

THE INFLUENCE OF PHOSPHATE ON THE HYDRATION OF CEMENT MINERALS STUDIED BY DTA AND TG

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ABSTRACT

A thermal analysis study of the effect of phosphate, in the concentration range 0.7–4.5%, on the hydration reaction of $3 \text{CaO} \cdot \text{SiO}_2 (\text{C}_3\text{S})$ is reported. The results are compared with strength development of phosphate cement reported by Nurse.

INTRODUCTION

The concentration of P_2O_5 in most cements is in the 0.2–0.3% range, but phosphates may be present in larger amounts in the raw material used in the production of cement. In these cases the phosphate enters the clinker. Some standards (B.S.) allow up to 2.25% P_2O_5 in the cement, provided certain working procedures are maintained. Phosphate reduces strength development because it causes the partial decomposition of C_3S into C_2S (β -dicalcium silicate) and free-lime, and itself forms a solid solution P_{55} with the C_2S , depicted as $\text{P}_{55}\text{-C}_2\text{S}$. Nurse¹ showed that for every percent P_2O_5 present in cement, the concentration of C_3S is reduced by 9.9% and the C_2S , now in solid solution, grows by 10.9%. Since C_3S is the main strength-developing component in cement, its decrease and the subsequent increase in C_2S causes the overall decrease in strength development. These findings were later confirmed by Hartman and Haegerman² and by Steinour³. Simanovskaja and Vodzinskaja⁴ showed that it was possible to use clinker containing a high percentage of phosphate provided enough CaF_2 was added to the mixture. In all cases the CaF_2 caused a reduction in the free-lime content.

The aim of this study was to follow by thermal analysis the hydration of phosphate - C_3S and to correlate the results with those found earlier on phosphate cement strength development.

EXPERIMENTAL

Neat C_3S (A, Table 1) was prepared from CaCO_3 and SiO_2 at 1550°C as

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TABLE 1

P₂O₅ AND FREE-LIME CONTENT

<i>Mineral</i>	<i>P₂O₅ by wt. %</i>	<i>P₂O₅ chem. anal. %</i>	<i>Free-lime by TG (%)</i>
A	—	—	1
B	0.70	0.62	7
C	1.50	1.38	13
D	2.25	2.08	18
E	4.50	4.32	26

described before⁵. In the same manner, CaCO₃, SiO₂ and Ca₃(PO₄)₂ were ground and heated to obtain C₃S containing 0.7, 1.5, 2.25 and 4.5% P₂O₅ (B–E, Table 1). In all cases, ca. 15 g material was prepared. Chemical analysis was performed by standard procedures^{6, 7}: SiO₂ by gravimetry and colorimetry, CaO by EDTA, and P₂O₅ by colorimetry (molybdenum blue). The analytical results obtained are shown in Table 1.

1 g of the minerals A–E were treated with 0.5 g water. The pastes obtained were separated into different tightly stoppered vials and kept at room temperature. The hydration process was stopped at various stages by grinding the sample and washing several times with cold acetone. Since the samples contained growing amounts of free-lime, these were obtained by TG from minimal (experimental) hydration time (which never exceeded 2 min).

TG data were collected from a Stanton–Redcroft instrument. The sample (50 mg) was heated from room temperature to 800°C at a rate of 7° min⁻¹ under dry nitrogen. DTA curves were obtained with a micro analyzer of BDL. The rate maintained was ≈ 5° min⁻¹ in air from ambient temperature to 800°C. The sensitivity was 1–2 μV/recorder span.

RESULTS AND DISCUSSION

There are two hydration products from the pure and phosphate minerals: a hydrated silicate of non-constant stoichiometry, CSH, which dehydrates gradually between 100–300°C with a maximum rate of dehydration at ca. 135°C, and Ca(OH)₂ which dehydrates sharply at ca. 500°C. This latter temperature is dependent on hydration age. At approximately 700°C there is a further loss of weight owing to the decomposition of carbonate formed from absorption of atmospheric CO₂. The loss of weight of CO₂ was translated into an equivalent amount of H₂O. The amount of initial free-lime determined by “2 min hydration” was reduced from the total Ca(OH)₂ formed at the various stages. These initial amounts are shown in the last column of Table 1. In Table 2 are shown the weight loss (in mg H₂O) from the net Ca(OH)₂ formed on hydration of the different minerals.

TABLE 2

WEIGHT LOSS OF WATER AT ca. 500°C

Age	Mineral				
	A	B	C	D	E
6 h	—	1.50	1.11	0.89	0
1 day	2.31	1.07	1.20	1.00	0.23
3 days	3.02	2.98	2.61	1.59	0.63
7 days	2.82	3.27	3.11	2.09	1.00
14 days	2.79	3.89	3.61	2.98	0.98
28 days	3.31	3.27	3.61	2.78	1.09
85 days	4.32	3.98	3.70	3.82	0.97

Table 2 shows that as a function of the amount of P_2O_5 in the mineral, the amount of $Ca(OH)_2$ formed grows smaller, that is, a distinct hindrance in the hydration is observed. In the neat C_3S (A) and in the minerals containing low amounts of P_2O_5 (B, C) there is a gradual growth of hydration with age. However, after 85 days, more $Ca(OH)_2$ is formed in A as compared to B and C, and after 1 day A displays a more advanced stage of hydration. In D and E, which contain high amounts of P_2O_5 , a strong retardation is observed. The behaviour of E ($\approx 4.5\%$ P_2O_5) is most dramatic: the hydration is checked after 7 days, after which no change occurs in the amount of $Ca(OH)_2$ formed with age.

These results are in good agreement with Nurse¹, who declares that 2.25% P_2O_5 is the maximum allowable amount in cement, and demonstrate the close resemblance between strength development on the one hand and hydration on the other, as observed from $Ca(OH)_2$ formation.

The DTA endotherms show peaks in two temperature regions: a broad, shallow band peaking ca. 130°C owing to dehydration of CSH, and 1–2 sharp bands peaking at ca. 500°C through dehydration of $Ca(OH)_2$. One of these latter peaks is due to the dehydration of the initial free-lime (represented by (2) in Table 3) and the second (1) to that of the $Ca(OH)_2$ formed in the course of hydration. The $Ca(OH)_2$ peaks show a shift in temperature closely associated with the degree of hydration, a phenomenon previously observed⁸. The peak temperature of all the bands grows with time to a limiting value.

Neat C_3S (A) shows only one band throughout the hydration period and is represented by (1) in Table 3. The single endotherm peaks at 485°C after 6 h, shifting to 519°C after 85 days. This behaviour has already been noted⁸. Obviously, this band represents only the dehydration of the $Ca(OH)_2$ formed during the hydration process and there is no evidence for the presence of free-lime in accordance with the results obtained by TG.

The minerals B, C and D each develop two endotherms (1) and (2). In mineral E, containing the maximal amount of phosphate, there is no observable $Ca(OH)_2$

formed from the hydration process, thus displaying only one endotherm, namely, that represented as (2). However, the endotherms are comparatively broad and a small (1) band may be hidden in the large (2) band. Table 3 and Figs. 1–5 summarize, this behaviour.

It should be borne in mind that the two bands are rather close, and probably

TABLE 3

PEAK TEMPERATURE^a OF DEHYDRATION ENDOTHERMS: (1) OF Ca(OH)_2 FORMED THROUGH THE HYDRATION PROCESS; (2) OF HYDRATED FREE-LIME

Time	Mineral			C		D		E
	A (1)	B (1)	(2)	(1)	(2)	(1)	(2)	
6 h	485	—	486	—	519	—	503	517
1 day	495	—	507	—	519	—	509	523
3 days	501	496	510	—	519	507	527	529
7 days	502	?	512	—	525	507	529	529
14 days	509	507	525	508	522	505	524	520
28 days	515	509	525	509	525	507	525	527
85 days	519	510	529	510	529	505	529	522

^a The values were not calibrated.

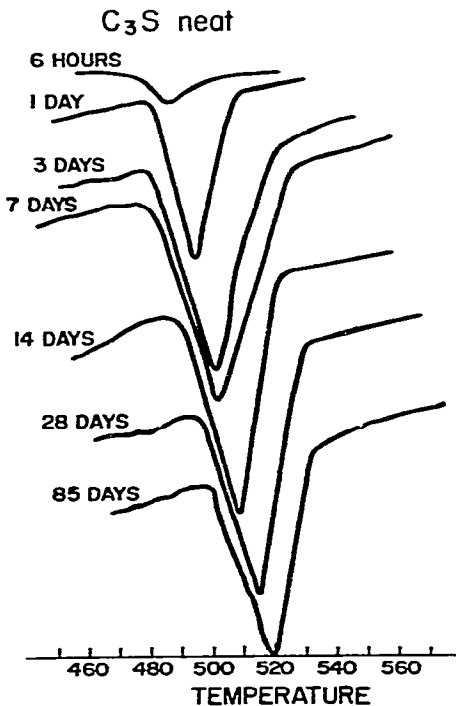


Fig. 1. Endotherm of neat C_3S (A) showing dehydration of Ca(OH)_2 and hydrated “free-lime” in the temperature range 460–550°C for ages between 6 hours and 85 days.

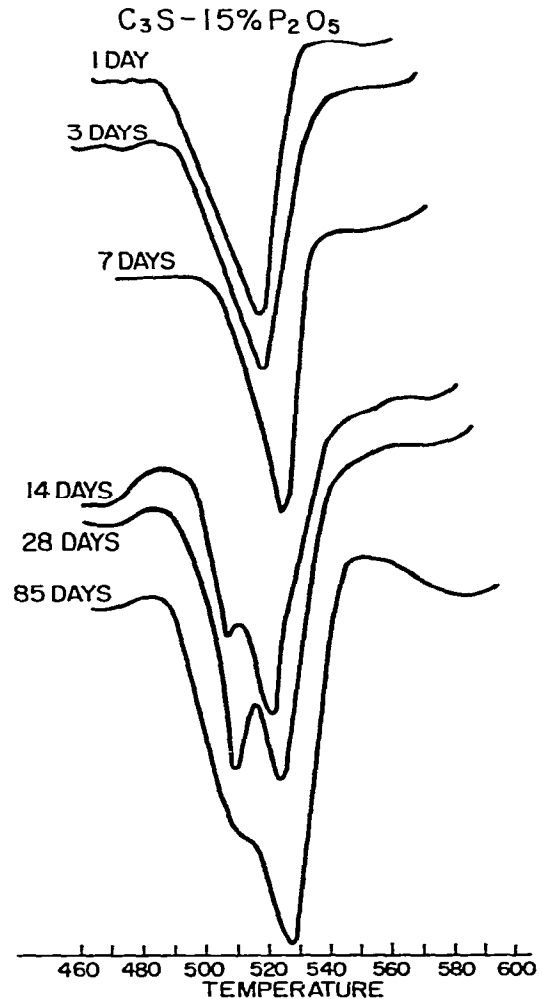
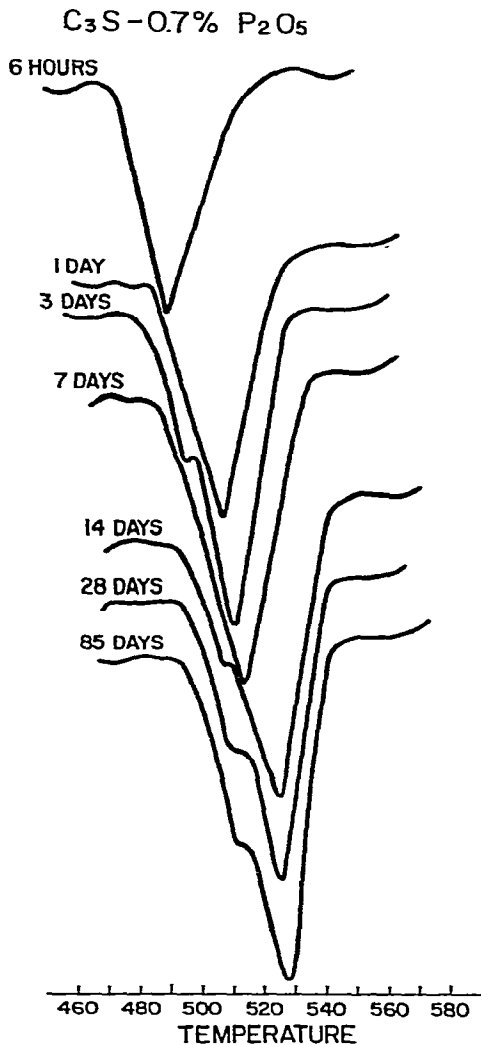


Fig. 2. Endotherm of C_3S containing $0.7\% P_2O_5$ (B) showing dehydration of $Ca(OH)_2$ and hydrated "free-lime" in the temperature range $460-550^\circ C$ for ages between 6 hours and 85 days.

Fig. 3. Endotherm of C_3S containing $1.5\% P_2O_5$ (C) showing dehydration of $Ca(OH)_2$ and hydrated "free-lime" in the temperature range $460-550^\circ C$ for ages between 1 and 85 days.

partly overlap, thus distorting the picture to some extent. Mineral B, which contains the minimal amount of phosphate, shows the well-known shifting of peak (1) in similarity to the same peak in A, but reaches a "younger" stage of hydration at 85 days in comparison to A; i.e., retardation is already under way. The free-lime peak (2) in B, C and D shifts only slightly and appears practically at a constant temperature in the last mineral E. Judging from peak temperatures of (1) (Table 3), there is little development of hydration in C and D and none, for all practical purposes, in E. In all the phosphate minerals the free-lime hydration peak (2) reaches the temperature $\approx 529^\circ C$, while the maximal value is only $519^\circ C$ for the neat C_3S . All this again proves that the "age" of lime, whether initially present or produced during the reaction, is responsible for the shift of the peak. The free-lime formed in accordance with the initial phosphate concentration can indicate qualitatively by DTA the extent

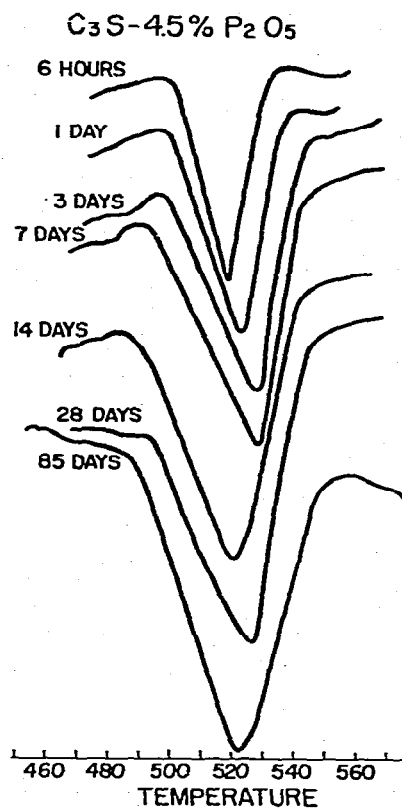
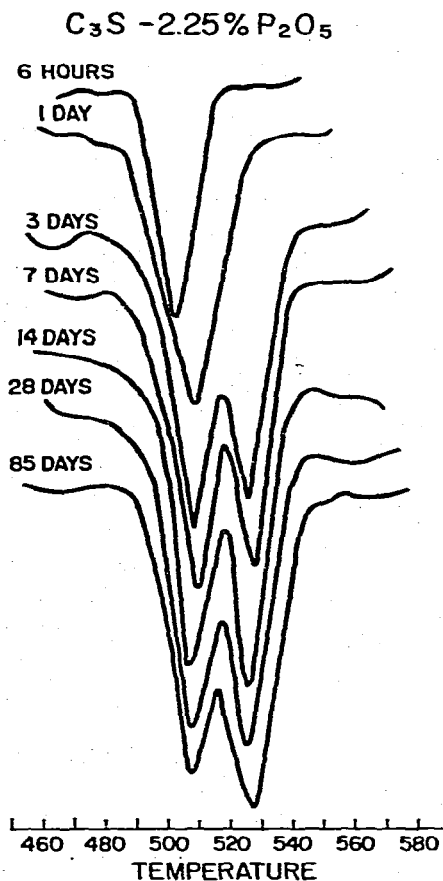


Fig. 4. Endotherm of C_3S containing 2.25% P_2O_5 (D) showing dehydration of $Ca(OH)_2$ and hydrated "free-lime" in the temperature range 460–550°C for ages between 6 hours and 85 days.

Fig. 5. Endotherm of C_3S containing 4.5% P_2O_5 (E) showing dehydration of $Ca(OH)_2$ and hydrated "free-lime" in the temperature range 460–550°C for ages between 6 hours and 85 days.

of the retardation of the hydration process. Above 1.5% P_2O_5 the hydration is reduced considerably: at 85 days the equivalent of ca. only 10 days hydration of neat C_3S is obtained; for 4.5% P_2O_5 practically no hydration is observed.

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