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PHASE TRANSITIONS IN TRIBOCHEMICALLY ACTIVATED NATURAL PHOSPHATES

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ABSTRACT

Kola apatite was ground in a planetary mill in the presence of additives and structural changes after the mechanochemical activation were examined by electron microscopy supplemented by DTA, IR and X-ray diffraction. The mechanochemical activation led to increase in defects in the apatite crystals and of apatite reactivity.

INTRODUCTION

Mechanochemical methods can be used for the production of phosphorus fertilizers from various natural phosphates [1, 2]. In such a way the problem of shortages of sulfuric and phosphoric acids may be partly solved. At the same time the mechanochemical activation of the raw phosphates increases the P_2O_5 content which can be utilized and the reactivity of the phosphates. It is known that the rate of the mechanochemical activation of solid materials is strongly dependent on the milling equipment, the medium, the additives and the time of treatment. The subject of this work is the mechanical and mechanochemical activation of apatite by the use of a planetary mill.

EXPERIMENTAL

As raw material Kola apatite with particle sizes 0.4 -0.071 mm and 39.4 wt% P_2O_5 was used. As additives pure NH_4NO_3, $CO(NH_2)_2$, $(NH_4)_2SO_4$ and KCl were used.

The process of mechanochemical treatment was carried out using a Fritsch planetary mill. The sample weight was 50 g while the reaction volume was 550 cm^3, and the grinding time - 15, 30, 60, 120 and 240 min.

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The structure changes of apatite after mechanochemical activation were studied by using DTA, X-ray (TUR M-61 apparatus using $Cu_{K\alpha}$ radiation and equipped with a Ni-filter), IR and especially EM techniques (using "Jeol" JEM-100 C and "Philips" EM-301 G electron microscopes). The reactivity of apatite was determined by chemical analysis of P_2O_5 in the solid and liquid phase, produced by decomposition of the activated samples with sulphuric acid (30% H_2SO_4). Specific surface area was measured using a "Sigma 28" Perkin Elmer gas chromatograph.

RESULTS AND DISCUSSION

The data obtained confirmed that reactivity of apatite and the soluble P_2O_5 in it, is increased due to the mechanochemical treatment. After 240 min of grinding the specific surface area increases by more than four times. It is shown in Fig. 1 that the specific surface area is strongly dependent on the time of treatment and on the nature of the additives. These surface area changes are related to the dissolution of P_2O_5 in 0.05 N H_2SO_4 from the natural and activated phosphate samples, as shown in Fig. 2. In Fig. 3 the dependence of reactivity (R) is plotted against time. R is the ratio of reactivity of tribochemically activated and non-activated phosphates.

Most of the samples were studied by X-ray powder diffraction. It was found that after a 60 min treatment some of the characteristic strong lines of the natural phosphate disappeared and some new lines appeared. The d values of the new lines were as follows: 1,028, 594, 446, 329, 241, 208, 166, 154, 144 pm, while the most intense lines which disappeared were 514, 313, 287, 249, 205, 176, 173, 145 and 142 pm. It is obvious that the tribomechanochemical activation results in a crystal rearrangement. Such crystal changes were also confirmed by IR spectroscopy. For example, the sample containing 90 wt% apatite and 10 wt% NH_4NO_3 treated for 60 min, has an IR spectrum without absorption bands at 760, 830 and 1570 cm^{-1} typical for the initial mixture, but shows new bands at 970 and 1640 cm^{-1}. From this it can be concluded that as a result of the tribochemical treatment new crystal defects and a new solid state are produced.The TG-DTA lead to the same conclusions.

The particle size and morphological crystal structure changes according to the time of treatment were studied by TEM and SEM techniques. Some of the important electron microscope observations are shown in Figs 4-8. Fig. 4 shows the microstructure of raw

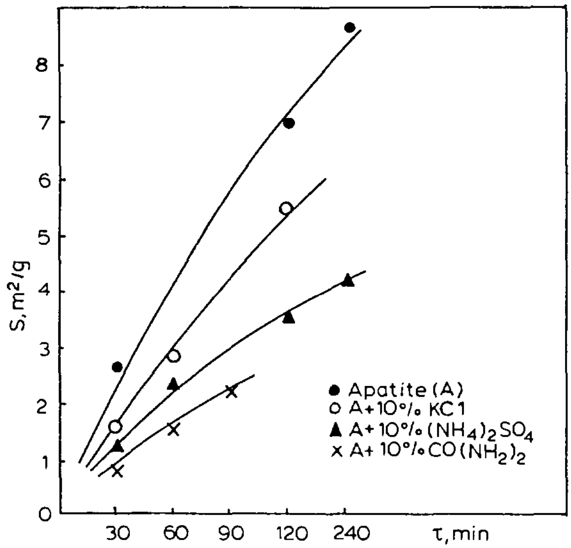

Fig.1. Dependence of specific surface area (S) on the time of treatment of Apatite and Apatite + additions

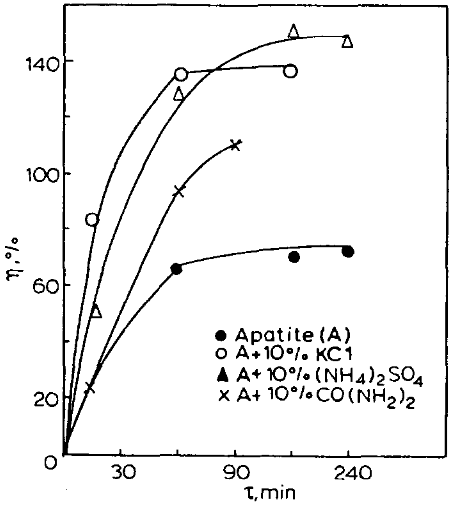

Fig.2. Rate of conversion of P_2O_5 insoluble to P_2O_5 soluble in 0.05 n H_2SO_4 (η) vs.time of treatment

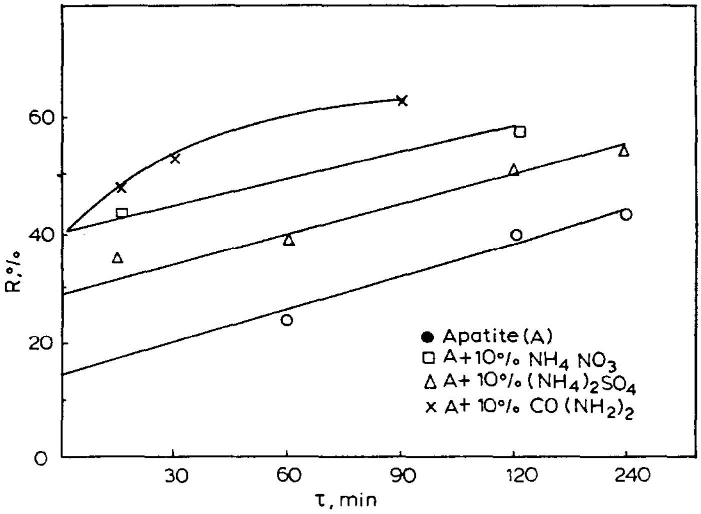

Fig.3. Reactivity (R) of Apatite and Apatite mixtures vs.time of treatment

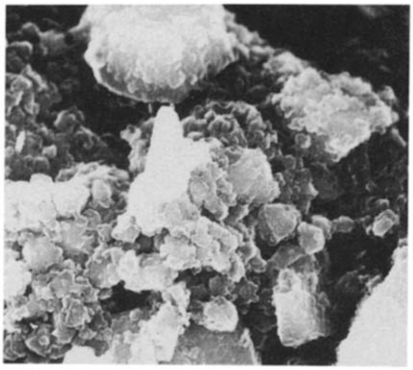

Fig.4. SEM photos of Apatite , x 1500

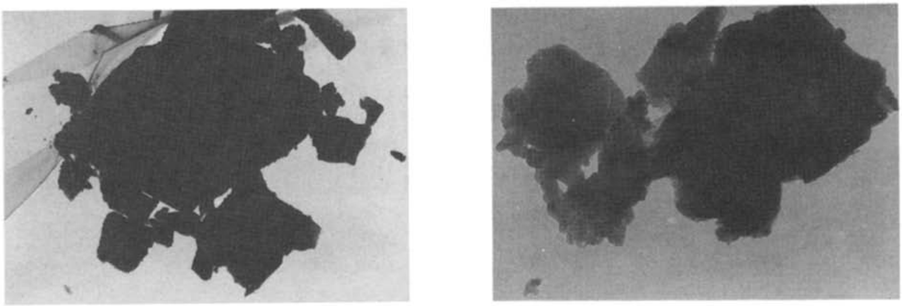

Fig.5. Transmission electron micrographs of Apatite+10%NH_4NO_3

a) x 2500 b) x 25000

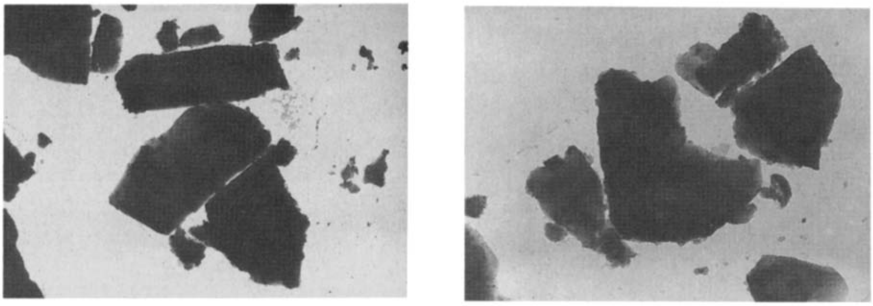

Fig.6. TEM photograph of Apatite + 10 % $CO(NH_2)_2$

a) x 9100 b) x 25000

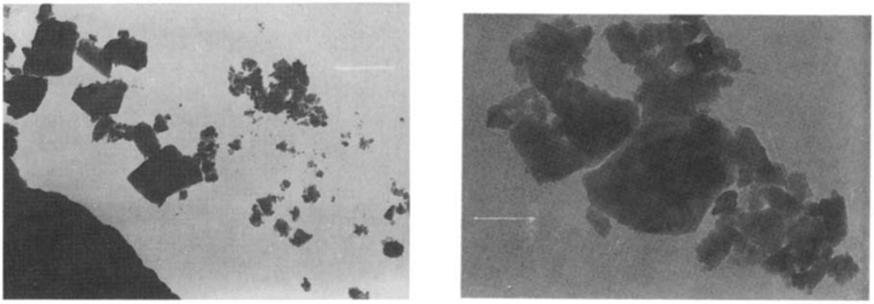

Fig.7. TEM photos of activated for 60 min Apatite + 10 % NH_4NO_3

a) x 9100 b) x 71000

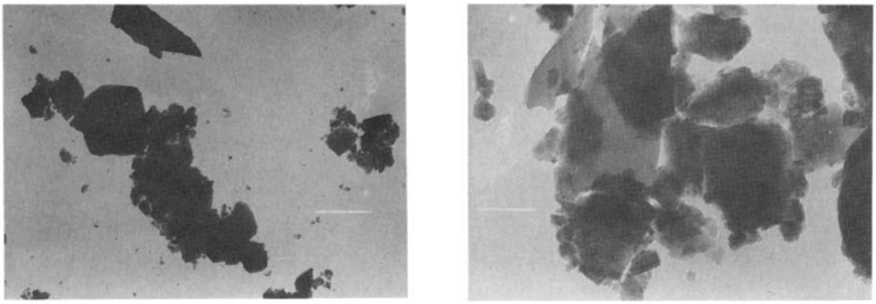

Fig.8. TEM photograph of 60 min activated mixture of Apatite + 10 % $CO(NH_2)_2$

a) x 9100 b) x 71000

apatite with no additives, while Figs 5 and 6 represent the initial mixtures of apatite and 10% NH_4NO_3 or 10% $CO(NH_2)_2$. As can be seen the particles are 0.05 to 2.0 μm in length and the apatite crystals have a hexagonal shape.

To show the effect of activation more clearly, the initial state of the mixture (Figs 4-6) can be compared with the same mixtures after 60 min. treatment (Figs 7-8). It is obvious that the particles decrease to 0.03 μm size and the crystal form has changed. At the same time the apatite crystals are more electron transparent because of size decrease and particle division. According to Bolderev et al. [3] and Chaikina et al. [4, 5] splitting during this treatment may take place in the plane [0001]. All these structural changes result in greater specific area and greater chemical reactivity of the natural Kola apatite.

CONCLUSIONS

Our investigations have shown that the structure of Kola apatite can be strongly affected by grinding in a planetary mill for 60 - 120 minutes. This effect differs in the presence of additives such as $CO(NH_2)_2$, NH_4NO_3, KCl, $(NH_4)_2SO_4$ etc. There is no uniform correlation between the specific surface area of the solid phase and its reactivity. The combination of physicochemical methods applied in our study did not provide clear information on the formation of new solid phases but did give much evidence of increase in defects and of apatite reactivity. The latter plays an important role in the manufacture of the natural phosphates and for this reason study in this field should be continued.

ACKNOWLEDGEMENT

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