Hydration process and rheological properties of cement pastes modified by orthophosphate addition

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Abstract

The use of cement by nuclear industry for confining low radioactive waste knows a constant increase. The interest bore to this material is due to its mechanical and chemical properties. However, these properties may be modified by the nature and the amount of wastes introduced with the mixing solution especially with large amount of phosphate. Precipitation of hydroxylapatite in the cement paste at the very beginning after mixing was emphasized from a particular concentration of orthophosphate. It was also found that this phenomenon leads to an early rigidification of the cement paste. From a kinetics point of view, the evolution of hydration was both delayed and slowed down according to a pessimum of phosphate concentration. These results indicate a competition between a adsorption process of phosphate on the cement phases which delay the hydration of the cement pastes and a process of precipitation of hydroxylapatite which does not.
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1. Introduction

Nuclear industry has been developed for decades. Treatment of the radioactive wastes has become of great concern since ecological legislation turned more and more drastic.[1,2] A broad range of solutions is used to treat these wastes depending on the nature and toxicity of the wastes. Among them, cementation is a widely applied technique for the conditioning of low- and intermediate-level radioactive wastes.[3–5] In particular, the use of cement is an attractive procedure to immobilize evaporator concentrates from aqueous effluents treatment. Although cement's chemistry is broadly known because of its wide use for construction throughout the world, knowledge of the effect of mixing cement with concentrates of complex chemistry is still limited, especially those containing large amounts of phosphate. This study is devoted to bring additional information on hydration of ce-

ment pastes mixed with solutions of high ionic strength and containing a large amount of orthophosphate.

Hydration of cement can be described by two simultaneous processes. The first concerns the dissolution of the different phases composing cement. The second leads to the precipitation of hydrates from the initially dissolved species. Among the precipitated hydrates, the main hydration product is calcium silicate hydrate ($CaO–SiO_2–H_2O = C–S–H$).[6] This hydrate is generally recognized as responsible for the setting and hardening of cement.[6] The wide use of cement is due to this property.

Adding phosphate to the hydration solution induces changes on the normal hydration process. Phosphate compounds are reported in the literature to be retarders of cement hydration.[6–9] Setting time can be strongly delayed whereas hardening can be greatly lowered at least at early age. The magnitude of these effects is highly variable, depending both on the kind and the amount of phosphates used to perform the experiments.[12] Several assumptions are still under discussion to explain this phenomenon. One of them would be the forma-

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tion of precipitates over the cement grains, which might block the dissolution of the phases and explain the hydration delay.[6] This hypothesis is, however, controversial and an adsorption process of the oxoanions on the dissolution sites would nowadays seem more likely.[11] Moreover, recent studies have underscored an unexpected favorable effect of phosphate at high concentration in complex high concentrated solutions.[10] Thus, a thorough investigation of the mechanism taking place during hydration of cement in the presence of phosphate seems necessary to account for these opposite results. Focus has been placed in this paper on the influence of high concentrations of orthophosphates ($0–50 \, g \, L^{-1}$) on hydration and rheological properties of cement pastes at early age. In our study, the concentration of salt was fixed at $300 \, g \, L^{-1}$ to simulate the salinity of the evaporator concentrates by adding sodium nitrate.

From a chemical point of view, the aqueous phase of cement pastes is characterized by a high calcium concentration and a high pH. The presence of phosphate in such conditions is susceptible to lead to an apatite formation. This assumption was preliminary verified by using phosphates speciation calculation with PHREEQC speciation software.[11] Although the activity coefficients are not accurately computed in such high ionic strengths, results indicate that in each case we studied, the system was very supersaturated with respect to hydroxylapatite

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- = Ca_{10}(PO_4)_6(OH)_2$$

Its precipitation was already proposed by Ma and Brown[12] and suggested by Lieber.[8] Therefore, preliminary experiments were carried out with a model system to verify a possible competition of precipitation between calcium silicate hydrate and hydroxylapatite. The model system was composed of a mixture of lime and silica introduced in solution of different concentrations of phosphate. Without phosphate, this type of mixtures leads to the formation of C–S–H by pouzzolanic reaction.[13]

2. Experimental

2.1. Hydration of cement pastes

Experiments were performed by using a cement of the following type: CEM I PM-ES 52.5R (referred in the following as HTS). The phosphate solutions were prepared by dissolving $Na_3PO_4 \cdot 12H_2O$ in distilled water and by adjusting the salinity to $300 \, g \, L^{-1}$ with a supplementary addition of

$NaNO_3$. Both chemicals were provided by Sigma–Aldrich. The investigated phosphate and nitrate concentrations as well as the corresponding ionic strength in solutions are given in Table 1. The water to cement ratio (w/c) was fixed to 0.3 in each experiment.

2.2. CaO–SiO₂ mixed in presence of phosphates

Different mixtures of CaO and SiO_2 were added to phosphate solutions ($0, 5, 10 \, g \, L^{-1}$). Lime was obtained by decarbonation overnight at $1000 \, °C$ of calcium carbonate provided by Aldrich. We used amorphous precipitated silica provided by Rhodia with a specific area of $230 \, m^2 \, g^{-1}$. The molar Ca/Si ratio and the liquid to solid ratio of the mixtures were, respectively, fixed to 0.8 and 50. The mixtures were stirred in thermoregulated bath at $25 \, °C$ for different times ranging from 1 h to 10 days. In such conditions, lime and silica dissolve to give high pH solution in which C–S–H precipitate in absence of phosphate. Samples were filtered and washed first with an alcohol–water mix, then with pure alcohol. Solids were analyzed by X-ray diffraction using an Inel CPS 120 position sensitive detector and a Cu Kα radiation ($\lambda_{Cu K\alpha_1} = 1.54056 \, Å$, acquisition time was 2 h, voltage 40 kV and intensity 40 mA).

2.3. Isothermal microcalorimetry

A high sensitivity ($0.1 \, \mu W$) isothermal Tian-Calvet type microcalorimeter was used to follow the hydration of cement pastes. This study required to record the thermal flow as soon as possible after mixing. A nacelle, which was pushed down to the bottom of the calorimetric chamber without friction, was used to prevent any extra undesirable heat. The heat evolution rate curve was mainly representative of the rate of hydration of silicate phases of cement and the cumulated heat which was representative of the degree of hydration, was calculated by integrating the thermal flow values (Fig. 1). The different steps of the hydration mechanism could be deduced from the sigmoid cumulated heat curve. The first step was characterized by an acceleration period, which corresponded to the nucleation of C–S–H and to the growth of the nuclei on the surface. Then, the reaction slowed down due to the covering of the particles constituting cement by C–S–H. The reaction was then, limited by the diffusion of reactants through the layer of C–S–H.[6]

For the experiments, a part of the paste mixed for the rheometric experiments (about 1 g) was put in the nacelle. Thus, parts of the same sample were examined by rheometry and calorimetry.

Table 1
Concentrations of PO_4^{3-}, $Na_3PO_4 \cdot 12H_2O$ and $NaNO_3$ and ionic strength of the hydrating solutions

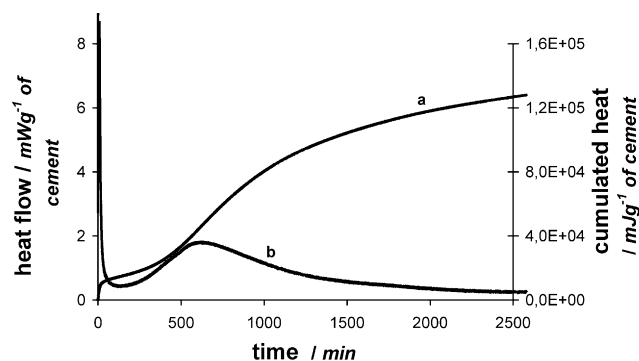| $[PO_4^{3-}]$ ($g \, L^{-1}$)	0	7	10	15	18	20	25	30	40	50
$[NaNO_3]$ ($g \, L^{-1}$)	300	287.9	282.7	274.1	268.8	265.5	257	248.2	230.9	213.7
$[Na_3PO_4 \cdot 12H_2O]$ ($g \, L^{-1}$)	0	28	40	60	72	80	100	120	160	200
Ionic strength	3.53	3.60	3.63	3.68	3.71	3.73	3.77	3.82	3.92	4.02

Fig. 1. Heat evolution rate curve and cumulated heat vs. time during the hydration of a HTS cement paste. (a) Cumulated heat and (b) heat flow (w/c = 0.3).

2.4. Dynamic mode rheometry

The evolution of the viscoelastic properties of the pastes was followed by dynamic mode rheology using a controlled strain rheometer (ARES Rheometrics Scientific, USA).

To perform the experiments, a cement paste sample was subjected to a sinusoidal shear strain defined by

$$\gamma = \gamma_0\, e^{i\omega t}$$

at constant frequency (ω). The resulting stress was measured by the intermediary of the torque and was also sinusoidal with a δ phase lag with respect to the applied strain

$$\tau = \tau_0\, e^{i\omega t + \delta}$$

Within the linear viscoelasticity range, using oscillatory mode, the relation between shear strain and stress was given by the following expression

$$\tau = G^*(\omega)\gamma$$

G^*, the complex shear modulus, being expressed as the sum of the shear storage modulus (G') and the shear loss modulus (G'') as

$$G^* = G' + iG''$$

The shear strain value was chosen within the linear viscoelasticity range of the cement paste, so as to avoid destructive measurements. Indeed, above a particular value of the shear strain called critical strain γ_c, the destructuration of the material would occur. In case of cement pastes, the limit of the linear viscoelastic domain has been shown to occur when the strain reaches 0.03%.[14,15]

A mixing-type tool (Fig. 2) composed of a helicoidal ribbon and a cell was used for the rheological measurements. This special tool was designed to maintain a saturated water atmosphere within the cell containing the sample, thus preventing the cement paste to dry.

Cement pastes were prepared by mixing 40 g of cement and 12 ml of solution for 2 min. They were then transferred into the rheometer cell and mixed again for 30 s. Mixing and transfer both induced strains which were relaxed before
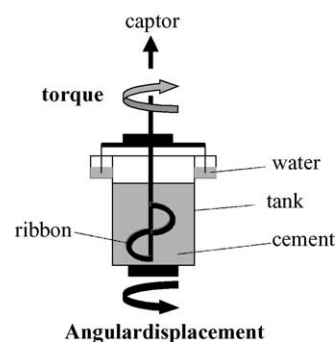

Fig. 2. Non-conventional geometry used for rheological investigations.

recording the data by operating a high amplitude strain (5%) at high frequency ($10\,\mathrm{rad\,s^{-1}}$) for 45 s. Experiments were then performed using a 0.005% shear strain and a $5\,\mathrm{rad\,s^{-1}}$ frequency.

During cement paste hydration, the shear storage modulus (G') rapidly became much more important than the shear loss modulus (G''), therefore, only the G' modulus was analyzed subsequently.

3. Results

3.1. CaO–SiO₂ mixed in phosphate solutions

Solutions containing lime, silica and sodium phosphate were prepared in order to determine the phases susceptible to precipitate in the CaO–SiO₂–P₂O₅–H₂O system in conditions close to the cement hydration in highly concentrated phosphate solutions. The X-ray diffraction patterns of the products obtained after 1 h and 10 days of stirring are plotted in Fig. 3. Without phosphates, as expected, C–S–H was the only compound detected. When an increasing amount
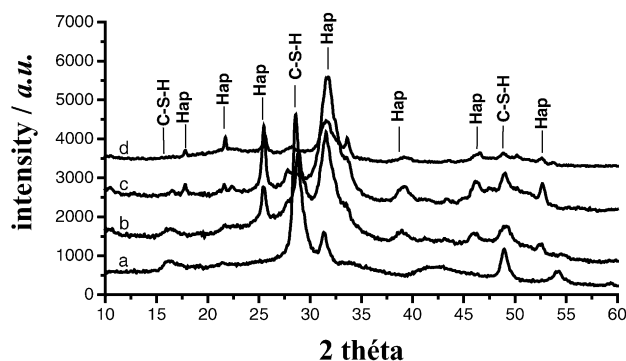

Fig. 3. X-ray diffraction pattern of the reaction products obtained from mixtures of lime, amorphous silica and phosphate solutions. (a) Solution with lime and silica only after 10 days, (b) lime, silica and a $5\,\mathrm{g\,L^{-1}}$ phosphate solution after 10 days, (c) lime, silica and a $10\,\mathrm{g\,L^{-1}}$ phosphate solution after 1 h, and (d) lime, silica and a $10\,\mathrm{g\,L^{-1}}$ phosphate solution after 10 days. The main peaks of hydroxylapatite and C–S–H are indicated ($\lambda_{\mathrm{Cu\,K\alpha_1}}$ = 1.54056 Å).
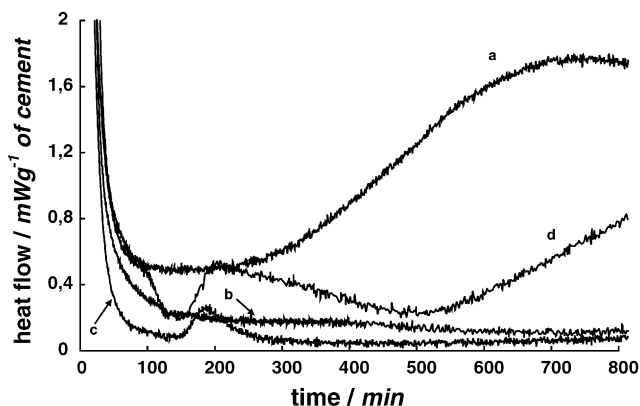
Fig. 4. Heat evolution rate curves of hydration of cement pastes at constant salinity for different concentrations of phosphate: (a) without phosphate, (b) $10 \, g \, L^{-1}$, (c) $40 \, g \, L^{-1}$ and (d) $50 \, g \, L^{-1}$.

Fig. 5. Cumulated heat vs. time for cement pastes hydrated with variable amounts of phosphates varying from 0 to $50 \, g \, L^{-1}$ in hydration solution: (a) $0 \, g \, L^{-1}$ without nitrate, (b) $0 \, g \, L^{-1}$ with $300 \, g \, L^{-1}$ of nitrate, (c) $10 \, g \, L^{-1}$, (d) $20 \, g \, L^{-1}$, (e) $30 \, g \, L^{-1}$, (f) $40 \, g \, L^{-1}$ and (g) $50 \, g \, L^{-1}$.

of phosphate ions was added to the solution in which CaO and SiO_2 are suspended, a decrease in C–S–H peaks was observed together with a progressive increase of the hydroxylapatite peaks (diffraction patterns a, b and d). The results show that hydroxylapatite precipitates preferentially with respect to C–S–H. Moreover, diffraction pattern c indicates that hydroxylapatite can precipitate within the very first minutes after mixing.

3.2. Heat flow evolution during the hydration of cement pastes in presence of phosphates

Fig. 4 shows the heat evolution rate of cement pastes at the beginning of hydration for different concentrations of phosphate in hydration solutions. After an initial increase due to the pure dissolution of cement, the thermal flow dropped down. For phosphate concentrations ranging from 40 to $50 \, g \, L^{-1}$, an endothermic component was clearly observed in the first 200 min, which indicated the occurrence of an additional reaction.

Given the fact that hydroxylapatite was previously identified in mixes of CaO, SiO_2 and phosphates, this endothermic component could be ascribed to the precipitation of hydroxylapatite. This hypothesis is strengthened by the endothermic enthalpy of precipitation of hydroxylapatite ($\Delta H_{prec} = 174 \, kJ \, mol^{-1}$), as calculated from literature data.[16] A deconvolution of the different peaks would have been precious to estimate the surface of each component and verify whether hydroxylapatite was really the species which precipitates. Unfortunately, this treatment is not possible because of the numerous reactions occurring simultaneously within the system.

3.3. Phosphate influence on hydration rate of the cement pastes

The cumulated heat curves, corresponding to hydration of cement mixed with the different phosphate solutions are
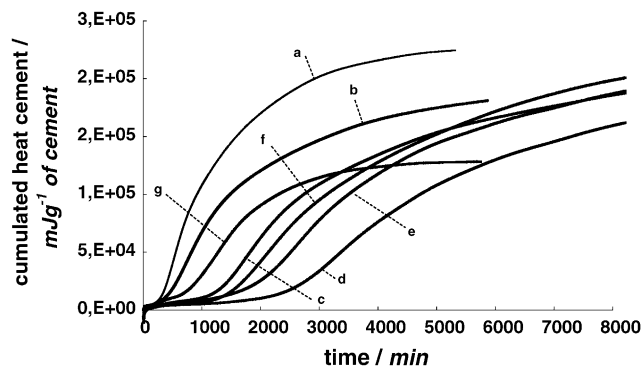
shown in Fig. 5. In all cases, the percentage of hydration when reaction became limited by diffusion was lower when cement was hydrated in high salt concentrated solution and more with phosphate than in the case of the neat cement paste. On the other hand, the maximum rate of hydration (the slope at the inflexion point on the cumulated heat curve) was also lower. In addition the delay to observe a significant increase of the percentage of hydration was longer when cement was hydrated in phosphate solutions. For a phosphate concentration within the range $0–20 \, g \, L^{-1}$ in the hydration solution, the acceleration period was all the more delayed as the phosphate concentration increased. A decrease of this delay was then observed for phosphate concentrations above $25 \, g \, L^{-1}$. A progressive decrease of the hydration rate during the acceleration period was also noticed for phosphate concentrations within the range $0–20 \, g \, L^{-1}$. For higher concentrations, the hydration rate increased again, but without exceeding the rate recorded for the phosphate free solution. It is also important to notice that a large amount of nitrate ($300 \, g \, L^{-1}$) did not change the time for which the reaction accelerated. Thus, delays observed with phosphate solution could not be attributed to a sodium nitrate effect.

3.4. Viscoelastic properties at early age of cement pastes hydrated for different concentrations of phosphates

Evolution of the viscoelastic properties of cement pastes containing increasing amounts of phosphate (0, 7, 15, 20, 30, 40, and $50 \, g \, L^{-1}$) was followed by dynamical rheometry. The graphs plotting the evolution of the storage modulus with the hydration time for the different cement pastes are shown in Fig. 6 (phosphate concentrations ranging from 0 to $18 \, g \, L^{-1}$) and Fig. 7 (phosphate ranging from 25 to $50 \, g \, L^{-1}$). Comparing the storage moduli at fixed time showed that the higher the phosphate concentration within the range $0–18 \, g \, L^{-1}$, the smaller the elastic modulus. When the phosphate concentration exceeded $25 \, g \, L^{-1}$, a change in the cement pastes behavior was observed. The elastic moduli severely increased during the very first minutes of hydration and reached higher
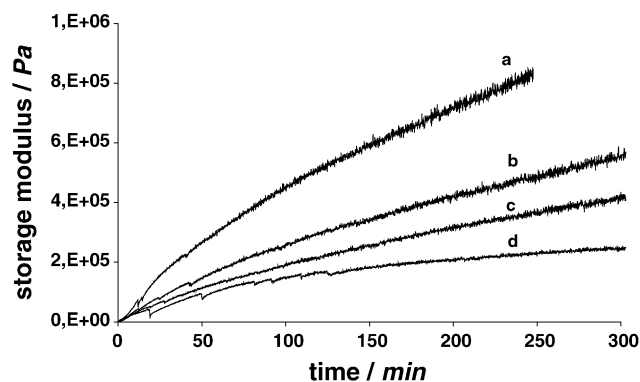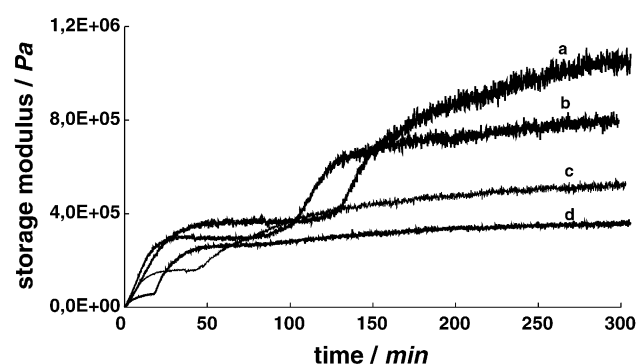
Fig. 6. Storage modulus evolution of cement pastes hydrating in phosphate solution (phosphate concentration ranging from 0 to $18 \, \mathrm{g \, L^{-1}}$): (a) $0 \, \mathrm{g \, L^{-1}}$ with nitrate, (b) $7 \, \mathrm{g \, L^{-1}}$, (c) $10 \, \mathrm{g \, L^{-1}}$ and (d) $18 \, \mathrm{g \, L^{-1}}$.

Fig. 7. Storage modulus evolution of cement pastes hydrating in phosphate solutions (phosphate concentration ranging from 25 to $50 \, \mathrm{g \, L^{-1}}$): (a) $50 \, \mathrm{g \, L^{-1}}$, (b) $40 \, \mathrm{g \, L^{-1}}$, (c) $30 \, \mathrm{g \, L^{-1}}$, and (d) $25 \, \mathrm{g \, L^{-1}}$.

values than in absence of phosphate. This dramatic increase was followed by a leveling-off period. The higher the phosphate concentration, the higher the modulus on the level and the higher the plateau. Then, the elastic moduli increased again.

4. Discussion

Both chemical and mechanical evolutions of the cement pastes during hydration show a discontinuity when the phosphate concentration increases in the hydration solution. From the kinetics point of view, Fig. 8 shows that the maximum rate of hydration decreases and then increases when the phosphate concentration increases in solution. On the contrary, the delay to observe a significant acceleration of hydration increases and then decreases as the phosphate concentration increases (Fig. 9). In both cases, the discontinuity occurs for a phosphate concentration close to $20 \, \mathrm{g \, L^{-1}}$.

As for the viscoelastic behavior revealed by dynamic mode rheometry of the cement paste, Fig. 10 shows the values of the storage modulus after 250 min of hydration in the different phosphate solutions. Once again, the evolution is discontinuous: the storage modulus is decreasing when the phosphate
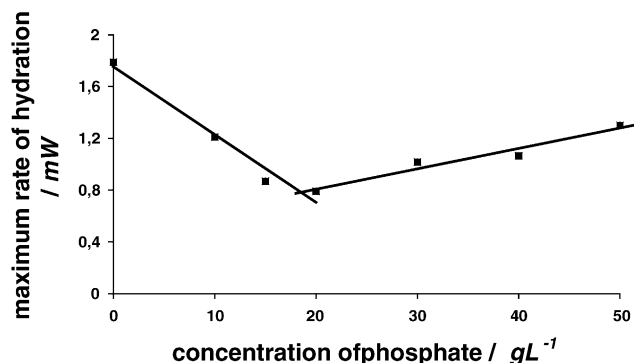

Fig. 8. Evolution of the maximum rate of hydration of HTS cement paste vs. the concentration of phosphate.
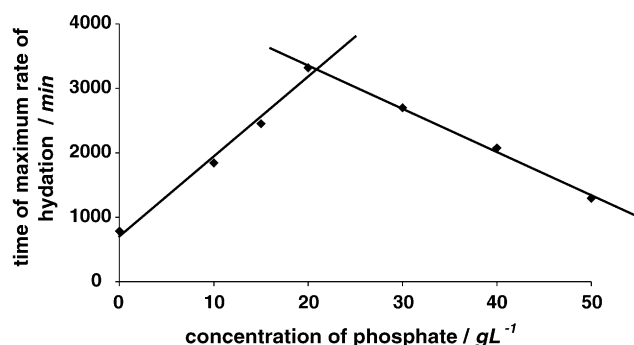

Fig. 9. Evolution of the time for which the rate of hydration of HTS cement is maximum vs. the concentration of phosphate.

concentration increases up to $20 \, \mathrm{g \, L^{-1}}$ but then is increasing when the concentration goes increasing above this value. These results give evidence for different roles of phosphate ions in the hydration process.

On the other hand, a severe initial increase of the elastic moduli is observed in the case of pastes hydrated in solutions with a phosphate concentrations above $25 \, \mathrm{g \, L^{-1}}$. The study of hydration at early age by isothermal microcalorimetry has shown the endothermic formation of an additional species in the same range of phosphate concentrations. Moreover, the trials which were performed on a simplified system showed
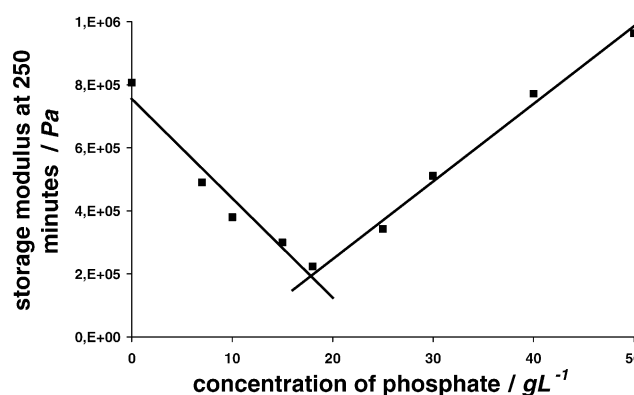

Fig. 10. Evolution of the value of the storage modulus after 250 min in function of the concentration of phosphate in solution.
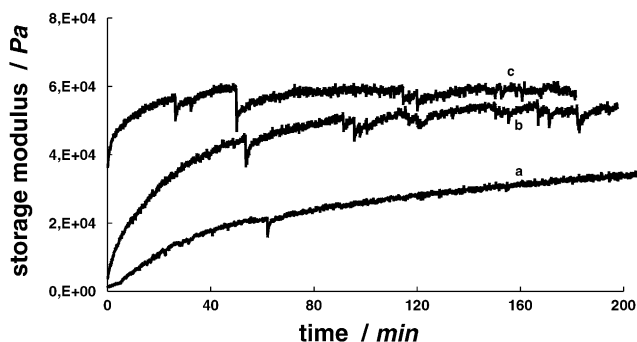
Fig. 11. Evolution of storage modulus for mixtures composed of lime and quartz sand with phosphate solutions of different concentrations as indicated on the curves, $l/s = 0.48$. (a) $0 \, g \, L^{-1}$, (b) $2.5 \, g \, L^{-1}$, and (c) $10 \, g \, L^{-1}$.

the possibility of a favored precipitation of hydroxylapatite with respect to C–S–H. All these elements suggest a precipitation of hydroxylapatite in the cement paste during the very beginning of hydration. Such a hypothesis was already suggested by Lieber[8] and Ma and Brown.[12] This precipitation would be responsible for the early rigidification of the paste in spite of the low degree of hydration.

In order to support this assumption, additional runs were carried out by recording the evolution of the storage modulus of a model system. These models were composed of mixtures of lime (3 g), quartz sand simulating the granular medium of cement (26 g) and phosphate solutions with concentration ranging from 0 to $10 \, g \, L^{-1}$ (14 ml). Quartz sand was used as an inert matrix because contrary to cement's case, with sand there is no formation of C–S–H. From the lime, which dissolves and phosphate contained in solution, the precipitation of hydroxylapatite was unavoidable. Results presented in Fig. 11 shows that the storage modulus increased together with the initial phosphate concentration, which was related to the amount of precipitated hydroxylapatite. Such results may be transposed to the hydrating cement paste and mean that the precipitation of hydroxylapatite can account for the early hardening of the cement paste for a phosphate concentration above $25 \, g \, L^{-1}$. Unfortunately, the percentage of hydroxylapatite supposed to precipitate is less than 2% so it is not possible to check its presence in the paste by classical analytical methods such as X-ray diffraction.

For lower concentrations, during hydration of cement, even though the solution is probably also supersaturated with respect to hydroxylapatite, an adsorption of phosphate ions inhibiting the dissolution of the cement particles seem more likely, as Lieber suggested it.[8] This might explain the increasing delay observed before the acceleration period when the phosphate concentration increases within the range $0–25 \, g \, L^{-1}$. Moreover, this is consistent with the lower amount of C–S–H formed at early age, as shown by the decreasing storage modulus in this range of concentration. For phosphate concentrations exceeding $25 \, g \, L^{-1}$, the phosphate ions might be less and less adsorbed because they precipitate into hydroxylapatite, which thus leads to a lower delay before

the acceleration period in the hydration of cement pastes. The reason why such high phosphate concentration is necessary to precipitate hydroxylapatite has still to be elucidated.

5. Conclusion

The systematic study of the hydration of cement pastes in concentrated phosphate solution confirmed the retarding effect of phosphate. However, a pessimum of delay was emphasized for a concentration of phosphate close to $25 \, g \, L^{-1}$. Moreover, rheological investigation of the cement pastes with increasing amount of phosphate also showed a discontinuity of behavior for a similar phosphate concentration. The origin of the decreasing delay and the discontinuity observed in the rheological properties can be explained by the formation of hydroxylapatite above a phosphate concentration of $25 \, g \, L^{-1}$. We have shown that this compound participates to the early rigidification of the cement paste. Below this concentration, an adsorption of the phosphate on the different phases constituting cement is very likely as it was already suggested.

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