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FORMATION OF LIQUID PHASE DURING HEATING CALCIUM DIHYDROPHOSPHATE AND PHOSPHATE ROCKS

Meeme Pyldme, Tallinn Polytechnic Institute, Tallinn,
U.S.S.R.

ABSTRACT

Solution formation in heating calcium dihydrophosphate and triple superphosphate granules in its own water evolved in dependence of conditions has been shown. Melting characteristics of the Karatau phosphorite by particle size and density, and recomendations for their calcination have been given. It was found that the phosphoric acid-thermal process of Kovdor apatite in a rotary kiln takes place with the participation of melt.

INTRODUCTION

Investigations were performed with the complex use of DTG, DTA, thermoelectrometry (conductance), X-ray phase analysis and scanning electron microscope. DTA and DTG analysis was carried out with the Derivatograph (Hungarian Optical Works), X-ray on a diffractometer DRON-05 ("Burevestnic", U.S.S.R.) and microscopic investigations on a "TESLA" instrument BS-300 (Czechoslovakia). The materials used were the reagent $Ca(H_2PO_4)_2 \cdot H_2O$, commercial granulated triple superphosphate (TSP), Karatau phosphorite and Kovdor apatite with addition of H_3PO_4. All these materials are connected with investigations of thermal processes: getting regulated solubility fertilizers, calcination of low grade phosphorites and producing defluorinated phosphatic feed supplement. $Ca(H_2PO_4)_2 \cdot H_2O$ crystals and phosphorites were heated by means of a derivatograph furnace. Thermal dehydration of TSP was provided in laboratory electrical and gas fluidized bed furnaces with variation of temperature ($200 \div 400^\circ C$) and heating time.

RESULTS AND DISCUSSION

It was found, that formation of the liquid phase (LP) during heating $Ca(H_2PO_4)_2 \cdot H_2O$ and TSP below the temperature of $550^\circ C$ had been directly connected with conditions of heating. Increasing electrical conductivity (EC) of the $Ca(H_2PO_4)_2 \cdot H_2O$ tablet showed the formation of solution or melt of the electrolyte at temperatures IIO-$430^\circ C$ (Fig.I.). Phosphoric acid can't appear in the ca-

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pacity of an electrolyte, as H_3PO_4 is also formed during heating magnesium dihydrophosphate [I], but EC of the $Mg(H_2PO_4)_2 \cdot 2H_2O$ tablet doesn't change.

Changes of surface and form of the $Ca(H_2PO_4)_2 \cdot H_2O$ crystals showed proceeding of the dehydration process more or less with their dissolution. On the crystals, heated up to I80°C under the higher H_2O vapor pressure (Fig.2.), can be seen secondary crystals, formed as the result of cooling the solution of $Ca(H_2PO_4)_2 \cdot H_2O$ thermal dehydration products in water evolved. At the same time the surface of some crystals, heated with separation of water vapor, shows unhomogenous structure (Fig.3.): a part of the crystal is dissolved, a part is cracked. Most of the crystals are cracked without any visible signs of solubilization.As the maximums of the EC and the DTG curves are at the same temperatures, it can be concluded, that crystal and constitution water take part in the formation of the solution.

It was found, that TSP granules were expanded and became more porous because of the formation LP and water vapor evaporation (Fig.4.). As a result their volume density and strength decreased accordingly by I.2-2.3 and 2.5-6.3 times (from 50 to 8-2 kg/cm^2).

Samples with various chemical and mineralogical compositions, made by fractionation phosphorites by particle sizes and density, were used in the investigations of phosphorite fusibility. Main attention was paid to melting beginning temperature (MBT) determination. MBT was determined by DTA curves for all samples studied. To find correlation between the phosphorite composition and MBT their quantitative mineralogical composition was determined by X-ray analysis. The chemical composition on the basis of latter was found. Differences between the determined and calculated chemical compositions indicated the content of X-ray amorphous substances in all samples. A correlation between MBT and the chemical composition was not found. Among cristalline minerals in the phosphorites studied illite has the lowest melting point, but MBT of these samples are different. It was found, that MBT are determined by the content of silicate (crystalline and amorphous) and carbonate minerals. The last raise the MBT, as CaO and MgO react with clay minerals forming higher melting substances. For the samples investigated a linear dependence was found between MBT and ratio of SiO_2 in silicates/CO_2 total in the range of

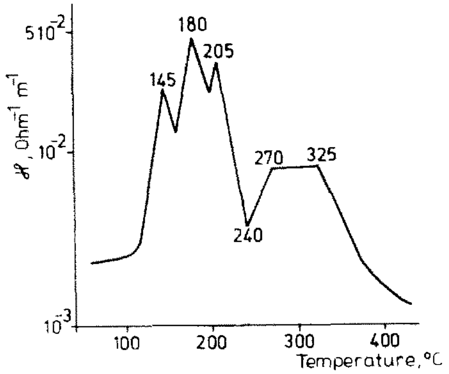

Fig.I. Relationship between EC $Ca(H_2PO_4)_2\cdot H_2O$ and temperature in dynamic heating I2°/min.

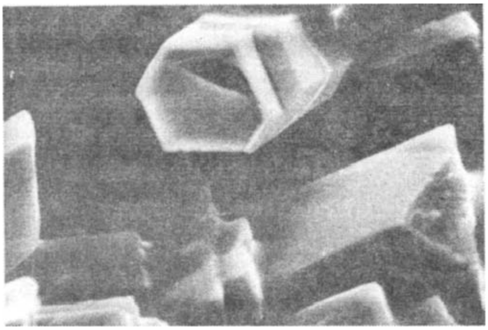

Fig.2. The surface of $Ca(H_2PO_4)_2\cdot H_2O$ crystal, heated in labyrint sample holder up to I80°C with heating rate 5°/min.

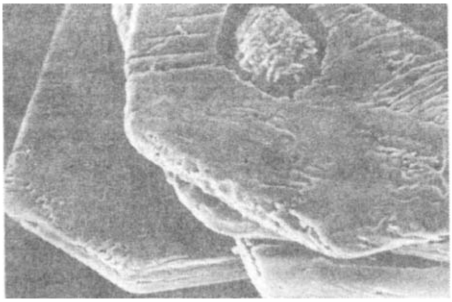

Fig.3. The surface of $Ca(H_2PO_4)_2\cdot H_2O$ crystal, heated on plate sample holder up to I80°C with heating rate 5°/min.

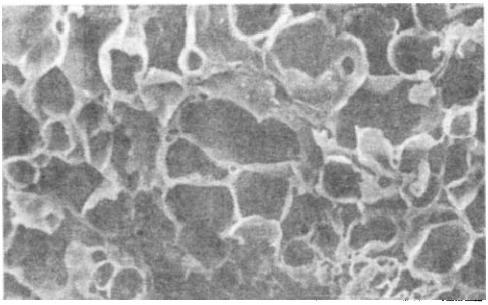

Fig.4. The surface of slitted TSP granula, heated at temperature 350°C during I5 min.

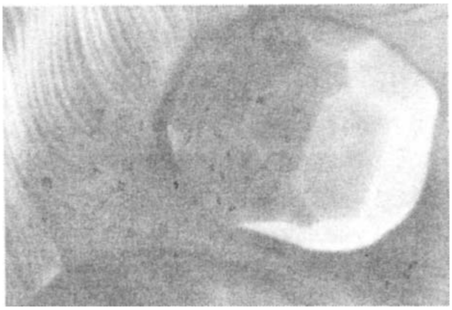

Fig.5. The surface of bro[illegible] lump of Kovdor apatite defluorinated product.

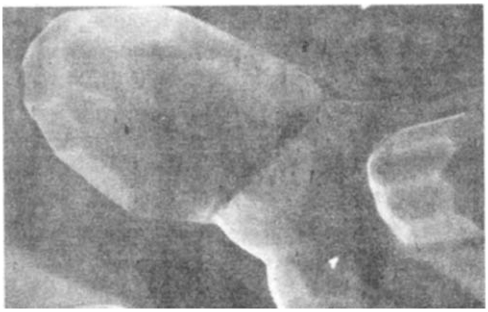

Fig.6. Single crystals of $Ca_{(9-n)}Mg_n(PO_4)_6$.

I020-I250°C. Phosphorite fractions from 2.70 to 3.00 g/cm^3 of fractions 0.04-0.I5 and 0.5-3.0 mm was studied by the above mentioned method. It was found, that the smallest and lightest fractions, which contained more clay minerals and less dolomite and calcite,had the lowest MBT. Quarz at temperature II00°C doesn't become sticky and cause melting. Thus, with a wiew to stabilization of the calcination process it is expedient to carry it out separately with small+easy and large+heavy fractions.

In the manufacture of the defluorinated phosphate by phosphoric acid-thermal method there are problems as a result of the formation of big clots and getting an unconditional product. It was found,that heating products from an industrial rotary kiln contain a glassy phase beside crystals of $Ca_{(9-n)}Mg_n(PO_4)_6$, where $n<2$, and uncomposed apatite (Fig.5.). By these samples it was found,that growing of single crystals (Fig.6.) take place in kiln.

The peculiarity of the Kovdor apatite concentrate is its phosphate mineral nature - fluorhydroxy-apatite and impurity of forsterite, in addition to dolomite and calcite. At the first stage of the process actualy impurities react with H_3PO_4 forming calcium and magnesium hydro- and dihydrophosphates. In heating they at first dehydrate, later react with apatite and residual impurities. By the phase diagram system formed: $Ca(PO_3)_2$-$Mg(PO_3)_2$-$Ca_2P_2O_7$-$Ca_3(PO_4)_2$-$Mg_3(PO_4)_2$ [2] LP can be form at 935°C.On the influence of amorphous SiO_2 on the heating product fusion can't be predicted because of the absence of corresponding data. The MBT couldn't be fixed exactly by DTA. The dependence EC on temperature was found to be very suitable to determine MBT: rapid increasing EC fixes the formation of the melt. Resulting these investigations it has been ascertained, that H_3PO_4 addition to Kovdor apatite concentrate decreases MBT of the system and primary LP forms at 900-II20°C, in dependence of kind and quantity of impurity minerals and quantity of added H_3PO_4. As during repeated heating LP was formed at higher temperature, it can be concluded that primary LP reacts with apatite and residual impurities forming calcium-magnesium phosphate and more refractory amorphous substances.

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