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INFLUENCE OF SILICIC ACID AND GLAUCONITE ON THERMAL DEHYDRATION OF $Ca(H_2PO_4)_2 \cdot H_2O$

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The thermal dehydration of mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$ with silicic acid and glauconite was studied by thermal (under dynamic and quasi-isothermal-quasi-isobaric conditions), X-ray and chromatographic analyses.

It was found that the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ is accelerated in the mixtures. $SiO_2 \cdot nH_2O$ and glauconite react with the intermediates of dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$, and silicophosphates and Al, K, Fe-phosphates are formed, respectively. The total degree of polymerization of calcium polyphosphates is lower in the mixtures than in $Ca(PO_3)_2$ itself.

Previous research has shown the thermal decomposition of $Ca(H_2PO_4)_2 \cdot H_2O$ to be a complicated polycondensation process in the course of which, depending on the experimental conditions, H_3PO_4, $CaH_2P_2O_7$, $Ca_3(HP_2O_7)_2$ and many other forms of polyphosphates are formed as intermediates. The end-product is high-polymeric calcium phosphate, $Ca(PO_3)_2$ [1].

The aim of this research was to study the interactions of mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$ with amorphous $SiO_2 \cdot nH_2O$ and glauconite in the course of heating in air up to complete dehydration.

Experimental

Thermal analysis was carried out with a Q-Derivatograph (MOM, Budapest) under dynamic conditions and under quasi-isothermal-quasi-isobaric conditions (*Q*), with simultaneous TG, DTG and DTA examinations.

Under dynamic conditions, the heating rate was 10 deg/min^{-1}, the amount of the sample was about 900 mg in the conventional platinum crucible.

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Under quasi-isothermal-quasi-isobaric conditions, the heating of the furnace was controlled so that the weight change was not over 0.5 $mg.min^{-1}$. The amount of the sample in the labyrinth sample holder was about 300 mg.

For the mixtures with glauconite, where the quantity of water liberated from glauconite (up to 400°) is 1.4%, Δm^* (%) was calculated for $Ca(H_2PO_4)_2 \cdot H_2O$.

Samples for chemical, chromatographic and X-ray analyses were obtained by heating $Ca(H_2PO_4)_2 \cdot H_2O$ and the mixtures in an open crucible (2000 mg) up to the given temperature in the Derivatograph furnace at a rate of 2.5 deg/min^{-1}, and then cooled at once.

X-ray diffraction measurements were carried out with a Dron 3M (USSR) instrument (CoK_α). The results are given in Table 1.

Table 1 Main composition of products in heated mixtures $Ca(H_2PO_4)_2 \cdot H_2O$ with $SiO_2 \cdot nH_2O$ and glauconite by X-ray diffraction analysis

Temperature, °C	$Ca(H_2PO_4)_2 \cdot H_2O$ +50% $SiO_2 \cdot nH_2O$	$Ca(H_2PO_4)_2 \cdot H_2O$ +50% glauconite
250	$CaHPO_4$	$CaHPO_4$
	$CaH_2P_2O_7$	Glauconite
	Amorphous phase	Amorphous phase
400	γ-$Ca_2P_2O_7$	γ-$Ca_2P_2O_7$
	δ-$Ca(PO_3)_2$	Glauconite
	Amorphous phase	$K(Al, Fe)P_2O_7$ [4]
		Amorphous phase
600	γ-$Ca_2P_2O_7$	γ-$Ca_2P_2O_7$
	δ-$Ca(PO_3)_2$	δ-$Ca(PO_3)_2$
	$xSiO_2 \cdot yP_2O_7$ [5]	$K(Al, Fe)P_2O_7$
	Amorphous phase	

For paper-chromatographic analysis, the well-known method [2] was used. Ion-exchange on Dowex 50W was used for the dissolution of polymeric phosphates. The contents of water-soluble P_2O_5, CaO and K_2O were determined (Table 2).

Chemicals

The $Ca(H_2PO_4)_2 \cdot H_2O$ used was a p.a. preparation (CaO = 21.94%, P_2O_5 = 55.35%, H_2O = 22.70%).

Amorphous $SiO_2 \cdot nH_2O$ was prepared by saturation of a solution of $Na_2O \cdot 3SiO_2$ with HCl, washed with water to remove Cl^- and dried at 90° to constant weight (SiO_2 = 93.22%, H_2O = 6.78%).

Glauconite was from the Maardu deposit (SiO_2 = 51.06%, Fe_2O_3 = 20.34%, Al_2O_3 = 10.67%, K_2O = 8.98%, H_2O = 5.60%).

Table 2 Content of water-soluble and ion-exchange soluble phosphates in heated $Ca(H_2PO_4)_2 \cdot H_2O$ and its mixtures with $SiO_2 \cdot nH_2O$ (50%) and glauconite (50%)

Sample	$Ca(H_2PO_4)_2 \cdot H_2O$			$Ca(H_2PO_4)_2 \cdot H_2O$ + $SiO_2 \cdot nH_2O$			$Ca(H_2PO_4)_2 \cdot H_2O$ + glauconite		
Temperature, °C	250	400	600	250	400	600	250	400	600
Content of total P_2O_5, %	62.5	67.8	69.5	29.9	31.2	31.5	29.1	30.2	31.0
Ion-exchange soluble, P_2O_5, % relative to total P_2O_5									
Monophosphate	30	10	2	60	10	10	60	3	6
Diphosphate	27	24		13	30	20	10	30	30
Polyphosphate ($n \geq 3$)	27			10	30	25	15	30	10
Sum of phosphates	84.4	34.3	1.9	82.9	67.0	54.6	85.1	62.8	45.8
Water-soluble P_2O_5, % relative to total P_2O_5									
Monophosphate	30	10	1	50	10	10	40	5	2
Diphosphate	20	5		10	8	4	10	7	
Polyphosphate ($n \geq 3$)	20	3		1	22		15	5	
Sum of phosphates	72.6	17.9	1.1	61.0	40.8	13.6	65.8	17.1	2.5
K_2O, relative %	0	0	0	0	0	0	9.1	5.6	3.9
CaO, relative %	62.9	6.5	1.0	56.0	25.2	3.9	32.8	14.6	1.5

Results and discussion

The results of the thermal analysis show that under dynamic heating at a rate of 10 deg/min^{-1}, $Ca(H_2PO_4)_2 \cdot H_2O$ decomposes in five stages (Fig. 1), with maximum rates at about 190, 255, 280, 365 and 440°. 1.5 mole of water is lost in the first step, 0.75 mole in the 2nd and 3rd steps, and the last 0.75 mole of water in the 4th and 5th steps.

Under Q conditions, the course of the decomposition is somewhat modified (Fig. 2). It was found that, in spite of the progressive nature of the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$, the compositions of the intermediate samples are strongly heterogeneous [1, 2].

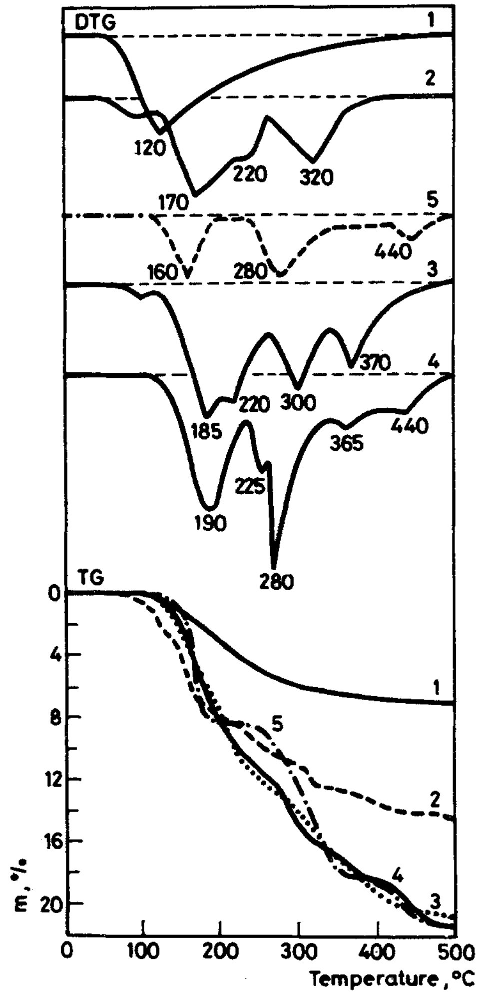

Fig. 1 Dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$, $SiO_2 \cdot nH_2O$ and their mixtures under dynamic conditions (10 deg·min^{-1}). Open crucible .1 - $SiO_2 \cdot nH_2O$; 2 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 50% $SiO_2 \cdot nH_2O$; 3 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 20% quartz; 4 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 5% $SiO_2 \cdot nH_2O$; 5 - $Ca(H_2PO_4)_2 \cdot H_2O$

Mixtures with $SiO_2 \cdot nH_2O$

The addition of 5% $SiO_2 \cdot nH_2O$ to $Ca(H_2PO_4)_2 \cdot H_2O$ changes the forms of the DTG, Q-TG and Q-DTA curves significantly (Figs 1 and 2). Under dynamic heating, dehydration occurs in stage 4. The last step, at 440°, disappears. If there is 50% of $SiO_2 \cdot nH_2O$ in the mixture, dehydration occurs in stage 3: the first step with maximum rate is at 170°. The change to the lower temperature is partially caused by the dilution effect (see curve 3 in Fig. 1 – $Ca(H_2PO_4)_2 \cdot H_2O + 20\%$ quartz). The second step is at 220° and the third at 320°. Dehydration in the mixture comes to an end at 420°, i.e. at a temperature 80 deg lower than for $Ca(H_2PO_4)_2 \cdot H_2O$.

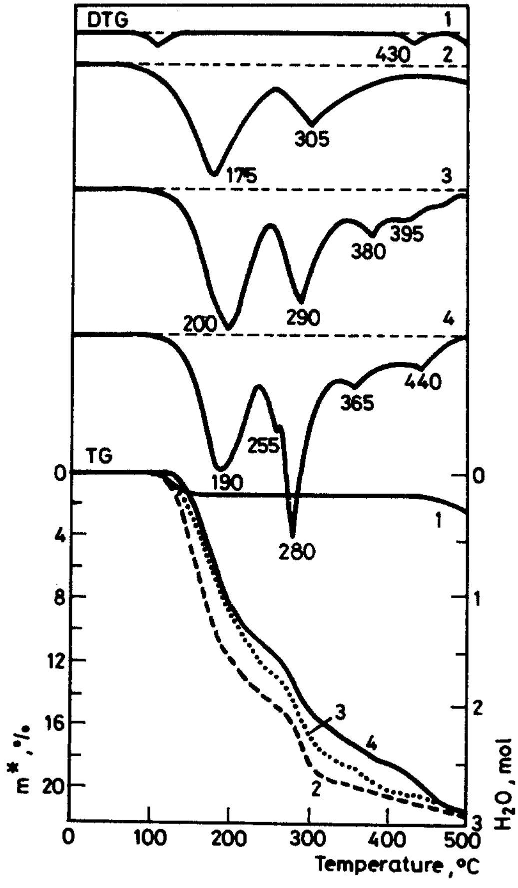

Fig. 2 Dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ and its mixtures with $SiO_2 \cdot nH_2O$ under quasi-isothermal-quasi-isobaric conditions. 1 - $Ca(H_2PO_4)_2 \cdot H_2O + 50\%$ $SiO_2 \cdot nH_2O$; 2 - $Ca(H_2PO_4)_2 \cdot H_2O + 5\%$ $SiO_2 \cdot nH_2O$; 3 - $Ca(H_2PO_4)_2 \cdot H_2O$;

Under Q conditions, the graduality of the decomposition and the changes caused by the impurities are more distinctly observed (Fig. 2). $SiO_2 \cdot nH_2O$ accelerates the dehydration significantly at temperatures over 265° (when 2 moles of H_2O is liberated), and the amount of water liberated up to 330° increases.

The results of chromatographic analysis (Table 2) show that the content of monophosphate in the mixture with $SiO_2 \cdot nH_2O$ (50%) is twice that in pure $Ca(H_2PO_4)_2 \cdot H_2O$ heated up to 250°, whereas the content of water-soluble P_2O_5 is 11.6% lower in the mixture. It could be concluded that the H_3PO_4 formed during the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ interacts with $SiO_2 \cdot nH_2O$. As a result, the polycondensation of calcium phosphates decreases. $CaHPO_4$ is formed in the mixture (Table 1).

During heating from 250° to 600°, the content of monophosphates decreases. As a result of the dehydration of $CaHPO_4$, γ-$Ca_2P_2O_7$ is formed (Table 1). The content of diphosphate is higher and the content of long-chain polyphosphates (insoluble by ion-exchange) is lower in the mixture than in the products heating of of the pure salt.

Mixtures with glauconite

Dehydration of the mixture with 5% of glauconite in an uncovered crucible occurs in four stages (Fig. 3). The temperatures of the maximum rates of steps 1, 3 and 4 increase by 10-15 deg (the 2nd step disappears), but the TG curves indicate acceleration of the loss of water from the mixture. The temperature of the last step is 45 deg lower than for the pure salt.

From the mixture with 50% of glauconite, water is liberated in 2 stages, with maximum rates at 175° and 305°. 1.5 moles of H_2O is lost from $Ca(H_2PO_4)_2 \cdot H_2O$ during heating up to 240°, and from the mixtures with 5% or 50% of glauconite at 230° and 180°.

The Q-TG curves also indicate the accelerating effect of glauconite on the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ in the first step, and is completed at a temperature 50 deg lower under Q conditions.

In the mixture with glauconite (50%) heated up to 250°, the content of water-soluble monophosphate is 1.5 times lower than that in the ion-exchange-soluble one (Table 2). The results of X-ray analysis indicate that the content of $CaHPO_4$ is analogous with that in the mixture with $SiO_2 \cdot nH_2O$. The interaction of glauconite with the intermediates of dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ indicates an increase in the water-soluble K_2O content in the heated mixtures, which does not occur with glauconite itself (Table 2). During heating up to 400°, the content of diphosphate in the mixture increases up to 30 relative %. At the same time, the content of insoluble (by ion-exchange) polyphosphates is lower than in the heating products of $Ca(H_2PO_4)_2 \cdot H_2O$. The X-ray analysis results show the contents of Al, Fe, K-phosphates (Table 1). $Ca(H_2PO_4)_2 \cdot H_2O$ does not decompose 100% in the reaction giving H_3PO_4 during heating, and therefore there is $Ca(PO_3)_2$ in the dehydrated mixture too, which coincides with the results in [3].

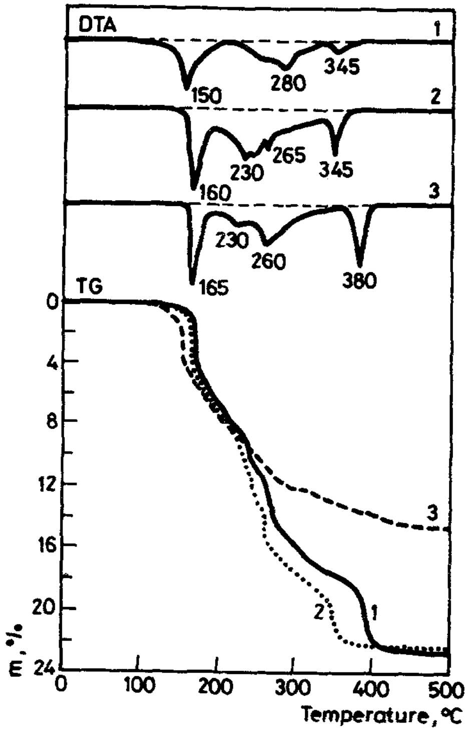

Fig. 3 Dehydration of glauconite, $Ca(H_2PO_4)_2 \cdot H_2O$ and their mixtures under dynamic conditions (10 deg·min^{-1}). Open crucible. 1 - glauconite; 2 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 50% glauconite; 3 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 5% glauconite; 4 - $Ca(H_2PO_4)_2 \cdot H_2O$

Conclusions

It has been established that $SiO_2 \cdot nH_2O$ and glauconite react with the intermediates of dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ on heating. New phosphates (silicophosphates and Al, K, Fe mixed phosphates) are formed, and accordingly the degree of polymerization of the calcium polyphosphates decreases. The dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ is accelerated. Glauconite affects the loss of water from $Ca(H_2PO_4)_2 \cdot H_2O$ from the beginning of dehydration and does this more thoroughly than $SiO_2 \cdot nH_2O$.

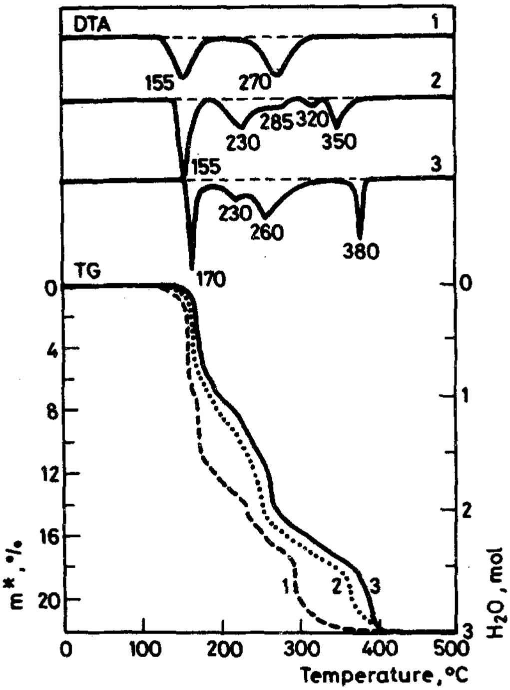

Fig. 4 Dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ and its mixtures with glauconite under quasi-isothermal-quasi-isobaric conditions. 1 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 50% glauconite; 2 - $Ca(H_2PO_4)_2 \cdot H_2O$ + 5% glauconite; 3 - $Ca(H_2PO_4)_2 \cdot H_2O$

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Zusammenfassung — Mittels röntgenographischer, chromatographischer und thermischer (unter dynamischen und quasi-isothermen-quasi-isobaren Bedingungen) Analyse wurde die thermische Dehydratation eines Gemisches aus $Ca(H_2PO_4)_2 \cdot H_2O$, Kieselsäure und Glaukonit untersucht.

Es wurde festgestellt, daß die Dehydratation von $Ca(H_2PO_4)_2 \cdot H_2O$ im Gemisch beschleunigt abläuft. $SiO_2 \cdot nH_2O$ und Glaukonit reagieren mit den Zwischenprodukten der Dehydratation von $Ca(H_2PO_4)_2 \cdot H_2O$ und formen Silikophosphate und Al,K,Fe-Phosphate. Der totale Polymerisationsgrad von Calciumpolyphosphat ist im Gemisch geringer als in $Ca(PO_3)_2$ selbst.