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Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems

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Struvite, an important reaction product in magnesium ammonium phosphate cement systems, was synthesized in the laboratory. The elevated-temperature dehydration and then room-temperature hydration characteristics of the dehydrated products were studied by thermogravimetric analyses and X-ray diffraction techniques. From isothermal experiments, struvite is found to be thermally unstable in air at temperatures above 50 °C. Struvite can lose part or all of its ammonia and water molecules depending on the time and temperature of heat treatment, ultimately forming magnesium hydrogen phosphate. This decomposed product is X-ray amorphous and upon room-temperature rehydration can form struvite, unknown hydrates or newberyite, alone or in combination with each other, depending on the amount of ammonia left in the structure. However, when struvite is heated in excess water, it only loses its water of crystallization to form the monohydrate, dittmarite. Dittmarite is thermally more stable than struvite and like struvite also forms magnesium hydrogen phosphate on decomposition. At room temperature and in the presence of excess water, dittmarite can slowly transform to the hexahydrate, struvite. The consequence of structural similarities between struvite and dittmarite and conditions under which they may be present in cured cements are described.

1. Introduction

Crystalline magnesium ammonium phosphate hydrates frequently form as unwanted insoluble impurity phases in liquid fertilizers during ammoniation of merchant-grade phosphoric acids [1]. A few of them also form as final reaction products when magnesium phosphate-based cement systems designed for dental or rapid road-repair work react with water at room temperature [2]. The major reaction product in all these cement systems has always been identified as the hexahydrate, struvite ($NH_4MgPO_4 \cdot 6H_2O$). However, lower hydrates, namely the monohydrate, dittmarite ($NH_4MgPO_4 \cdot H_2O$) and the tetrahydrate, schertelite [$(NH_4)_2MgH_2(PO_4)_2 \cdot 4H_2O$] have also been reportedly identified in these systems in small quantities. Based on these observations, various investigators have proposed reaction schemes when magnesium oxide (MgO) reacts with monoammonium dihydrogen phosphate ($NH_4H_2PO_4$) in the presence of water [2]. Dittmarite and/or schertelite have been postulated to form as intermediate reaction products before they transform to the more stable hexahydrate, struvite.

The setting reactions of magnesium phosphate-based cement systems are very rapid and exothermic. If proper care is not adopted, the adiabatic accumulation of heat in a massive cement pour can raise the temperature quite easily above the boiling point of water. This rise in temperature has been blamed for job failures due to the loss of compressive strength in these systems [3]. Thus, it is important to study the thermal stability of the reaction products of these systems.

A systematic investigation was carried out in our laboratory to understand the phase relationships of various reaction products in these cementitious systems at different temperatures. In this paper, the hydration/dehydration behaviour of struvite at various temperatures up to the boiling point of water, and the mechanism of its transformation to dittmarite, are reported.

2. Experimental procedure

Struvite was synthesized in the laboratory by mixing solutions of reagent-grade magnesium nitrate and ammoniacal ammonium dihydrogen phosphate with each other. The fine white precipitate that formed after the reaction was allowed to settle at room temperature for 15 min before it was filtered under suction. The precipitate was thoroughly washed several times with deionized water to free it from any nitrate and phosphate ions. The white residue was finally washed with acetone and dried under suction to remove the last traces of water. The semi-dry solid struvite was then

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transferred to a Petri dish and allowed to dry completely in air at room temperature.

Powder X-ray diffraction (XRD) was carried out on a computer-controlled Rigaku Rotaflex system using nickel-filtered Cu$K\alpha$ radiation and a graphite monochromator at a scan rate of 2° (2θ) min^{-1}.

The thermogravimetric analysis (TGA) work was performed on a DuPont 2100 Thermal Analysis system and also on a Perkin Elmer 1700 DTA unit under static air and at a heating rate of 5 °C min^{-1}. System software on both instruments permitted the conversion of the TGA curve to its derivative mode (DTGA) by providing a rate of weight loss curve as a function of temperature.

The room-temperature infrared (IR) spectra for selected samples were recorded in the wavenumber range of 400 to 4000 cm^{-1} on a Nicolet Model 740 FTIR spectrophotometer using the standard KBr disc technique.

Deionized water was used throughout the study.

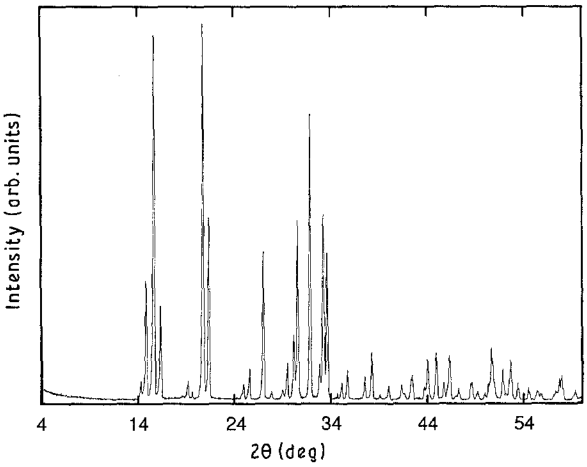

Figure 1 Powder XRD pattern for synthetic struvite.

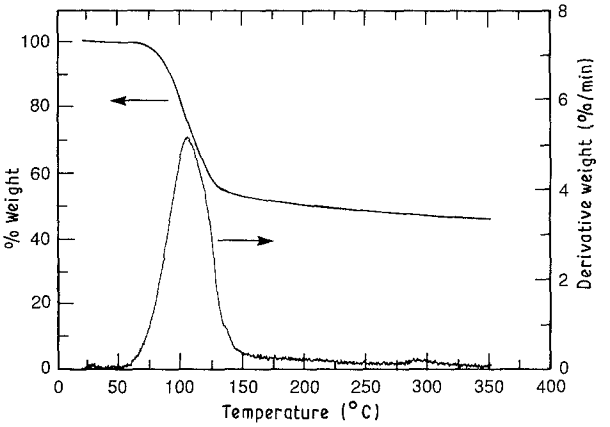

Figure 2 TGA/DTGA curves for synthetic struvite.

3. Results and discussion

The powder XRD pattern of synthetic struvite shown in Fig. 1 matches very well with that of the published pattern for struvite and is thus considered to be a single-phase material. The TGA/DTGA curves for this struvite are also shown in Fig. 2, where the DTGA curve shows a large weight loss peak at ~106 °C and is assigned to be the characteristic decomposition temperature for struvite. However, it can also be noticed in Fig. 2 that the weight loss begins to start at a temperature of ~55 °C and is complete when the temperature reaches ~250 °C. At this point, the actual weight loss is estimated as ~50% of the original weight and this weight loss corresponds to the following decomposition reaction for struvite:

$$NH_4MgPO_4{\cdot}6H_2O \rightarrow MgHPO_4 + NH_3\uparrow + 6H_2O\uparrow$$

The simultaneous loss of both NH_3 and H_2O molecules from the struvite structure presumably occurs gradually as a function of temperature rather than at distinct steps. Otherwise, double peaks would have appeared in the corresponding DTGA curve.

To study the isothermal decomposition/dehydration characteristics of struvite, it was subjected to various isothermal heat treatments in a temperature-controlled electric oven at temperatures ranging from 50 to 98 °C for different lengths of time. The samples after each heat treatment were analysed by XRD and TGA/DTGA techniques. It was observed that struvite lost adsorbed water only when heated at 50 °C for 5 days without showing any sign of decomposition. However, struvite appeared to be unstable at higher temperatures starting from 55 °C. The TGA/DTGA curves for struvite samples heat-treated at different temperatures for various lengths of time are shown in Fig. 3. The crystallinity of the final products as determined by XRD is also shown on these figures. An analysis of these figures clearly shows that depending on the temperature and/or length of the heat treatment, struvite can be rendered totally X-ray amorphous. Whenever the product is partly crystalline, the signature of the crystalline struvite pattern is still preserved and superimposed on a broad amorphous hump in the XRD pattern. But dittmarite was never detected by XRD in any of the heat-treated samples. It is thus conceivable that struvite starts to become X-ray non-crystalline as soon as NH_3 and H_2O molecules are expelled from its crystal structure, resulting in weight loss. The non-crystallinity of the resultant products is also characterized by a broad peak in the DTGA curves. If struvite is only partially amorphized (as at 70 °C for 1 h, Fig. 3b), the decomposition peak is shifted towards lower temperatures. Thus, the struvite decomposition temperature is affected by the degree of crystallinity or the crystallite size. Similarly, the decomposition peak shifts towards lower temperature as the amorphization temperature increases up to ~ 80 °C, after which it appears to remain constant.

Interesting results were obtained when the thermally treated struvite samples were rehydrated at room temperature in excess water. Depending on the thermal history, a few new phases (unknown and newberyite) in addition to struvite are formed. Typical TGA/DTGA curves for two selected rehydrated samples are shown in Fig. 4. Based on these experiments, it can be predicted that upon rehydration, struvite will only form if some NH_3 molecules are still present in the structure. Surprisingly, this was the case

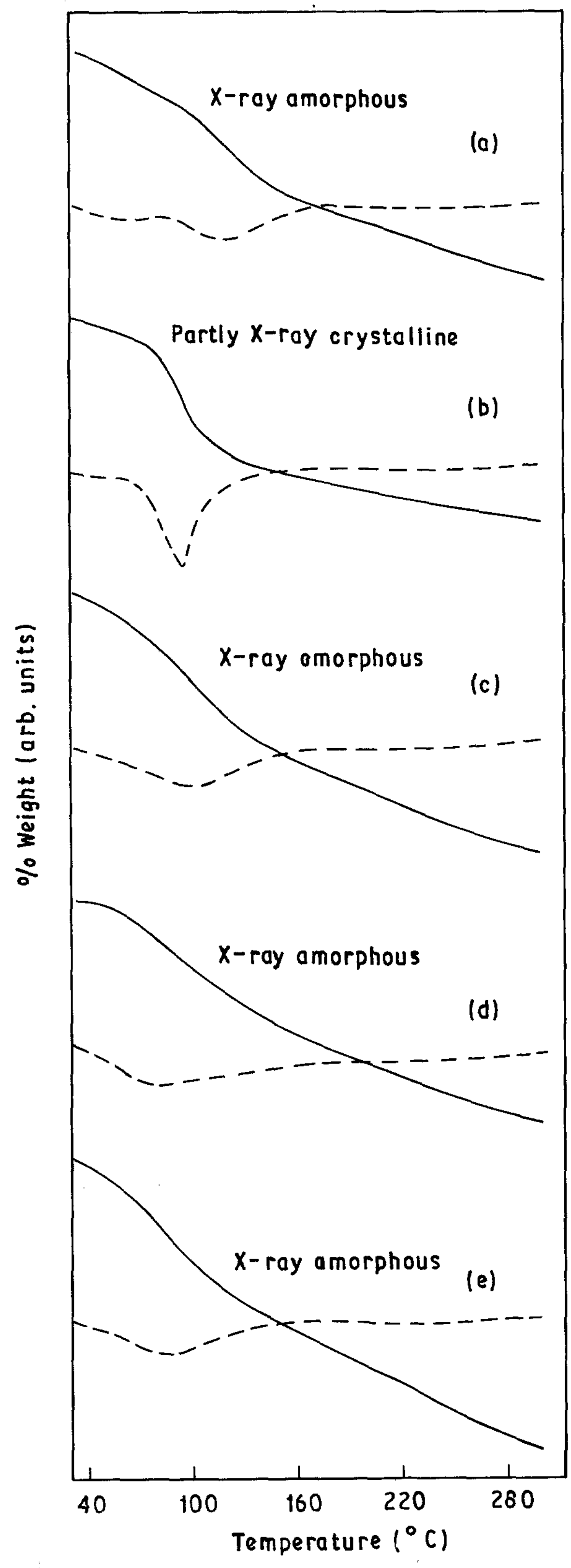

Figure 3 TGA/DTGA curves for synthetic struvite heated at (a) 55 °C for 4 days, 18 h; (b) 70 °C for 1 h; (c) 70 °C for 3 h; (d) 83 °C for 2 h; and (e) 98 °C for 2 days, 12 h.

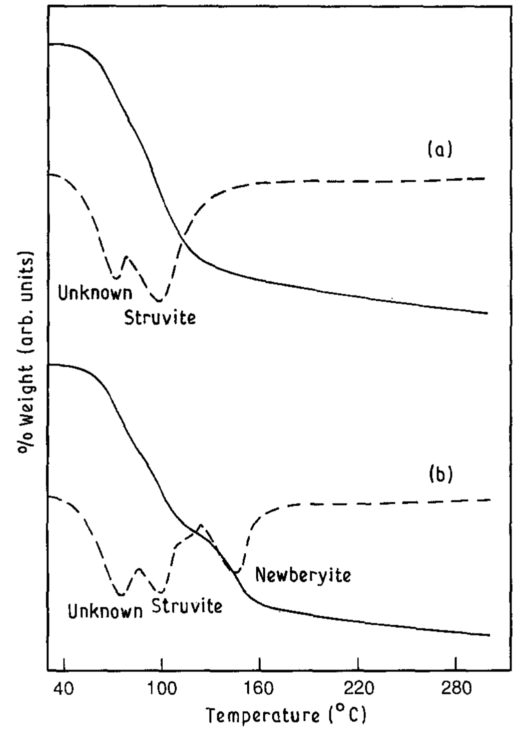

Figure 4 TGA/DTGA curves for hydrated samples of Fig. 3: (a) sample of Fig. 3a rehydrated for 1 h and (b) sample of Fig. 3e rehydrated for 5 days.

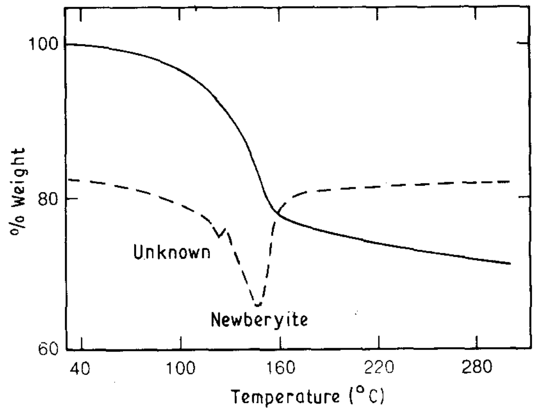

Figure 5 TGA/DTGA curves for the sample of Fig. 4b heated at 55 °C for 20 h.

for the sample of Fig. 3e, since some struvite still formed upon rehydration of this sample, as noticed in Fig. 4b. It was not possible to determine if the unknown phase decomposing at a temperature lower than that of struvite contained any ammonia. In any case, formation of both struvite and newberyite in a rehydrated sample (Fig. 4b) shows the complex character of thermally amorphized struvite which is probably biphasic. When this rehydrated sample (of Fig. 4b) is again dehydrated at 55 °C for 20 h, the low-temperature unknown phase and struvite are no longer detectable in its TGA/DTGA curves (Fig. 5). Newberyite and a new unknown phase, being more stable than struvite, are not affected by this heat treatment. Furthermore, dittmarite could not be detected in any of these rehydrated samples by the XRD technique.

Although struvite is the main reaction product in commercial magnesium phosphate cement systems, sometimes the monohydrate, dittmarite, also forms in these systems. Thus, further investigation was carried out with synthetic struvite to explore the conditions under which this elusive dittmarite phase can form in these cement systems. Frazier *et al.* [1] have reported observing the formation of dittmarite in ammoniated magnesium-contaminated merchant-grade phosphoric acids at higher temperatures.

When struvite was boiled in excess water, the final product was found to be completely converted to dittmarite, depending on the time of boiling. It was also discovered that single-phase dittmarite could be synthesized in the laboratory in the same manner as described earlier for struvite, except that the two solutions had to be mixed at boiling temperatures. The powder XRD pattern and TGA/DTGA curves for synthetic dittmarite are shown in Figs 6 and 7, respectively. The weight loss curves in Fig. 7 clearly show that dittmarite is more stable than struvite and its decomposition temperature is ~221 °C. The small peaks appearing below ~150 °C in the DTGA curve of Fig. 7 are due to a small amount of impurities not detectable by the X-ray technique. The percentage weight loss obtained from Fig. 7 corresponds to the decomposition of dittmarite via the following reaction scheme:

$$NH_4MgPO_4 \cdot H_2O \rightarrow MgHPO_4 + NH_3\uparrow + H_2O\uparrow$$

Since only one large weight loss peak appears in the DTGA curve for dittmarite, its dehydration and/or decomposition behaviour appears to be very similar to that of struvite as discussed earlier, i.e. through simultaneous expulsion of both NH_3 and H_2O molecules. In spite of this similarity, struvite and dittmarite decompose at two widely different temperatures.

To study the room-temperature hydrolytic stability of dittmarite, powdered dittmarite was placed in deionized water for various lengths of time and the resulting solid after drying was examined by the XRD technique. It was observed that dittmarite slowly hydrated and transformed to the more stable hexahydrate, struvite, with time. An XRD pattern for dittmarite hydrated for 24 h at room temperature is shown in Fig. 8. This figure shows the gradual transformation of dittmarite to struvite, representing a mixed-phase X-ray pattern.

The difference in chemical composition and thermal stability between struvite and dittmarite is related to the nature of various bonds present in their crystal structures, and may be observed in their IR spectra. The room-temperature IR spectra for struvite and dittmarite are shown in Fig. 9. As can be seen in this

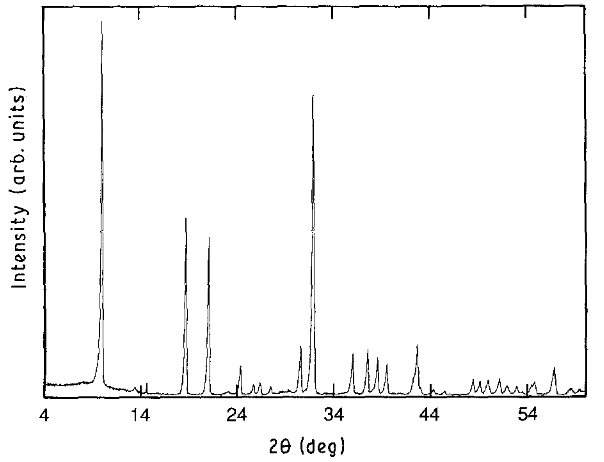

Figure 6 Powder XRD pattern for synthetic dittmarite.

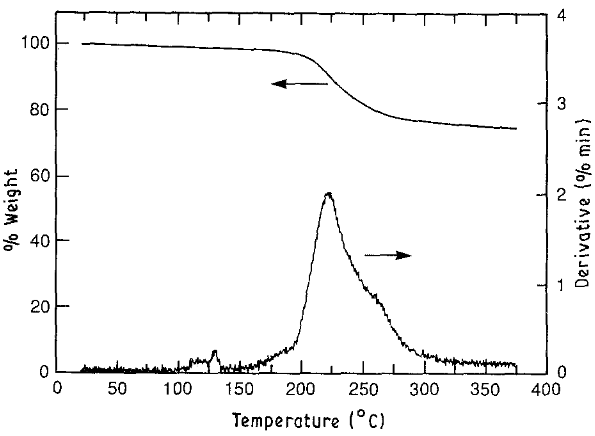

Figure 7 TGA/DTGA curves for synthetic dittmarite.

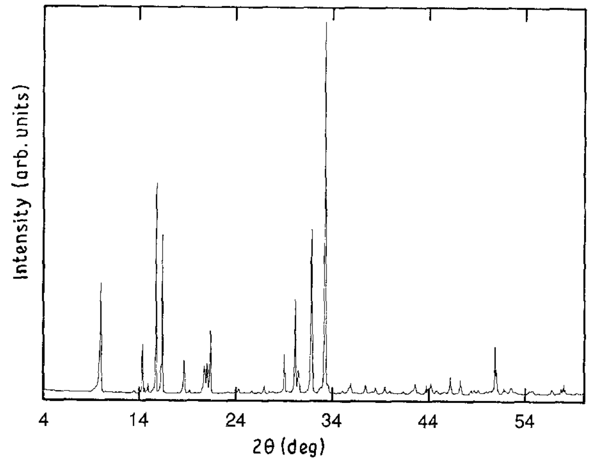

Figure 8 Powder XRD pattern for dittmarite hydrated for 1 day.

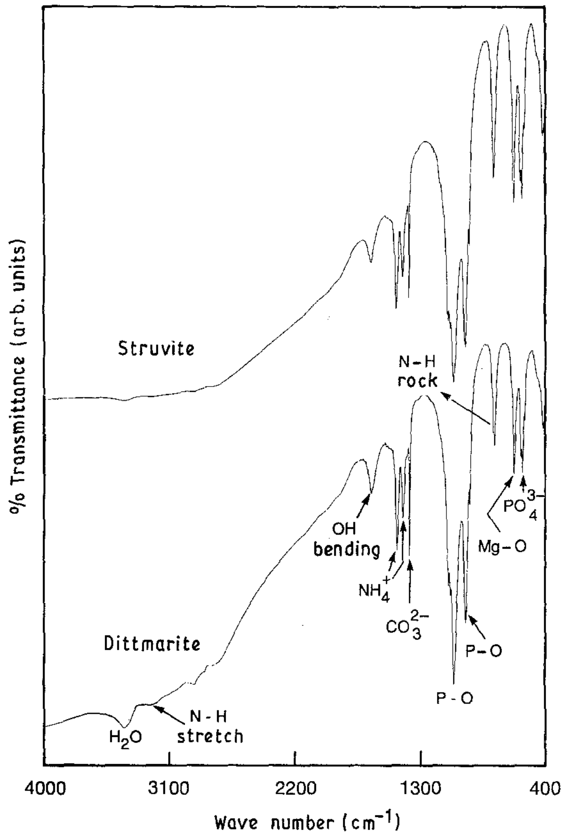

Figure 9 Transmission IR spectra for synthetic struvite and dittmarite.

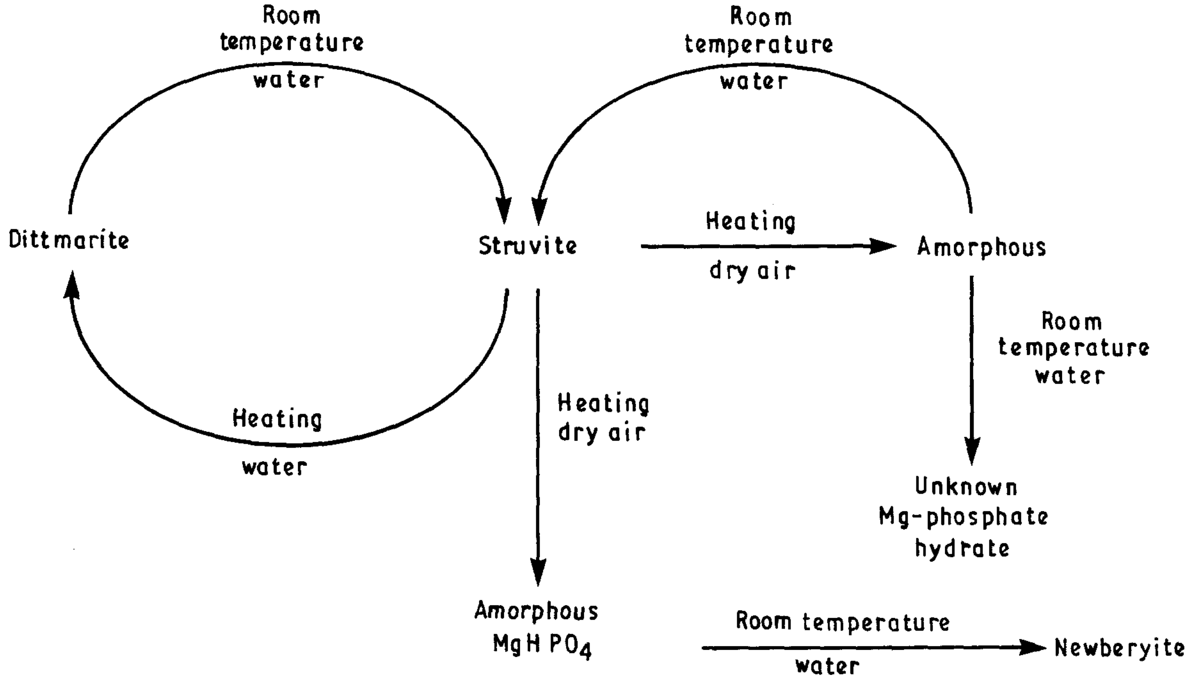

Figure 10 Schematic diagram of the reaction mechanisms and relationships among various products studied and identified during the present study.

figure, the two spectra match very closely and virtually no shift is observed in the position of any peak. The vibrations due to the P–O–P linkage characteristic of the orthophosphate ion are observed in both patterns at ~1000 and ~580 cm^{-1}. Thus, the two compounds seem to be structurally related especially in terms of the nitrogen and the hydroxyl groups, and the difference might be in the way the extra water molecules are linked. These extra water molecules make the struvite structure thermally less stable than dittmarite.

4. Summary and conclusions

From the foregoing discussion it is postulated that crystalline struvite decomposes, giving off NH_3 and H_2O molecules, starting from a temperature of 55 °C in air. Thus, struvite is thermally stable up to this temperature. However, the resultant decomposition product is X-ray amorphous and chemically corresponds to $MgHPO_4$ as determined by weight loss measurements via TGA. The dehydrated struvite, upon rehydration, will form newberyite if all the NH_3 molecules are lost from the structure. Otherwise, depending on the relative proportion of the ammonium ions left in the structure, it can rehydrate back to struvite at room temperature.

On the other hand, when struvite is heated to higher temperature in the presence of excess water, it loses five water molecules from its structure and forms the monohydrate, dittmarite. Dittmarite can also pick up extra water molecules at room temperature and can reversibly transform to struvite. It thus appears that the presence of excess water or very moderate hydrostatic pressure can prevent the loss of NH_3 molecules from struvite. In other words, struvite is more stable in water than it is in air. The hydration/dehydration characteristics of the struvite–dittmarite pair as determined in this study can be expressed schematically and are shown in Fig. 10. The exact temperature at which struvite decomposes to dittmarite was not measured accurately and is estimated to be ~60 °C.

Finally, this study was not intended to delineate the mechanisms of setting reactions in the magnesium phosphate cement systems. None the less, important clues are provided as to the nature of reaction products that are sometimes detected in these systems. It is shown that the ultimate nature of reaction products in these rapid-setting magnesium phosphate-based cement systems will depend on many job- and curing-related factors.

Acknowledgement

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