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EFFECT OF P_2O_5 CONTENT IN PHOSPHOGYPSUM ON ITS THERMAL DECOMPOSITION TO CaCO AND SO_2

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The effect of P_2O_5 on the thermal decomposition of phosphogypsum to phospholime and sulphur dioxide has been studied.

During the production of phosphoric acid, chemical gypsum is obtained, known as phosphogypsum due to the inevitable content of phosphorus. The phosphorus content in the phosphogypsum, estimated as P_2O_5, is mostly within the limits 0.4 to 2.0%. This constant admixture has a very significant effect on the selection of the phosphogypsum processing and on the optimizing of the selected process [1, 2].

The experimental samples, consisting of mixed $CaSO_4$ and P_2O_5, were subjected to thermal treatment by the procedures and under the conditions described previously [3]. Different phosphorus-containing raw materials and products were applied, as P_2O_5 in phosphogypsum results from undecomposed phosphates and from the incomplete washing off of P_2O_5 during filtration. Table 1 presents the compositions of the samples and the thermal treatment conditions. After treatment, the samples were subjected to X-ray and infra-red spectroscopic analysis. The X-ray phase analysis was carried out using a TUR–MG1 diffractometer with CuK_α radiation, with a Ni-filter. The resulting X-ray diagrams are shown in Fig. 1.

For thermally treated mixtures of $CaSO_4$ and natural phosphates in a reducing atmosphere at 1150°, besides the main phases of $CaSO_4$–II and CaO, the presence of a small quantity of calcium pyrophosphate $Ca_2P_2O_7$ was identified. With sample C–14.3.0, containing a mixture of $CaSO_4$ and 5% P_2O_5 as apatite, the presence of $2CaO \cdot P_2O_5$ was shown by lines with $d = 3.186$, 3.079, 2.814, 2.714, 2.629 and 1.698 Å. The presence of dicalcium phosphate in sample C–17.3 *a*, consisting of mixed $CaSO_4$ and 5% P_2O_5 as phosphorite, was demonstrated by lines with $d = 3.176$, 3.079, 2.783, 2.629 and 1.725 Å.

When $CaSO_4$ mixed with P_2O_5 as $Ca(H_2PO_4)_2 \cdot 2H_2O$ and the sample (C–28.3.*d*) was treated thermally in a reducing medium at 1150°, the existence of a new phase, $3CaO \cdot P_2O_5$, was evidenced by lines with $d = 4.084$, 3.440, 3.198, 2.909, 2.780,

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Table 1 Investigated samples of $CaSO_4 + 5\%\ P_2O_5$ and conditions of their thermal treatment

Sample	P_2O_5, as	*T* of treatment, °C	Time of treatment, min	Gas medium, %
C–14.3.*a*	Apatite	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.8$ Ar
C–17.3.*a*	phosphorite	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.8$ Ar
C–28.3.*a*	$Ca(H_2PO_4)_2 \cdot 2H_2O$	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.8$ Ar
C–31.2.*a*	$CaHPO_4 \cdot 2H_2O$	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.4$ Ar
C–34.2.*a*	H_3PO_4	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.8$ Ar
B–6	H_3PO_4	1150	60	$3.2\,H_2 + 12\,CO_2 +$ $+ 84.8$ Ar

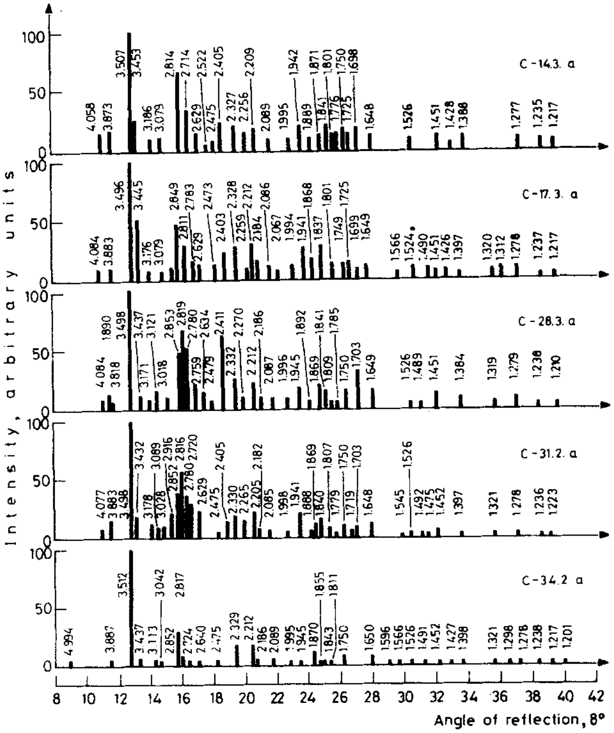

Fig. 1 Röntgenograms of different samples of the system $CaSO_4$—P_2O_5

2.634, 2.270, 2.212, 1.892, 1.785 and 1.750 Å, along with the presence of $2CaO \cdot P_2O_5$. The quantity of dicalcium phosphate was greater, as observed from a comparison of the most intense lines—2.819 and 2.909 Å.

When P_2O_5 was added to $CaSO_4$ as $CaHPO_4 \cdot 2H_2O$ and the sample (C–31.2.*a*) was treated therminally at 1150° in a reducing medium, the presence of $2CaO \cdot P_2O_5$ was evidenced along with $3CaO \cdot P_2O_5$. The quantity of $2CaO \cdot P_2O_5$ was approximately equal to that of $3CaO \cdot P_2O_5$, as shown by the equal intensities of the lines at 3.062 and 2.874 Å.

With sample C–34.2.*a*, in which the quantity of P_2O_5 was equal to that in the previous samples but was introduced as H_3PO_4, the quantity of $3CaO \cdot P_2O_5$ was considerably greater than that of $2CaO \cdot P_2O_5$, as evidenced by its plentiful line spectrum and the higher intensity of the lines.

The presence of the phases $2CaO \cdot P_2O_5$ and $3CaO \cdot P_2O_5$ was established after the thermal treatment of sample B–6 in an inert atmosphere, which suggests that

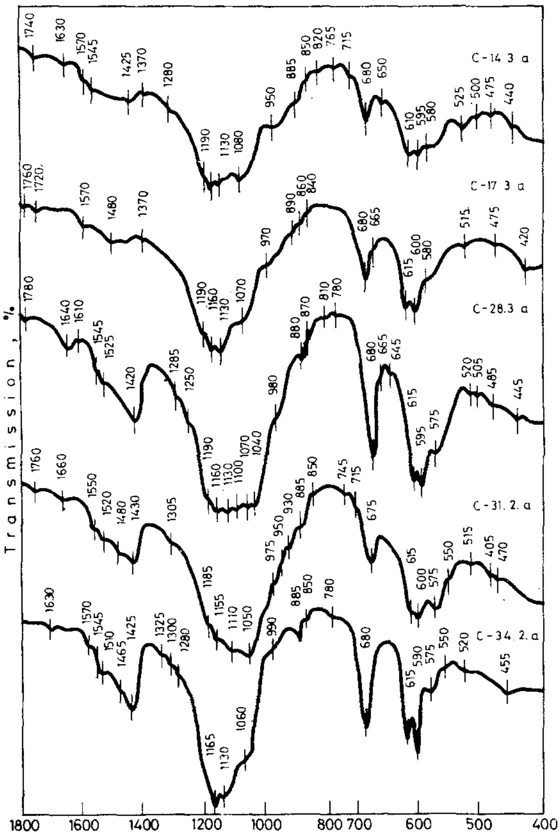

Fig. 2 Infrared spectra of different samples of the system $CaSO_{42}O_5$

their formation is dependent on the temperature rather than on the gaseous medium in the process of thermal decomposition.

The data from the infra-red spectroscopic (Fig. 2), recorded with a UR–10 (Karl Zeiss) double-beam spectrophotometer applying KBr tablets, confirm the X-ray phase analysis information. The infra-red absorption spectra of the samples investigated, along with the characteristic absorption bands of the insoluble anhydride, reflect the absorption bands of the new phases, which are not very distinct, but still indicative of CaO and $Ca(OH)_2$. The absorption bands for $3CaO \cdot P_2O_5$ for samples treated in a reducing medium are particularly clear and readily identified.

The X-ray diagrams and the spectrograms of the different samples exhibit great differences in spectra and line intensities, both for the prepared phosphate, and the $CaSO_4$–II, and the CaO and $Ca(OH)_2$ resulting from the thermochemical decomposition of $CaSO_4$ to CaO and its interaction with P_2O_5 to different phosphates. As concerns the different P_2O_5 admixtures in waste phosphogypsum from quantitative and qualitative aspects, the corresponding optimum conditions of phosphogypsum decomposition need to be selected. This would ensure the stability and reliability of the technological processes and the high quality of the produced phospholime, allowing its application in different branches of the national economy.

References

1 I. Gruncharov, G. Bechev, I. Dombalov, P. Kirilov and Y. Pelovski, Trudy NIUIF, 243 (1983) 38–44.

2 V. Borisov, N. Videnov, N. Solodyankina, I. Dombalov, V. Skorobogatov, A. Ivanov and P. Kirilov, Khimicheskaya Promishlenost, 9 (1982) 29–30.

3 I. Gruncharov, G. Bechev, I. Dombalov and Y. Pelovski, Reports of "First National Conf. in Chemistry", November 26–28, Sofia, 1985.

Zusammenfassung — Es wurde der Einfluß von P_2O_5 auf die thermische Zersetzung von Phosphogips zu Phospholim und Schwefeldioxid untersucht.

Резюме — Изучено влияние пятиокиси фосфора на термическое разложение фосфогипса до фосфолима и двуокиси серы.