JOURNAL OF MATERIALS SCIENCE 14 (1979) 365–370

The microstructure and infra-red spectra of hydrated tricalcium silicate containing phosphate

LINA BEN-DOR, YAACOV RUBINSZTAIN*
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

The influence of phosphate, in the concentration range 0.7 to 4.5%, on the hydration reaction of tricalcium silicate was examined with a scanning electron microscope and an infra-red spectrometer. Correlation between the morphology and infra-red vibrations, on the one hand, and the free lime content dependence on the phosphate concentration, on the other, is discussed.

1. Introduction

Since the pioneering work of Nurse [1] it was known that P_2O_5 forms a solid solution with dicalcium silicate (C_2S†) of the cement clinker and reduces the content of tricalcium silicate (C_3S). Consequently the early strength falls as the P_2O_5 increases. Obviously, the free lime content also increases when C_3S containing phosphate "decomposes" to C_2S as is seen from the phase diagram of the system C_2S–C_3P–CaO (see e.g. [2]). The earlier studies of Nurse and of Gutt and their co-workers [1, 3, 4], the comprehensive review of Steinour [5] on the subject, covering the period between 1942 and 1956, and the more recent reports presented in Tokyo 1968 [6] all give an account of the phase equilibria of Portland cement minerals in presence of phosphate, the setting times and strengths of the hydrated material.

A more recent study of phosphatic Portland cements was presented in Moscow 1974 [7, 8] and continuous conduction calorimetry was used to follow the heat evolution especially at early ages. It was found that not more than 2.5 per cent P_2O_5 could be tolerated in Portland cement, as above this limit, setting times become too long and early strength very low.

It seemed useful to correlate these findings with the behaviour of C_3S in presence of phosphate by microscopy and vibrational spectrometry. A thermal (TG and DTA) study has been reported elsewhere [9]. A great many microscopic observations have been made on neat C_3S paste [10], but none on phosphate C_3S. The same is true for infra-red spectra.

2. Experimental procedure

2.1. Materials

Neat C_3S was prepared from $CaCO_3$ and SiO_2 [10]. The various minerals were prepared by introducing appropriate amounts of $Ca_3(PO_4)_2$ into the calcite–silica mixture before the treatment to 1550° C. The four minerals were thus prepared to contain 0.7, 1.5, 2.25 and 4.5% P_2O_5‡. The chemical analysis showed the P_2O_5 content to be within 0.1% of the calculated amount.

2.2. Preparation of samples

The samples were prepared by treating the minerals with water in a water/solid ratio of 0.5. The pastes were divided into different well-stoppered vials. At different "ages" from 6 h to 85 days, the hydration process was interrupted by breaking the "stone", washing it several times with cold acetone

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*This paper is in partial fulfilment of the MSc degree of Y. Rubinsztain, at the Hebrew University.
†$C = CaO$; $S = SiO_2$; $H = H_2O$; $C_2S = 2CaO \cdot SiO_2$; $C_3S = 3CaO \cdot SiO_2$; C–S–H = calcium silicate hydrate.
‡Percentages by weight.

Figure 1 C_3S–0.7% P_2O_5 hydrated 7 days (× 14 000).

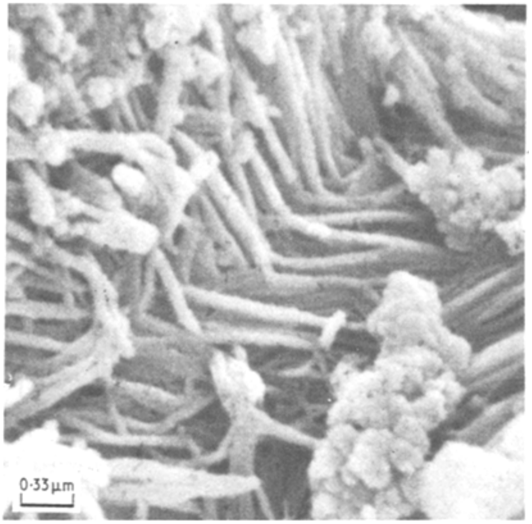


Figure 3 C_3S–0.7% P_2O_5 hydrated 85 days (× 21 000).

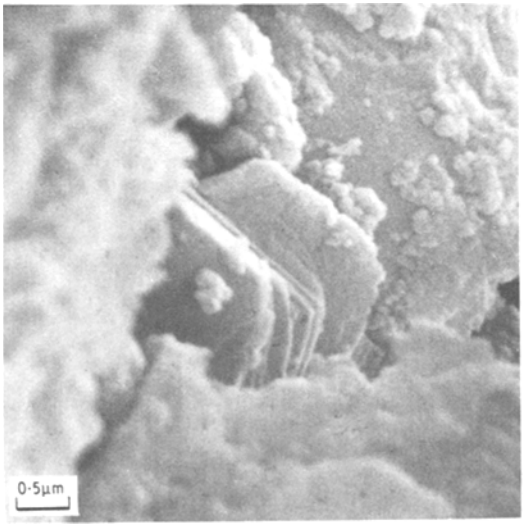


Figure 2 C_3S–0.7% P_2O_5 hydrated 28 days (× 14 000).

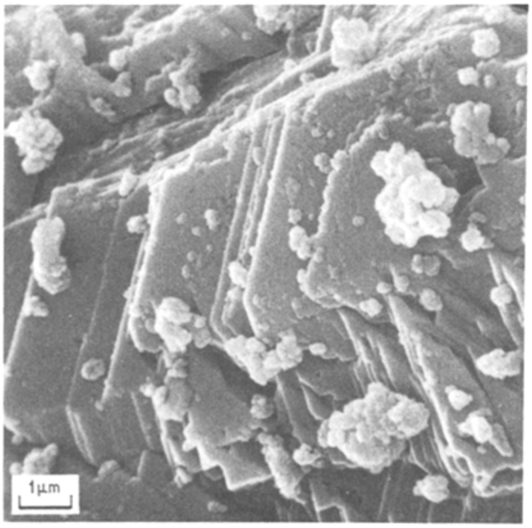


Figure 4 C_3S–0.7% P_2O_5 hydrated 85 days (× 7000).

and storing under vacuum until measurements were performed.

2.3. Methods of investigation

A stereoscan S4 of Cambridge Scientific Instruments was used. The samples were coated with a conductive layer of gold before scanning.

A Perkin–Elmer 457 grating infra-red spectrophotometer was used, with a pure 200 mg KBr disc in the reference beam. The KBr sample discs containing 1% of the ground minerals were produced by vacuum die and under pressure of 9 t cm^{-2}.

3. Results and discussion

3.1. Scanning electron microscope

The hydration products of C_3S are two: hexagonal plates of $Ca(OH)_2$ and acicular needles or honeycomb morphology of C–S–H gel ([10] and references therein). The C–S–H produced from C_2S is much the same chemically and morphologically as that produced from C_3S. A high concentration of phosphate is bound to affect the morphology of the hydration products.

Fig. 1 is a 7 day hydration of C_3S containing 0.7% P_2O_5. Notwithstanding the early stage of

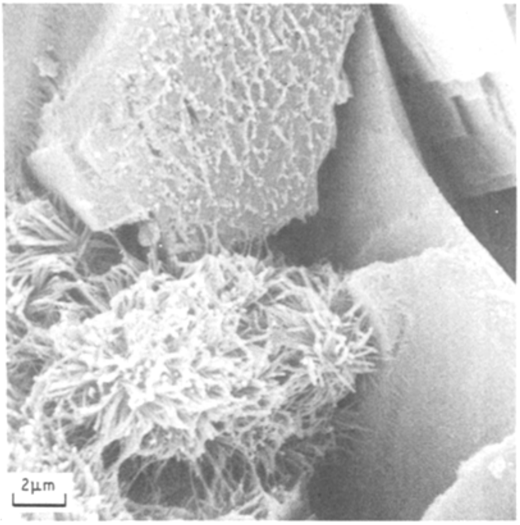


Figure 5 C_3S–1.5% P_2O_5 hydrated 85 days (X 3500).

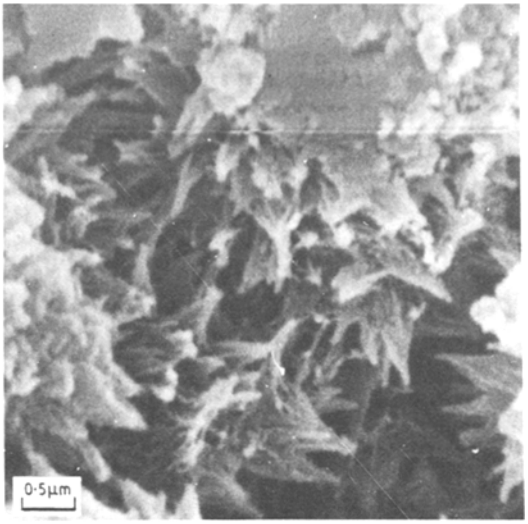


Figure 7 C_3S–2.25% P_2O_5 hydrated 7 days (X 14 000).

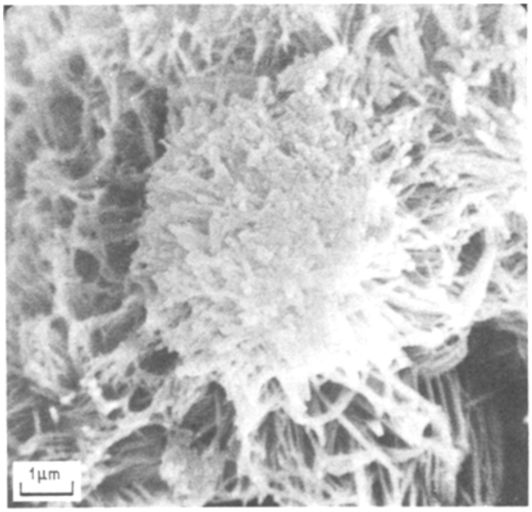


Figure 6 C_3S–1.5% P_2O_5 hydrated 85 days (X 7000).

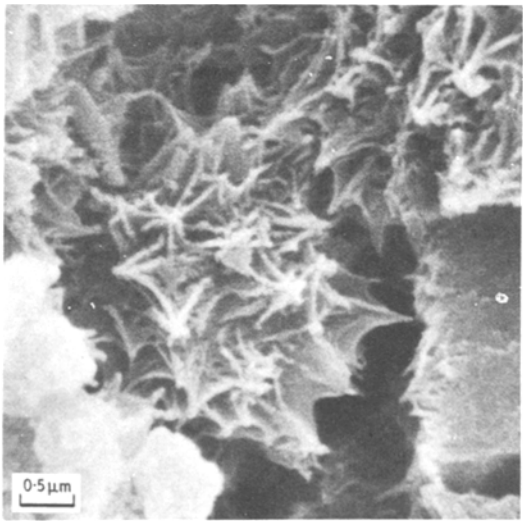


Figure 8 C_3S–2.25% P_2O_5 hydrated 14 days (X 14 000).

hydration, many plates of $Ca(OH)_2$ are clearly visible (enlargement 14 000 x). Fig. 2 (14 000 x) shows in the centre typical plates while the hydrated gel is starting to form (not in focus), after 28 days hydration. After 85 days, Fig. 3, the fibres (magnification x 21 000) of the "sponges" in between two $Ca(OH)_2$ plates (not visible in the picture) are seen, and Fig. 4 shows again the parallel hexagonal plates (7 000 x). Much the same morphology is seen for hydrated C_3S containing 1.5% P_2O_5. However, the bulk of the $Ca(OH)_2$ plates nearly covers the whole field of view. This is due, of course, to the high free lime content of the mineral which hydrates much faster than neat C_3S and is present in large amounts owing to the comparatively high P_2O_5 content. Fig. 5 shows the "honeycomb" C–S–H and the thick $Ca(OH)_2$ plates (3500 x) for 85 days hydration of C_3S–1.5% P_2O_5, and Fig. 6 is a detailed view of the sponge (7000 x). For minerals containing more than 1.5% P_2O_5 a morphology hitherto unobserved appears; instead of the delicate long fibres of C–S–H a "star-like" morphology appears. Figs. 7 and 8 show 7 day and 14 day hydration of C_3S–2.25% P_2O_5 (14 000 x) with the "stars" well characterized. Fig. 9 (7000 x) shows a rare view of the sponges (as well as the plates) and Fig. 10 which is a 2 x enlargement of the former shows clearly the appearance of an unhydrated grain for a mineral

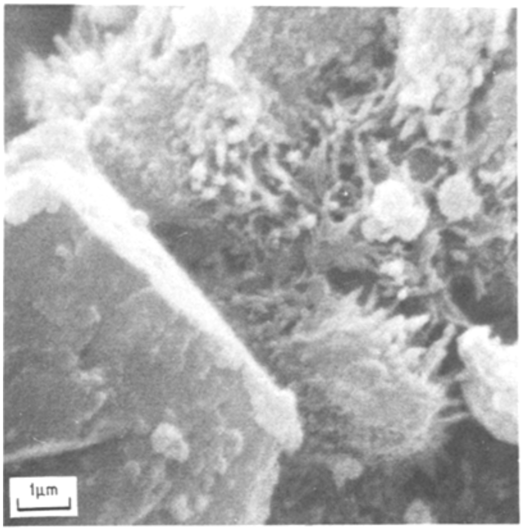


Figure 9 C_3S–4.5% P_2O_5 hydrated 28 days (× 7000).

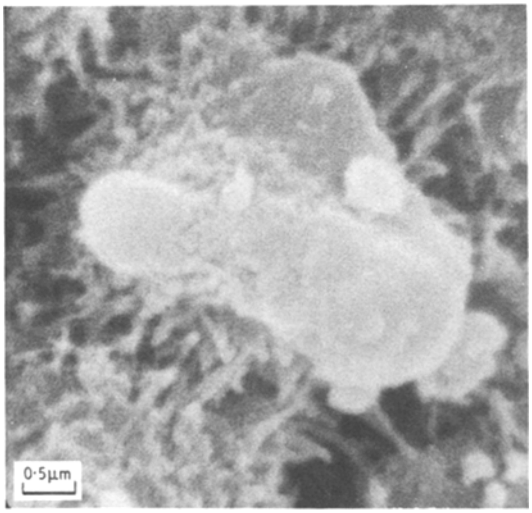


Figure 10 C_3S–4.5% P_2O_5 hydrated 28 days (× 14 000).

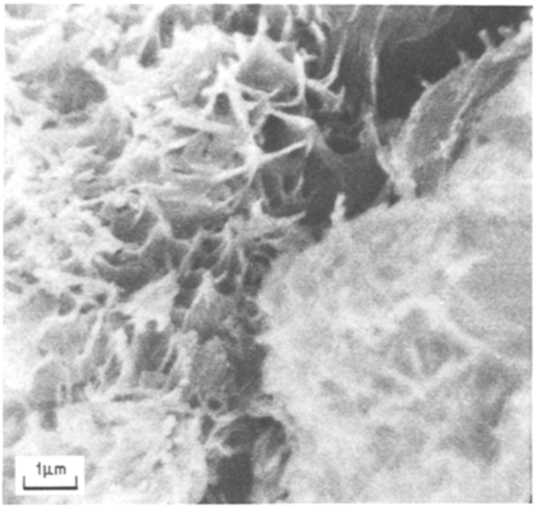


Figure 11 C_3S–4.5% P_2O_5 hydrated 85 days (× 7000).

containing 4.5% P_2O_5 (after 28 days hydration). Fig. 11 (7000 x) shows the morphology of the C–S–H after 85 days hydration.

Thus the morphology is clearly consistent with what has been observed for strength development of Portland cement with a high phosphate content (>0.4%):

(1) P_2O_5 tends to decompose C_3S liberating free lime which is clearly observed even for young hydration ages; the accumulation of the plates and their thickness being dependent on the initial phosphate concentration.

(2) There is less fibrous C–S–H material formed as a function of P_2O_5 content. Less C–S–H formed means lower strength of the structure.

(3) High P_2O_5 content ($\geqslant$2.25%) modifies the morphology to show a "star-like" structure instead of the "sponges" or "honeycombs".

(4) $Ca(OH)_2$ plates are never observed in the case of admixtures which accelerate the hydration of the neat mineral. Here, these plates are formed as a result of initial free lime and the retarding effect of P_2O_5.

3.2. Infra-red spectra

The hydrated minerals display two main regions of i.r. absorption: the OH stetching vibrations region between 3700 and 3200 cm^{-1} and the Si–O stretching vibrations of the SiO_4 group regions at between 1000 and 800 cm^{-1} and at 500 cm^{-1}. The behaviour of hydrated neat C_3S and β-C_2S in the i.r. have been discussed earlier [11].

The dry mineral containing 0.7% P_2O_5 already contains some free lime ($\approx$7% according to TG measurements) as is observed by the OH stretching vibration of $Ca(OH)_2$ at 3650 cm^{-1}. With hydration time this sharp band grows and simultaneously with it develops a broad shallow band due to associated OH, in the region 3550 to 3200 cm^{-1}. It is impossible to avoid some absorption of atmospheric CO_2 so that even the unhydrated minerals show a broad quite distinct band due to carbonate: 1500 to 1400 cm^{-1}. This band becomes more pronounced as the P_2O_5 concentration grows.

If one compares the OH vibrations of the

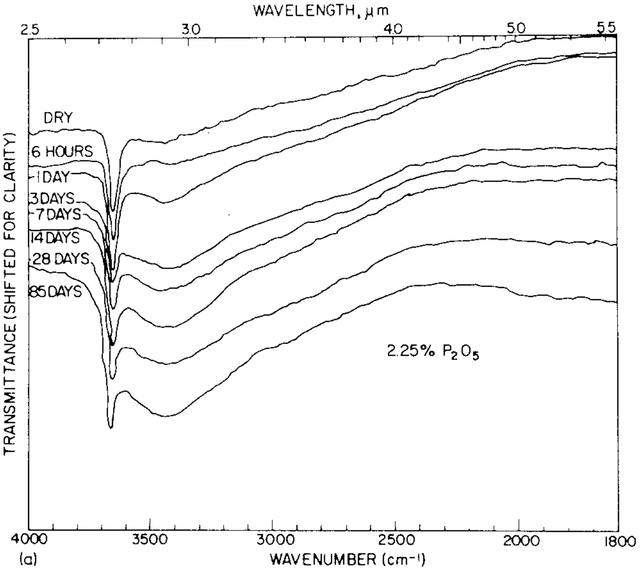
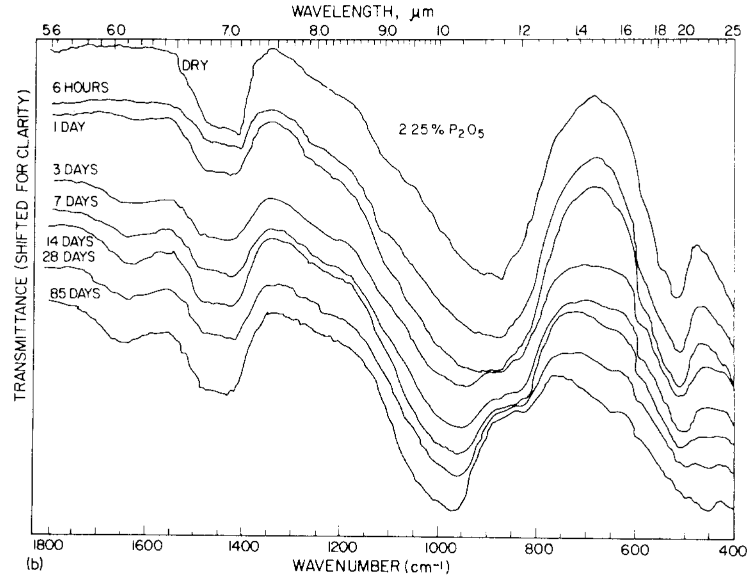


Figure 12 (a) Infra-red spectra of C_3S–2.25% P_2O_5 after 6 h to 85 days hydration in the range 4000 to 1800 cm^{-1}. (b) Infra-red spectra of C_3S–2.25% P_2O_5 after 6 h to 85 days hydration in the range 1800 to 400 cm^{-1}.



various minerals one clearly sees a dependence of their intensity with phosphate concentration, but for each mineral the intensity also grows with hydration time. This growth with age is less pronounced for minerals containing the highest P_2O_5 concentrations, namely, 2.25% and 4.5%, a result consistent with former thermal measurements, strength development of cement and the morphological aspects described above.

A weak ν_2 water band is detected at ≈ 1600 cm^{-1} for hydration times of 14 days and more for all minerals. In the higher energy region (valency vibration) of the Si–O stretch, the dry minerals show a wide intense absorption exhibiting some structure (four maxima) while in the lower energy region, deformation vibrations, a comparatively sharp strong band appears. With hydration age the valency vibrations lose intensity and structure and shift to higher energy: between 850 and 950 cm^{-1} to between 950 and 1050 cm^{-1}. At the same time the deformation vibrations become very broad and weak and practically disappear for 85 days hydration. These effects are caused by low crystallinity of the C–S–H gel formed and the association of the initial well-defined SiO_4 tetrahedra to larger structures. The vibrational spectra of one of the minerals containing 2.25% P_2O_5, as a function of hydration, is shown as an example in Figs. 12a and b.

In conclusion, the morphology and the i.r. analysis concur with the well-known harmful influence of phosphate on Portland cement and its minerals.

References

1. R. W. NURSE, *J. Appl. Chem.* 2 (1952) 708.
2. W. GUTT, Proceedings of the Fifth International Symposium on the Chemistry of Cement, 1968, Vol. I (The Cement Association of Japan, Tokyo, 1969) p. 93.
3. R. W. NURSE, J. H. WELCH and W. GUTT, *J. Chem. Soc.* (1959) 1077.
4. J. H. WELCH and W. GUTT, *ibid.* (1961) 4442.
5. H. H. STEINOUR, Portland Cement Association, Bull. 85 (1957).
6. Proceedings of the Fifth International Symposium on the Chemistry of Cement, (The Cement Association of Japan, Tokyo, 1969) 1968, Vol. I, pp. 77, 93 and 340.
7. Proceedings of the Sixth International Symposium on Chemistry of Cement, 1974.
8. W. GUTT and M. A. SMITH, BRE Current Paper CP 95/74.
9. L. BEN-DOR and Y. RUBINSZTAIN, *Thermochim. Acta* (to be published).
10. L. BEN-DOR and D. PEREZ, *J. Mater. Sci.* 9 (1974) 423.
11. *Idem, Thermochim. Acta* **12** (1975) 81.

Received 31 March and accepted 6 July 1978.