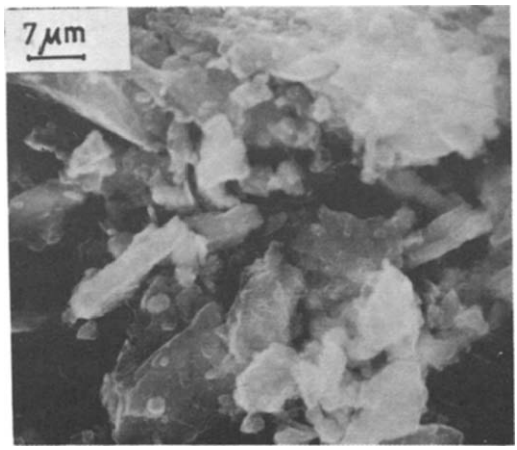

Fig.7. SEM-view of a sample of PPG + 5% of gudron treated thermally at 1100°C in a reducing atmosphere; x 1 500

The main part of calcium sulphate turns into anhydrite II at 500°C. The electron-microscope view of a fragment of the granule shows small residuals of dihydrate and semi-hydrate with vague forms /Fig.4/ which are not seen at the X-radiography. The elongated crystals of anhydrite II /Fig.4/ are clearly seen.

When the decomposition of PPG with 5% of gudron activator already takes place at 1050°C, crystal phases of $CaSO_4$ and CaO are observed. Usually, the larger elongated crystals from $CaSO_4$ with the size of 2-3μ are fundamental for the newly formed rounded small crystals of CaO with the size of 0,05μ /Fig.5/. The microquantities of gudron residuals, such as a layer which carry and embrace part of the small crystals of $CaSO_4$ and CaO are observed at 1050°C even at 1100°C. A series of microphotographs in Fig. 6 illustrate exactly such a layer surrounded by elongated $CaSO_4$ crystals and CaO monocrystals /the sample is powder of ground granules/.

The results from the scanning electron-microscopy are similar /Fig.7 /. Evidently, the good adhesion of gudron is a prerequisite for a more active diffusion of some of the inorganic solid elements and the obtained reducing gas components of gudron in the subcrystal and intercrystal structure of phosphogypsum. Most probably, the defects in the structure of phosphogypsum together with the simultaneous decrease of the partial pressure of oxygen inside the granules,determine the registered lower temperature of initiation of thermochemical decomposition and higher velocity constants at comparatively lower temperatures.

CONCLUSION

The results from the analysis of the microphotographs (TEM and SEM) of the solid products (granule surface, fragment from the inside of the granule, powder from ground granules) of phosphorite phosphogypsum with 5% of gudron activator treated thermally at different

temperatures together with the data from the X-ray phase analyses and the chemical analysés explain some aspects of the mechanism and the microkinetics of the process of thermochemical decomposition of phosphorite phosphogypsum. They confirm the existing correlation between the microstructure of the initial, the intermediate and the final products with their composition and specific surface, as well as the kinetical effectivity of the process of thermochemical decomposition of phosphogypsum.

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