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The thermal dehydration of the $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 system. Part 1. Mechanism

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Abstract

The thermal dehydration of the $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 system has been studied by a continuous thermogravimetric mode method, and by a batch method, heating the mixtures in the molar ratios $SiO_2/Ca(H_2PO_4)_2 \cdot H_2O = 0.5, 1, 2$ and 3 at 150, 185, 245, 275, 320, 430 and 780°C. The batches, after cooling, were examined by X-ray diffraction (XRD) and infrared spectroscopy (IR) to identify the intermediate and final products. The final products were mainly $Ca(PO_3)_2$ and SiP_2O_7, while pyro- and triphosphates and $Si(HPO_4)_2$ were detected as intermediate products. The quantity of SiO_2 present affects the dehydration which takes place in five stages. The removal of water molecules in the first, second and fourth stages was increased, and in the third and fifth stages was decreased on increasing the amount of SiO_2.

Keywords: $Ca(H_2PO_4)_2$–SiO_2 system; Dehydration; DTA; IR; TG; Thermal treatment; XRD

1. Introduction

An important step in the production of phosphate fertilizers, such as calcium polyphosphates, is the acid-thermal treatment of the phosphate raw materials, which is accompanied by condensation of the intermediate acidic salts, mainly $Ca(H_2PO_4)_2 \cdot H_2O$. The thermal polycondensation of $Ca(H_2PO_4)_2 \cdot H_2O$ has been studied previously [1, 2]. In the case where the raw phosphate materials contain silicate gangue, it is interesting to study the thermal decomposition of the $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 system.

Our previous thermogravimetric study has shown that the mechanism of the dehydration of the above system is very complicated. The amount of SiO_2 present has

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an influence on the dehydration which is different from that of the pure $Ca(H_2PO_4)_2 \cdot H_2O$ [3,4]. A recent study [5] of the thermal dehydration of the systems of $Ca(H_2PO_4)_2 \cdot H_2O$ with amorphous $SiO_2 \cdot nH_2O$ and with glauconite revealed that $SiO_2 \cdot nH_2O$ and glauconite react with the phosphate intermediates producing silicophosphates and, at the same time, decreasing the degree of polymerisation of the calcium polyphosphates, whereas the dehydration processes are accelerated.

The aim of this research is the detailed study of the influence of amorphous SiO_2 on the thermal treatment of $Ca(H_2PO_4)_2 \cdot H_2O$ up to 780°C.

2. Experimental and results

The raw materials used were commercial $Ca(H_2PO_4)_2 \cdot H_2O$ (CP) and amorphous SiO_2 (S). The $Ca(H_2PO_4)_2 \cdot H_2O$ (Merck, extra pure) had the composition 56.5% P_2O_5, 21.5% CaO and 21.7% H_2O. The free H_3PO_4 content was determined after washing with acetone, and was found to be 2.97% H_3PO_4 (or 2.15% P_2O_5). The CP used in each case had been washed with acetone to remove the free H_3PO_4. The amorphous SiO_2 was anhydrous of particle size < 400 mesh (Silicon IV oxide 99.5%, Ventron GMBH). The IR spectra of the raw materials are shown in Fig. 3a, below.

Mixtures of the two solids in molar ratios $R = S/CP = 0.5, 1, 2$ and 3, were prepared by mixing corresponding amounts of each in a porcelain mortar with vigorous grinding. Thermal analysis of the mixtures was carried out using a derivatograph $TRDA_3$-H (Chyo Balance Corporation), which provided signals for the temperature (T), thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA). The data were collected and stored in a PC by an amplifier/multiplexer board model PCLD-889 (Advantech Co., Ltd.). The thermal analysis graphs of the mixtures are shown in Fig. 1.

Samples (6–10 g) from the above mixtures were heated separately in porcelain crucibles at 150, 185, 245, 275, 320, 430 and 780°C for 4 h each. The choice of these heating temperatures was derived from the thermal analysis study. The weight losses per 100 parts of CP of these batch experiments are given in Table 1 and are also shown in Fig. 1, as a function of temperature, for comparison with the thermogravimetric results measured by continuous mode.

Each of the heating samples was examined by IR and XRD techniques. In the XRD studies, we used a Siemens D-500 diffractometer with Cu Kα radiation ($\lambda = 1.54060$ Å). The XRD patterns of the samples are shown in Fig. 2. IR spectra taken with a Perkin-Elmer 783 spectrophotometer are shown in Fig. 3.

3. Discussion

The thermogravimetric (TG) and differential thermal analysis (DTA) curves, as well as the batch experiments (Fig. 1), indicate that the SiO_2 content has an effect on the dehydration of the $Ca(H_2PO_4)_2 \cdot H_2O$. Thermal analysis of the pure $Ca(H_2PO_4)_2 \cdot H_2O$ (Fig. 1a) [2] shows that three moles of water are lost in five stages, the last being

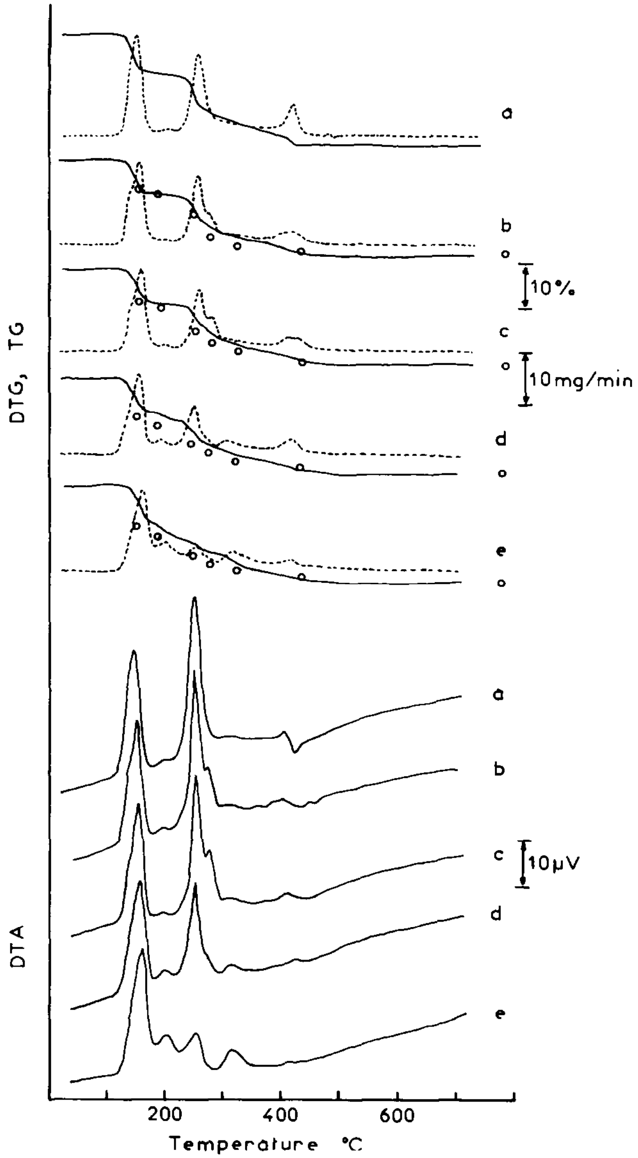


Fig. 1. TG, DTG and DTA curves for the thermal dehydration of pure $Ca(H_2PO_4)_2 \cdot H_2O$ (a) and the mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 with molar ratios S/CP of 0.5 (b), 1 (c), 2 (d) and 3 (e), at a heating rate of 5°C min^{-1}. The solid circles indicate the weight loss after 4 h of heating at the corresponding temperatures.

exothermic. The presence of SiO_2 changes the dehydration process. The first and third stages appear as a bimodal stage for $R = 0.5$ and 1. Table 2 shows the temperatures of the two peaks of the bimodal stages. The peak temperatures for all the mixtures are near to those of pure $Ca(H_2PO_4)_2 \cdot H_2O$. The mass losses from both batch (Table 1) and TG

Table 1
The weight losses per 100 parts of CP of the mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$ (CP) and amorphous SiO_2 (S) after 4 h heating at each temperature

Molar raito $R = S/CP$	Temperature/°C						
	150	185	245	275	320	430	780
0[a]	7.31	8.82	14.71	–	17.51	–	21.72
0.5	7.47	8.04	12.43	17.34	19.56	21.06	21.79
1	7.72	9.03	14.31	16.72	18.85	20.64	21.76
2	8.71	10.89	14.78	16.93	18.67	20.39	21.76
3	9.52	11.38	15.65	17.74	19.00	20.83	21.76

[a] From Ref. [3].

(Table 2, water molecules removal) experiments indicate that the first, second and fourth stages are increased, and the third and fifth stages decreased on increasing the amount of SiO_2.

The XRD patterns (Fig. 2) show that the crystalline phase of the initial $Ca(H_2PO_4)_2 \cdot H_2O$ is detected up to 320°C. The anhydrous $Ca(H_2PO_4)_2$ crystalline phase is detected for $R = 0.5$ up to 245°C, and for $R = 1$ up to 185°C. The crystalline phase $Ca_3H_2(P_2O_7)_2 \cdot H_2O$ appears from 245 to 320°C, while for $R = 3$ it appears up to 430°C. The appearance of the metaphosphate crystalline phases occurs after heating to 320°C for $R = 0.5$ and 2, after heating to 430°C for $R = 1$, and after heating to 780°C for $R = 3$. All the final heating products have the same XRD pattern ($Ca(PO_3)_2$ 9-0363), while some particular XRD patterns of $Ca_4P_6O_{19}$ and $Ca_3(PO_4)_2$ were identified in the heated mixtures with $R = 1$ (275°C) and $R = 2$ (320 and 430°C) respectively. The presence of phases in which the oxide ratio $r = CaO{:}P_2O_5$ is more than 1, which is the ratio of the initial materials, such as $Ca_3H_2(P_2O_7)_2 \cdot H_2O$ ($r = 1.5$), $Ca_4P_6O_{19}$ ($r = 1.333$) and $Ca_3(PO_4)_2$ ($r = 3$), results in the formation of free H_3PO_4

$$3[Ca(H_2PO_4)_2 \cdot H_2O] \rightarrow Ca_3H_2(P_2O_7)_2 \cdot H_2O + 2H_3PO_4 + H_2O \quad (1)$$

$$Ca_3H_2(P_2O_7)_2 \cdot H_2O + Ca(H_2PO_4)_2 \rightarrow Ca_4P_6O_{19} + 4H_2O \quad (2)$$

$$3Ca(H_2PO_4)_2 \rightarrow Ca_3(PO_4)_2 + 4H_3PO_4 \quad (3)$$

There is also the known anomalous transformation of $Ca(H_2PO_4)_2$ which produces free H_3PO_4

$$Ca(H_2PO_4)_2 \rightarrow CaHPO_4 + 4H_3PO_4 \quad (4)$$

It is possible for the free H_3PO_4 to react with the SiO_2 [6,7] yielding silicophosphates, such as $Si(HPO_4)_2$ which is concentrated to SiP_2O_7 at about 300°C [8]. So the increase of the fourth stage, which takes place in the same temperature range, is attributed to the above concentration. The final product was the δ-calcium metaphosphate, while the γ-form appears at 320 and 430°C for $R = 0.5$, and at 430°C for $R = 1$. The conversion of γ-calcium metaphosphate to the β-form, which is well known and

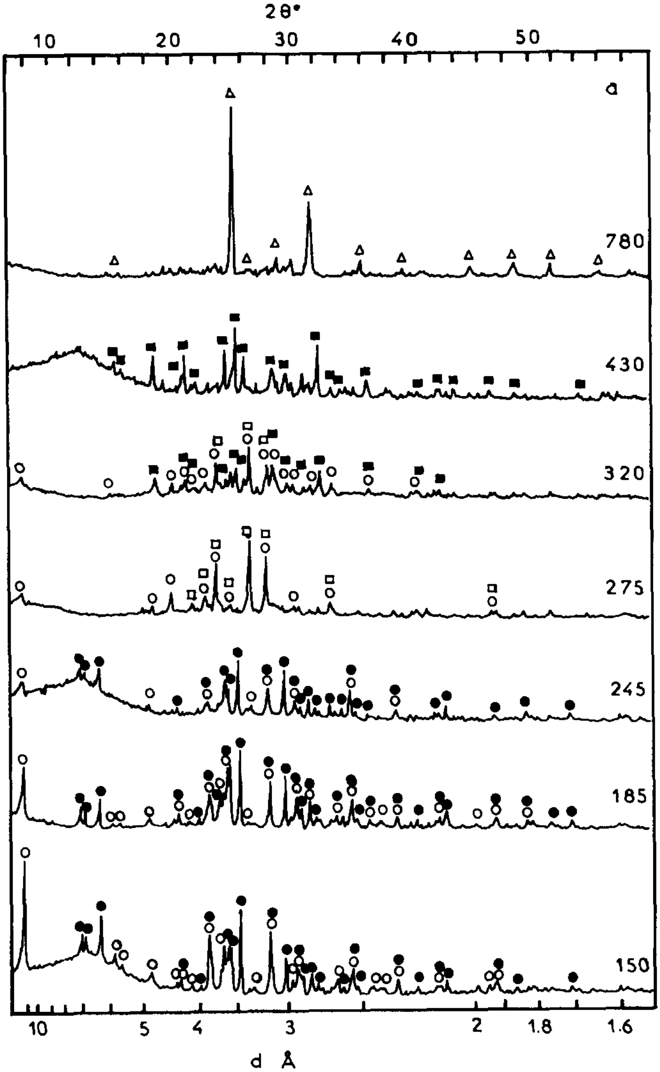


Fig. 2. XRD patterns of the $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 mixtures with molar ratios S/CP of 0.5 (a), 1 (b), 2 (c) and 3 (d), heated at the temperatures indicated: (○) $Ca(H_2PO_4)_2 \cdot H_2O$ 9-0347, (●) $Ca(H_2PO_4)_2$ 9-0390, (□) $Ca_3H_2(P_2O_7)_2 \cdot H_2O$ 22-0526, (■) γ-$Ca(PO_3)_2$ 17-0498, (△) δ-$Ca(PO_3)_2$ 9-0363, (▲) β-$Ca(P_2O_6)$ 11-0039, (◇) $Ca_4P_6O_{19}$ 15-0177 and (◆) $Ca_3(PO_4)_2$ 29-0359.

takes place at around 550°C [9, 10], was not observed here. The presence of SiO_2 favours the conversion of the calcium metaphosphate from the γ- to δ-form.

An unexpectedly small amount of $Ca(H_2PO_4)_2 \cdot H_2O$ appears after heating at 780°C for the $R = 3$ mixture, and is attributed on the hydrolysation of the metaphosphate with

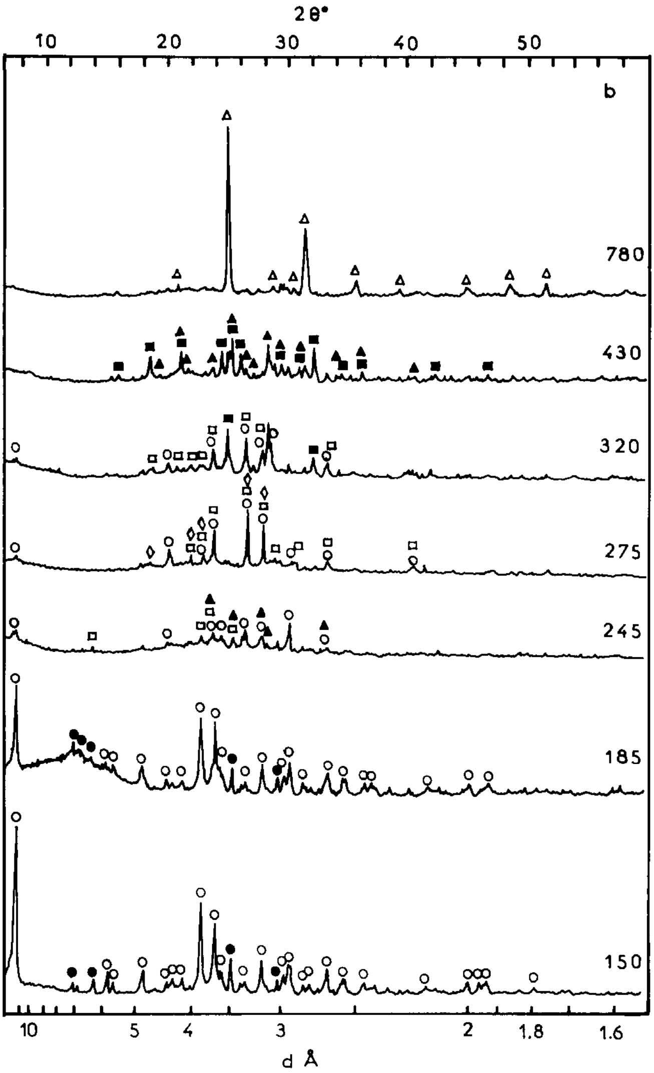


Fig. 2. (*Continued*).

the remaining zeolite water. There are some remaining unidentified peaks; for $R = 2$ at a heating temperature of 150°C corresponding to $d = 12.8484$, 3.4861, 3.3961 and 3.2215 Å, at a heating temperature of 185°C corresponding to $d = 12.7882$, 3.7338 and 3.3470 Å; for $R = 3$ at a heating temperature of 245°C corresponding to $d = 4.4238$ and 2.9465 Å, at a heating temperature of 275°C corresponding to $d = 4.4176$ and 2.9173 Å, at a heating temperature of 320°C corresponding to $d = 4.4106$ and 2.9098 Å, and at a heating temperature of 430°C corresponding to $d = 2.9166$ Å.

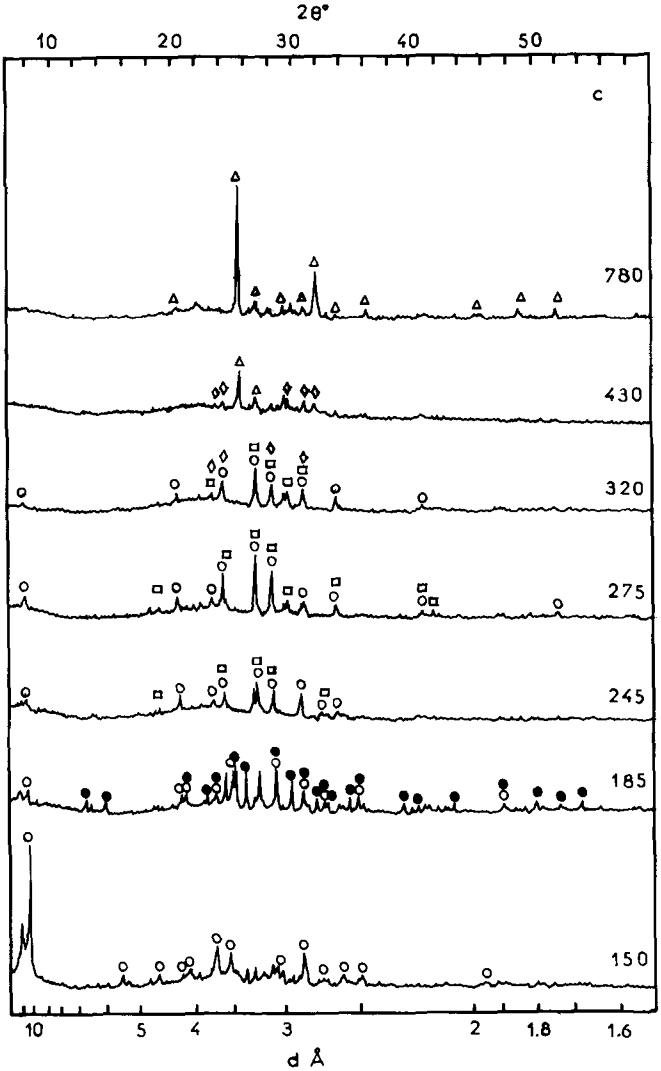


Fig. 2. (*Continued*).

The results obtained from the IR spectra (Fig. 3) are in agreement with the basic assumptions made previously on the basis of the XRD studies. The crystal water molecules of $Ca(H_2PO_4)_2 \cdot 2H_2O$ absorb at 3305–3485 cm^{-1} (stretching), at 1635–1670 cm^{-1} (bending in-plane), and at 660–687 cm^{-1} (liberation modes) according to the literature [11–13]. The adsorption bands for the stretching vibration of the crystal water are quite apparent up to 320°C, while for $R = 0.5$ and a heating temperature of 150, 185 and 245°C (Fig. 3b), two distinct peaks are observed at 3465–3485 and 3330

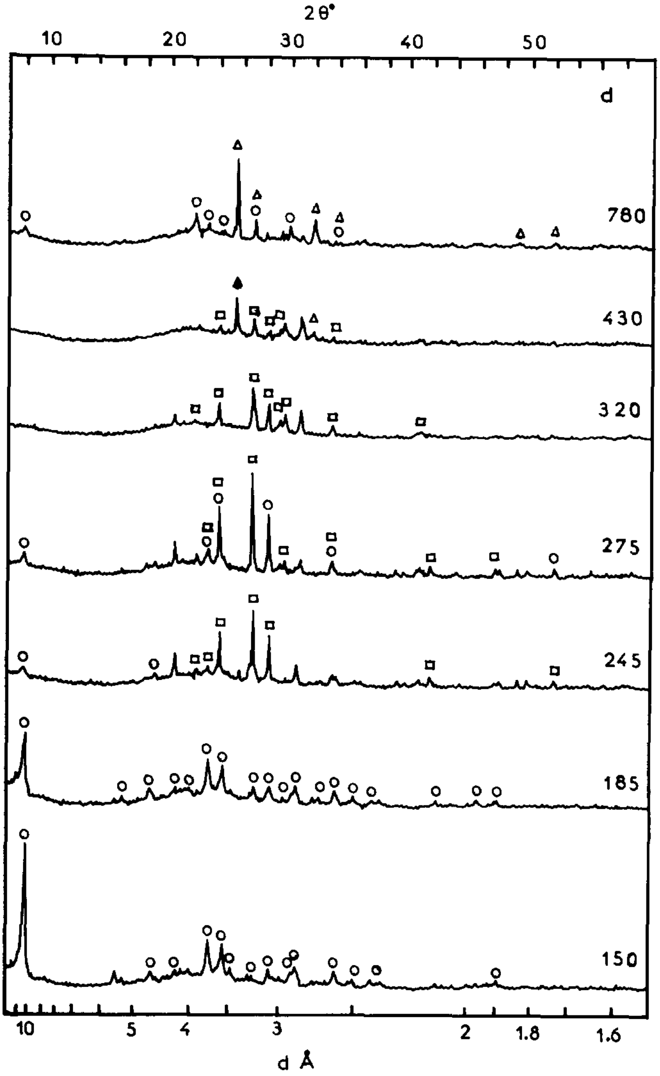
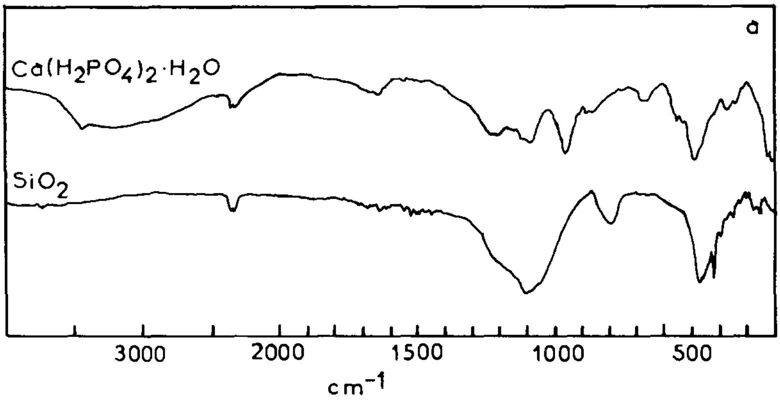


Fig. 2. (*Continued*).

cm^{-1} which indicate the presence of two different types of crystal water. The liberation mode vibrations are quite apparent up to 245°C for $R = 0.5$ (Fig. 3b), up to 185°C for $R = 1$ (Fig. 3c) and up to 150°C for $R = 2$ and 3 (Fig. 3d and Fig. 3e respectively). We also noticed that in all the spectra there are some very broad absorptions at around 3300 cm^{-1}, which correspond to zeolite water. As indicated in a study [14] on $Ca_2HP_3O_{10}$, the zeolite water remains up to 527°C.



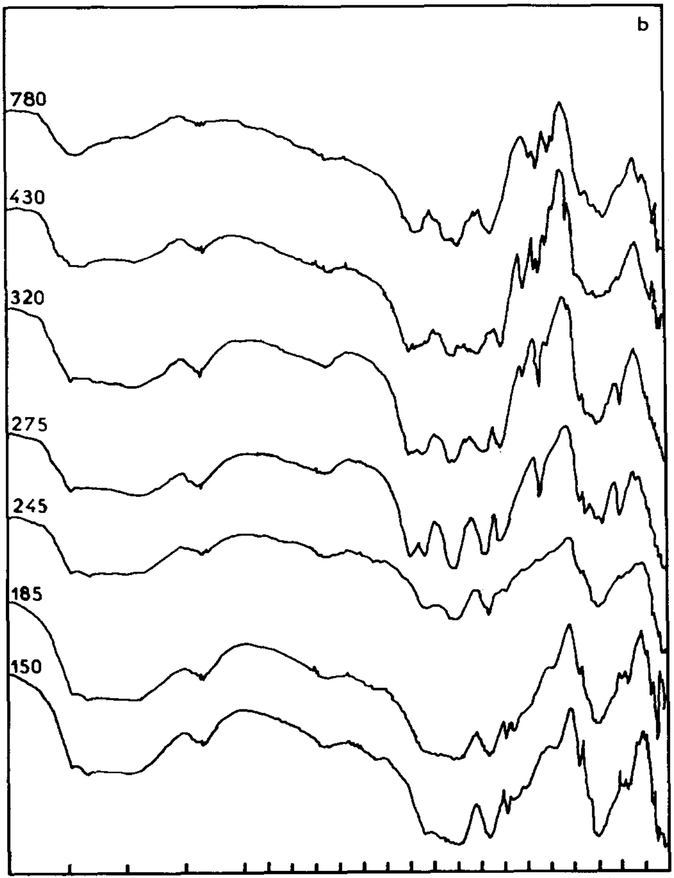


Fig. 3. IR spectra of the $Ca(H_2PO_4)_2 \cdot H_2O$–SiO_2 mixtures with molar ratios $R = S/CP$ of 0.5 (b), 1 (c), 2 (d) and 3 (e), heated at the temperatures indicated. The spectra of the initial components (a) are also shown.

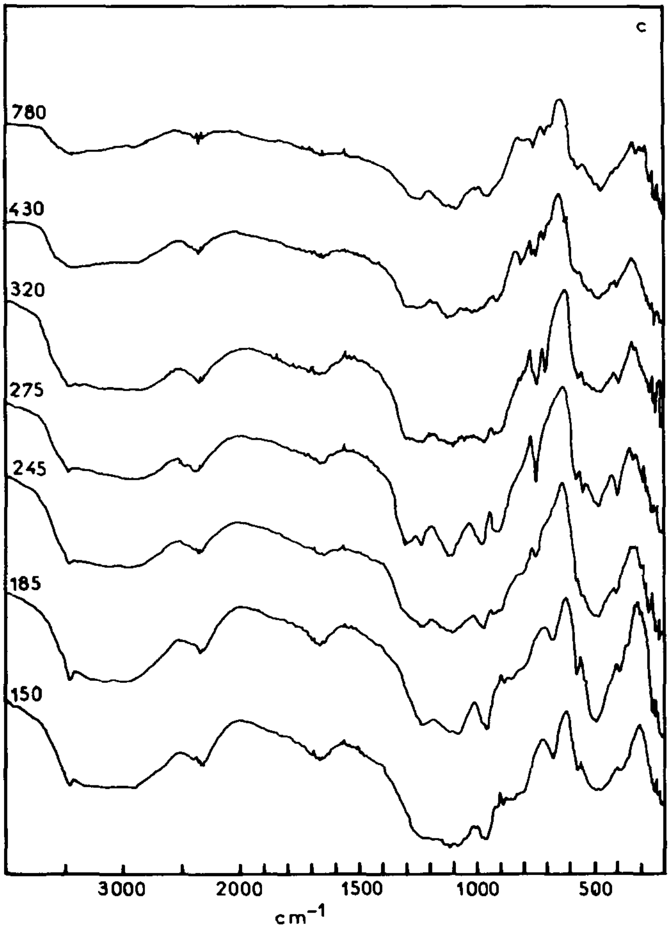


Fig. 3. (*Continued*).

The absorption bands of the acidic phosphoric group P–OH appear with a very broad band at 3200–2850 cm^{-1} (stretching), 1400–1200 cm^{-1} (δ) and at around 950 cm^{-1} (stretching), and are quite distinct up to 430°C. The absorption bands in the regions 3200–3050 cm^{-1} (stretching), approx. 1300 cm^{-1} (δ) (which are more distinct at 275–430°C) can be attributed to vibrations of the POH groups of $Si(HPO_4)_2$ [15].

The vibrations of the middle groups O–P–O (PO_2) of the poly- and metaphosphates which appear at 1300–1030 cm^{-1} overlap with those of the PO_3 terminal groups at 1200–1000 cm^{-1} (ν_{as}, ν_s). The absorption in the region approx. 670 cm^{-1}, which is attributed to the δ(PO) vibration mode of $Si(HPO_4)_2$ [15], appears up to 245°C. At temperatures 275 and 320°C, these absorptions are shifted to approx. 740 cm^{-1}, and for $R = 0.5$ and 1 at 430 and 780°C are split into two absorptions which are attributed to ν_s

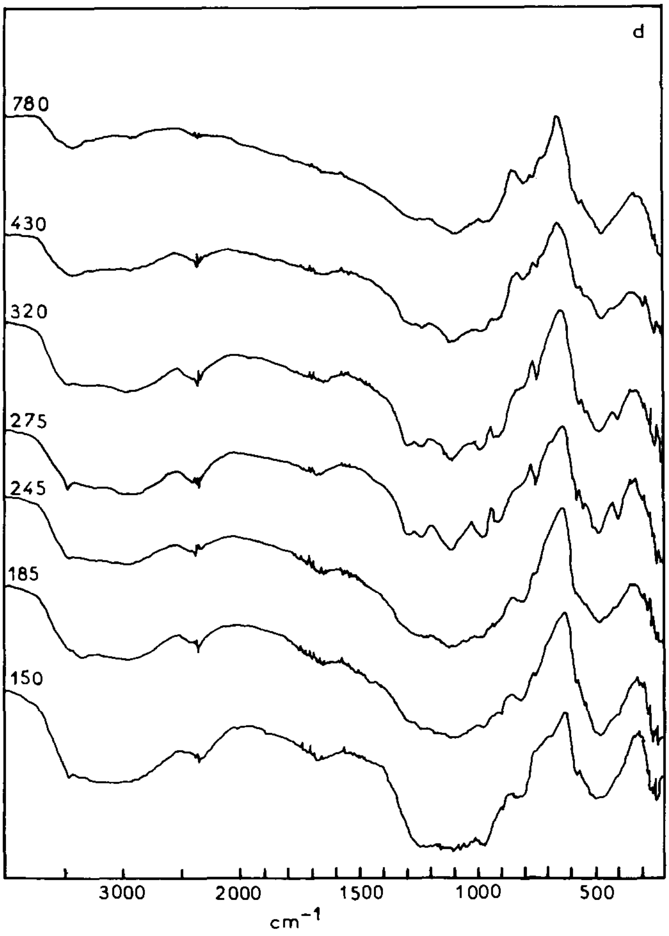


Fig. 3. (*Continued*).

of the POP groups of SiP_2O_7 [15]. This shows that $Si(HPO_4)_2$ is produced at the lower temperature, and, at higher temperatures, is concentrated into SiP_2O_7

$$Si(HPO_4)_2 \rightarrow SiP_2O_7 + H_2O \tag{5}$$

The absorption bands of the P–O–P bridging groups of the poly- and metaphosphates appear at 710–680 cm^{-1} (ν_{as}, ν_s) and they become more apparent above 320°C and much more distinct at 780°C. The reaction between SiO_2 and liberated H_3PO_4 would be expected to form new bonds and the absorption band of P–O–P appears at 1030 cm^{-1}, while the absorption band of the P–O–Si group would be expected in the region from 1098 to 1123 cm^{-1}, which is similar to the absorption band of the Si–O–Si group [16].

The absorption bands of amorphous SiO_2 (Fig. 3a) are in the regions 1107, 800 (ν_s), 467 (δ) and 419 cm^{-1}. The first three are characteristic of anhydrous amorphous silica

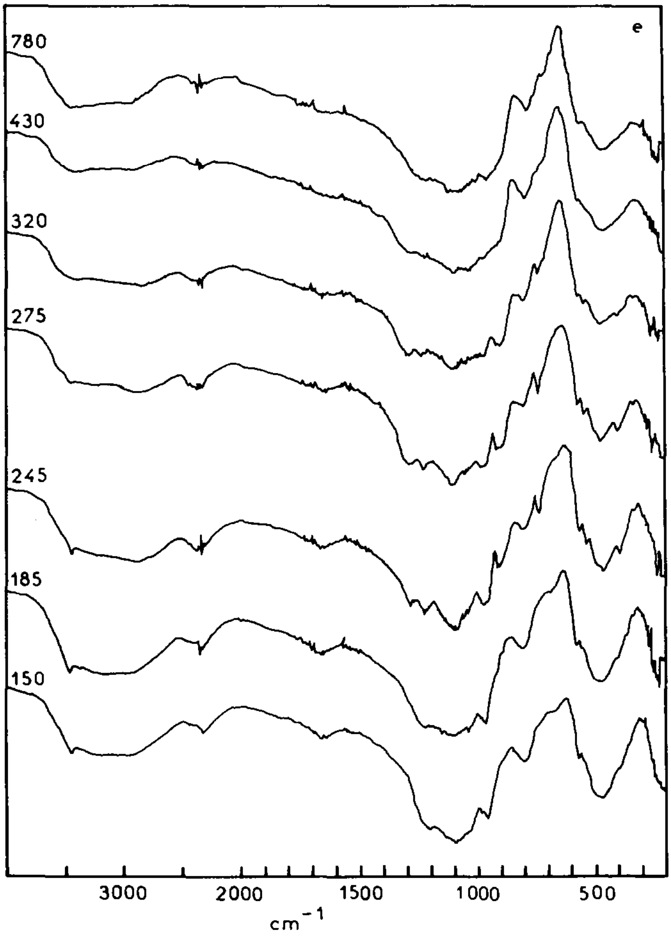


Fig. 3. (*Continued*).

and the last (419 cm^{-1}) indicates the presence of cristobalite [17]. The very broad band at 800 cm^{-1}, which does not overlap with the phosphate bands, for $R=0.5$ and 1, is virtually absent and appears again after 320°C as a very narrow absorption which is attributed to the γ(SiO) vibrations of SiP_2O_7 [15]. This confirms that reaction (5) takes place.

4. Conclusions

The dehydration of the $Ca(H_2PO_4)_2.H_2O–SiO_2$ system occurs in five stages and the amount of SiO_2 affects the removal of water molecules, generally, at lower temperatures. The mass loss of the first, second and fourth stages was increased, and that of the third and fifth stages was decreased as the amount of SiO_2 was increased.

Table 2
The water molecule removal (W_H) per molecule of CP of the mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$ (CP) with amorphous SiO_2 (S) and the maximum transformation temperatures (T_{max}/°C) from the TG and DTG curves

Stage	Molar ratio R = S/CP									
	0[a]		0.5		1		2		3	
	W_H	T_{max}	W_H	T_{max}	W_H	T_{max}	W_H	T_{max}	W_H	T_{max}
1	1.01	147	1.05	153	1.04	152	1.10	158	1.19	158
2	1.08	193	1.09	190	1.10	191	1.30	193	1.61	196
3	2.22	254	2.30	252 271	2.26	252 271	2.20	251	2.10	251
4	2.48	303	2.51	305	2.58	301	2.59	307	2.66	314
5	3	416	3	410	3	404–422	3	419	3	411

[a] From Ref. [3].

The dehydration process seems to take place by two mechanisms. One is the individual dehydration of the phosphate raw material via the production of pyro- and triphosphates as intermediate products, with the final product being δ- metaphosphate. This produces crystalline materials.

The other mechanism is the reaction of phosphates, possibly the free H_3PO_4 produced by the mechanism described above, with amorphous silica. At lower temperatures, the product was $Si(HPO_4)_2$, which at higher temperatures decomposed to SiP_2O_7. These products are amorphous.

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