

## **STUDY OF THE THERMAL DEHYDRATION OF $Mn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$**

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The dehydration and condensation reactions taking place during the calcination of  $Mn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$  has been followed by means of thermal analyses under quasi-isothermal-isobaric conditions. Isothermal calcination of starting binary dihydrogenphosphate has been also carried out in an electric oven at various temperatures. The reaction products obtained were analyzed by chromatography, IR-spectroscopy, X-ray diffraction analysis, and electron microscopy. The compositions of the calcinates were determined through extraction. The effect of the partial pressure of water vapour has been followed on course, of the condensation reactions and of the formation of the main product: binary cyclo-tetraphosphate (tetrametaphosphate)  $MnCaP_4O_{12}$ .

Recently, cyclo-tetraphosphates of some bivalent metals have proved to be significant inorganic compounds [1-3]. They have been tested as microadditives to fertilizers of long-term action, and some of them are special thermostable pigments-luminiscent [4, 5], anticorrosive [6, 8] or coloured [9]. However, the reaction mechanism of their formation from binary cyclo-tetraphosphates is not fully understood, and the respective reaction conditions need to be specified in more detail as well. The cyclo-tetraphosphates can be prepared by the calcination of the dihydrogenphosphate [1-3, 10] or mixtures containing phosphorus and bivalent metal in the corresponding ratio [1-3, 10, 12].

From a consideration of the results [13-15] on the thermal decomposition of  $Mn(H_2PO_4)_2 \cdot 2H_2O$ , obtained through thermogravimetry under quasi-isothermal-isobaric conditions, we presumed that the same experimental method could provide data on the thermal decomposition of  $Mn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ , necessary to complete our ideas about the con-

densation reaction course. The present communication gives an account of our experimental results on the above mentioned reaction because these processes and their course are considerably affected by thermoanalytical conditions and, in addition to that, the rate of temperature increase as well as the water vapour pressure in the calcination area have a distinct effect. These factors are technologically important for the synthesis of binary cyclo-tetraphosphate from starting binary dihydrogenphosphate or from the corresponding starting mixture of suitable Mn and Ca compounds with phosphoric acid.

It is to be mentioned that the possible existence of binary manganese calcium cyclo-tetraphosphates has not been presumed until recently [1-3]. Only the last papers of our workplace [16, 17] proved the existence of the  $Mn_{2-x}Ca_xP_4O_{12}$ , where  $x = (1; 0)$  (i. e. also  $MnCaP_4O_{12}$ ).

### Experimental

The composition of  $Mn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$  (light pink crystals), prepared by the authors was confirmed by X-ray diffraction analysis and its morphology by electron microscopy.

For elucidation of the changes in mass and enthalpy during calcination the sample was thermoanalyzed by the classical dynamic method (i. e. unisothermally) using a Derivatograph C apparatus [18] (Hungarian Optical Works MOM Budapest). The conventional measurement was carried out in an open crucible with the temperature increase of  $5 \text{ deg. min}^{-1}$ , sample weight of about 300 mg, in temperature interval from 30 to  $600^\circ$ , and in the presence of air (Fig. 1).

For separation of the individual processes taking place during the calcination, the sample was submitted to thermogravimetric examination under quasi-isothermal-isobaric conditions [18-20]. Decomposition rate:  $0.3 \text{ mg. min}^{-1}$ , atmosphere: air, sample weight: about 150 mg. There were used two types of sample holders (Fig. 2): multi-plate sample holder (curve 1), and labyrinth crucible (curve 2). The last arrangement mentioned makes it possible to trap the water vapour released during calcination. Its partial pressure was about 100 kPa and constant (quasi-isobaric conditions [18-20]). In the case of the multiplate sample holder the partial pressure of water vapour contacting, the sample was so low (about 1 kPa) that it could be neglected.

The conditions of the thermal analysis were then adopted for the preparation of the main condensation products and intermediates, i. e. by

calcination of  $\text{Mn}_{1/2}\text{Ca}_{1/4}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Fig. 3a) and for the sake of comparison of  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  in the electric oven having an adjusted temperature increase of  $2 \text{ deg. min}^{-1}$  (control system: Chinotherm 10A - Chinoim Budapest, Hungary). Reaching the temperature selected ahead (within the interval of  $80\text{-}600^\circ$ ); each sample was heated for 30 min isothermally in a flat corundum pan (curves 3 and 4) and in a set of closed corundum crucibles (curves 1 and 2). In the former case the circumstances were corresponding to the multiplate sample holder ( $p_{\text{H}_2\text{O}} = 1 \text{ kPa}$ ) and in the later one to the labyrinth crucible ( $p_{\text{H}_2\text{O}} = 100 \text{ kPa}$ ).

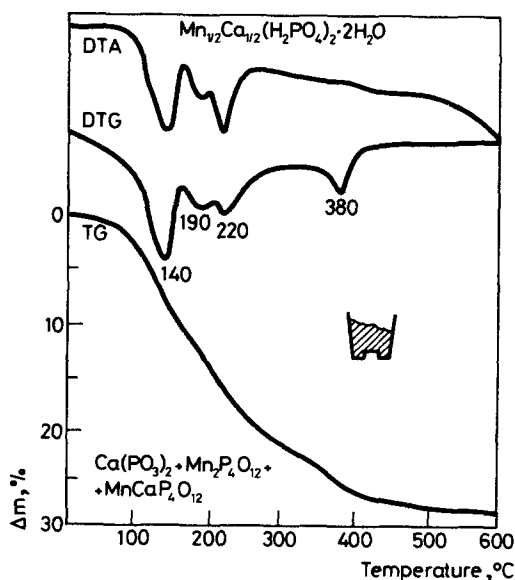


Fig. 1 Simultaneous TG, DTG, DTA curves of  $\text{Mn}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  under conventional circumstances

The samples calcinated at isothermal conditions were extracted with acetone. The phosphorus component of the extraction (in the form of phosphoric acid or diphosphoric acid from the dihydrogendiphosphate formed) is expressed by the weight decrease after the extraction of the calcinated sample and as the  $\text{P}_2\text{O}_5$  portion of the total amount in the calcinate. Then, the calcinates were extracted with water (curves 1 and 3), because the formed intermediate - dihydrogendiphosphate ( $\text{MeH}_2\text{P}_2\text{O}_7$ ) - is water soluble. The samples calcinated above  $120^\circ$  were extracted with  $0.3 \text{ M HCl}$ .

The final product of the heat treatment, the *c*-MnCaP<sub>4</sub>O<sub>12</sub> (or *c*-Mn<sub>2</sub>P<sub>4</sub>O<sub>12</sub> and Ca(PO<sub>3</sub>)<sub>2</sub>) remained insoluble (curves 2 and 4).

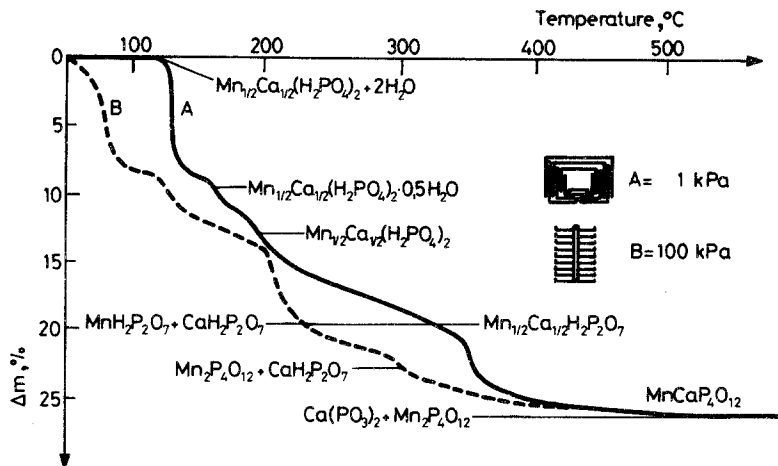


Fig. 2 Q-TG curves of  $\text{Mn}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  under quasi-isothermal-isobaric conditions using the polyplate sample holder (B) and the labyrinth crucible (A)

The calcinates and the individual products prepared in the thermal analysis at quasi-isothermal isobaric conditions were identified by means of instrumental analytical methods: chromatography [22], X-ray diffraction analysis [16, 25] (HZG-4, GDR) and electron microscopy [26] (Tesla BS 300, CSSR).

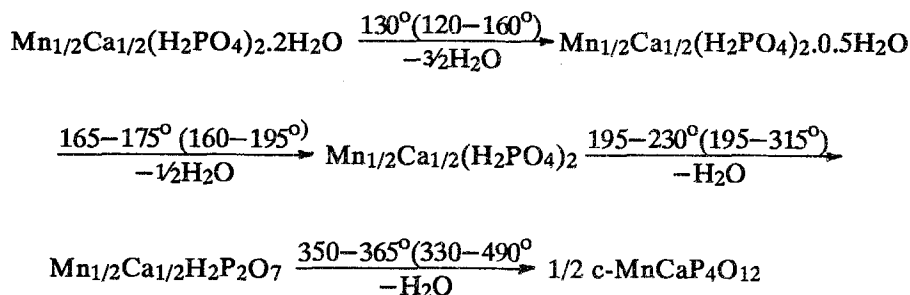
## Results and discussion

Figure 1 shows the simultaneous TG, DTG and DTA curves of manganese-calcium dihydrogenphosphate obtained by using a dynamic heating program. It can only be read of them that the water loss of the compound is a four step endothermal process. Since the partial processes strongly overlap, it is hard to define the magnitude of the weight changes connected with the individual processes, as well as to draw conclusions regarding the probable progress of the decomposition and the composition of the transitionally formed intermediate by stoichiometric calculations.

The thermal analysis under quasi-isothermal-isobaric conditions has already given some what more defined conception of the individual processes

(Fig. 2) taking place during calcination of the starting  $\text{Mn}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The course of the curves allowed to state two reaction mechanisms which are closely connected with the water vapour tension, within the grains. One of them holds for the vapour tension approaching 100 kPa (curve 2), on the contrary the other is preferred if the vapour tension is very low (curve 2). Only the former mechanism leads to the derived product of binary manganese-calcium cyclo-tetraphosphate. In the latter case the products of non-binary type are mostly produced. The X-ray analysis of the intermediary and end products verified this supposition.

Curve 2 in Fig. 2 shows the weight changes of the sample in the case if the examination was carried out by using the labyrinth crucible. Based on the course of this curve it is already possible to suppose the eventual mechanism of the water loss process.



Accordingly, first the sample lost 1.5 mole of water at  $130^\circ$  in quasi-isothermal way. The remaining 0.5 mole water of crystallization departed between  $160-195^\circ$ , with maximum rate at  $170^\circ$ , in an unisothermal way. The condition that the progress of the water departure in dependence of temperature occurred in the two sections in a different (isothermal and anisothermal) way indicates that the mechanism of the dehydration must have also been different.

Thereafter, the splitting of the constitutional water from the double salt  $\text{Mn}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2$  took also place in two steps and probably according to two different mechanism. First the crystalwater free sample lost viz. in a broad temperature interval between  $200$  and  $300^\circ$  gradually one mole of water. In contrast, the greater part of the other one mole of water became liberated in the vicinity of  $360^\circ$  while it was not necessary to increase the temperature significantly. However, the last traces of the water could be expelled from the sample only by the gradual increasing of the temperature with about 200 degrees. In the case of metal phosphates this latter

phenomenon can often be observed [19]. As a matter of fact it counts as an exception if the departure of water takes place in a rapid way.

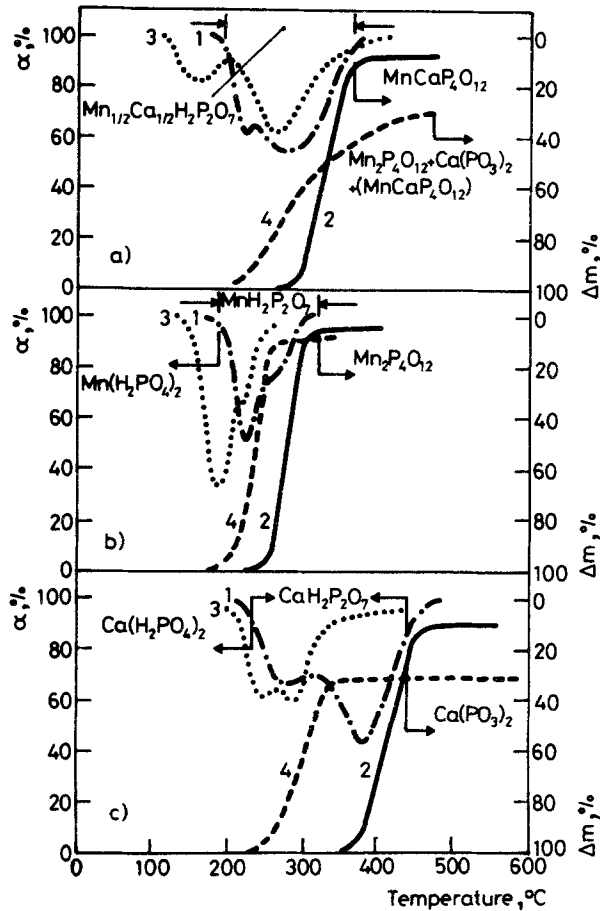


Fig. 3 Results of extraction of intermediates and end products obtained after calcination of  $\text{Mn}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (a);  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (b) and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (c) at various temperatures and various water vapour pressure: 100 kPa (curves 1 and 2) and 1 kPa (curves 3 and 4)

The fact that the intermediate  $\text{Mn}_{1/2}\text{Ca}_{1/2}\text{H}_2\text{P}_2\text{O}_7$  as well as the end product:  $\text{MnCaP}_4\text{O}_{12}$  are binary salts and not the simple mixtures of the corresponding manganese and calcium compounds, could convincingly be proved in experiments carried out by extraction. As it can be seen in Fig. 3, the course of curves 1 and 2 picture *a* do not show any likeness with those to

be seen in pictures *b* and *c*. Based on the results of electron microscopic and IA spectroscopic examinations of the calcinated samples and the extraction residues we also came to the above conclusion.

The binary calcium-manganese cyclo-tetraphosphate (*c*-MnCaP<sub>4</sub>O<sub>12</sub>) presents a new compound not mentioned in literature till now and which has become the subject of Czechoslovak patent [17]. Its crystal structure has been determined in monoclinic system - group C 2c with structure parameters:  $a = 1.2295(5)$  nm,  $b = 0.8688(4)$  nm,  $c = 1.0173(4)$  nm,  $\beta = 118.94(3)$ , the volume of an elementary cell  $V = 0.9510$  nm<sup>3</sup> and density 2.870 g.cm<sup>-3</sup> ( $\rho$  calculated) or 2.88 g.cm<sup>-3</sup> ( $\rho$  experimental).

The water loss process of Mn<sub>1/2</sub>Ca<sub>1/2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O took place in another way if the compound was examined on the multiplate sample holder in the presence of water vapour of about 1 kPa pressure under quasi-isothermal conditions. In this case namely the course of the curve (curve 1 in Fig. 2) differed from that of the Q-TG curves obtained by using the labyrinth crucible (curve 2). The former curve was not only shifted in the direction of lower temperatures, according to the lower water vapour content, but the break points presented themselves also at temperatures - different from those corresponding to the composition of the intermediates formed within the labyrinth crucible. The results of the extraction experiments (Fig. 3) similarly prove the change of the decomposition mechanism. According to these, in a significantly lower temperature range became the intermediates water soluble (curve 3 in Fig. 3) and the end product insoluble in 0.3 M HCl solution (curve 4) respectively.

Based on the analogy of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O [14] and Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O [27] as well as on earlier experiences [29] one can draw conclusions regarding the character of the changed reaction mechanism. Accordingly, it can be supposed that in the presence of water vapour of low partial pressure beside Mn<sub>1/2</sub>Ca<sub>1/2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.0.5H<sub>2</sub>O also hydrogenphosphate hydrates of other composition (Me<sup>II</sup>HPO<sub>4</sub>.*x*H<sub>2</sub>O; Me<sup>II</sup> = Mn, Ca) and phosphoric acid could be formed. After it these intermediary hydrates may lose their residual crystal water content while of the phosphoric acid diphosphoric acid may be formed [29].

The next process in the interval of 200-290° caused again the release of 1.5 water molecules. Parallel dimanganese cyclo-tetraphosphate (*c*-Mn<sub>2</sub>P<sub>4</sub>O<sub>12</sub>) and CaH<sub>2</sub>P<sub>2</sub>O<sub>7</sub> were formed [27]. With further temperature increase the latter compound was condensed in two steps. First calciumdihydrogendiphosphate (CaH<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) was formed (290-340°) and finally Ca(PO<sub>3</sub>)<sub>2</sub> (340-450°). The formation of only about 5% of *c*-MnCaP<sub>4</sub>O<sub>12</sub> could be detected.

Summing up, it can be stated that the fundamental difference between the mechanisms of the reactions taking place under two different conditions (100 and 1 kPa resp.) is, that in pure water vapour atmosphere of 100 kPa pressure the reactions take place in a uniform and unambiguous way (sec eqs), and the intermediary and end products are of binary type double salts, while in water vapour atmosphere of low (1 kPa) partial pressure the starting compound decomposes soon after the beginning, breaks up into its constituent parts and many partial reactions take place in a parallel way.

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**Zusammenfassung** – Dehydratations- und Kondensationsreaktion während der Kalzinierung von  $Mn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$  wurden unter quasi-isothermen-isobaren Bedingungen mittels Thermoanalyse untersucht. Die isotherme Kalzinierung der binären Dihydrogenphosphat-Ausgangssubstanz wurde bei verschiedenen Temperaturen auch in einem Elektroofen durchgeführt. Erhaltene Reaktionsprodukte wurden mittels Chromatographie, IR-Spektroskopie, Röntgendiffraktionsanalyse und Elektronenmikroskopie untersucht. Die Zusammensetzung der Kalzinierungsprodukte wurde über Auslaugen bestimmt. Weiterhin wurde der Einfluß des partiellen Druckes von Wasser auf den Verlauf der Kondensationsreaktionen und die Bildung des Hauptproduktes {binäres Cyclotetraphosphat (Tetramethaphosphat)  $MnCaP_4O_{12}$ } untersucht.