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Influence of orthophosphate ions on the dissolution of tricalcium silicate

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ABSTRACT

Tricalcium silicate dissolution in the presence of orthophosphate ions was monitored by measuring the concentrations of calcium and silicate ions in dilute suspensions using a special dissolution cell coupled to an optical emission spectrometer. Results show that increasing adsorption of orthophosphate ions slows down the dissolution of Ca_3SiO_5 and that a calcium-phosphate precipitate may form at certain orthophosphate concentrations. These observations are correlated with results of calorimetric experiments carried out during the hydration of silica-rich cement pastes in the presence of the same salts.

1. Introduction

The presence of mineral salts in the mixing solution of a Portland cement (PC) often results in modifying of the cement hydration process. Different cases may illustrate the situation whereby mineral salts are dissolved in the mixing solution. For example, in the concrete industry, it's common to add appropriate mineral salts to accelerate or delay the setting of cement whenever necessary. Low and intermediate level radioactive wastes containing soluble salts may be encapsulated by reaction with Portland cement, a process commonly known as cementation.

Depending on the nature and amount of mineral salts in the mixing solution, the modification in the PC hydration can occur differently (adsorption, precipitation, poisoning). Among the numerous interfering mineral salts, orthophosphates, which are found in large concentration in some radioactive effluents, are known to be strong retarders. Understanding of the different mechanisms involved in the retardation due to orthophosphate ions is therefore of great interest for conditioning such wastes.

PC is a polyphasic material mainly composed of calcium silicate phases. Its hydration, as well as the hydration of its main phase, tricalcium silicate, follows dissolution–precipitation processes. As soon as the particles of cement (or tricalcium silicate) are in contact with water, the different phases dissolve and lead to the precipitation of many more insoluble hydrates. The main hydration product of cement (as well as of tricalcium silicate) is a calcium silicate hydrate referred to C–S–H ($(CaO)_x$–SiO_2–$(H_2O)_y$) which is responsible for the setting and hardening of cement pastes.

Lieber [1] and Ma and Brown [2] have shown that mixing cement with solutions containing orthophosphate ions results in retarding cement hydration. Lieber [3] has also noted that the magnitude of the retardation depends on the nature and amount of phosphates dissolved in the mixing solution. To explain this result, he suggested that orthophosphate ions may adsorb on the surface of clinker particles and form a calcium-phosphate compound which prevents a normal hydration. More recently, Cau-Dit-Coumes and Courtois [4] and Bénard et al [5] have shown that the retardation is not a monotonous function of the concentration of orthophosphate ions. It increases with the phosphate content for low concentrations (0–0.2 mol L^{-1}) but then decreases when the phosphate concentration increases within the range 0.2–0.5 mol L^{-1}. Taking into account rheological measurements and phosphate speciation calculation, Bénard et al. suggested that this evolution is due to the precipitation of a calcium-phosphate compound when the orthophosphate ion concentration in the mixing solution exceeds a limit value.

Below this particular concentration, adsorption of orthophosphate ions may occur and thus delay hydration. It can be assumed that this adsorption reduces the dissolution of anhydrous phases and thus retards the tricalcium silicate hydration process.

In order to check this assumption, we chose to simplify the system by studying pure tricalcium silicate dissolution in the presence of orthophosphate ions. This study was carried out with diluted suspensions because the dissolution process occurs very quickly and it is therefore difficult to follow not to say impossible in a paste. The advantage of the method is a possible continuous titration of the calcium and silica concentrations which results from Ca_3SiO_5 dissolution. Technically we used a special dissolution cell coupled to an

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Table 1
Chemical composition of the silica-rich cement (mass percent)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
68.05	22.95	2.70	1.90	0.80	0.16	0.17	2.25

optical emission spectrometer. Different experiments were performed with two water-to-C_3S weight ratios (50 and 200) and with increasing orthophosphate concentrations. Moreover, in order to examine a possible influence of the orthophosphate counter ions, either sodium or potassium orthophosphate were used. These results were then compared to those obtained by calorimetry with pure silica-rich cement pastes. Experiments with pastes are part of a larger study which also includes the measurement of dimensional variations under wet curing of mortars [5,6].

2. Materials

Dissolution experiments were performed with a pure tricalcium silicate while calorimetric measurements were carried out with silica-rich Portland cement (CEM I PM-ES 52,5R according to European standard EN 197-1) the composition of which is detailed in Tables 1 and 2. Both cement and tricalcium silicates were provided by Lafarge. The orthophosphate solutions were prepared by dissolving in distilled water either $Na_3PO_4, 12H_2O$ or K_3PO_4, both provided by SIGMA-ALDRICH.

3. Experimental methods

3.1. Monitoring tricalcium silicate dissolution

A special set up was used to compare the dissolution rate of pure tricalcium silicate in the presence of increasing orthophosphate concentrations. This set up was composed of a dissolution cell which was coupled to an ICP-OES VISTA PRO Varian spectrometer with axial detection system. It helped us to follow both continuously and simultaneously the concentrations of the different species in the suspension solution. The main advantage of this device was that we could obtain measurements at very short intervals (10 s) with very low concentrated solutions containing different species.

The dissolution cell was composed of a reactor which was screwed on a filtration system. The porosity of the filter was set at 0.1 µm, in order to prevent tricalcium silicate particles from going towards the spectrometer. Stirring was provided by a rotating helix located in the middle of the cell and connected to a variable speed motor set at 1100 rpm. The cell was hermetically closed and flushed with argon diverted from the spectrometer to prevent carbonation of the solution. A part of the solution was pumped to the nebulizer of the spectrometer. The fraction depleted for analysis was very small and most of the derived solution was reintroduced in the dissolution cell; over 1 h of experiment the liquid-to-solid ratio varies less than 0.06% [7]. The uncertainty of the analyses by ICP-OES was below 3%.

Table 3 summarizes the wavelengths used to determine the concentrations of the different species.

3.2. Determining the rates of appearance of calcium and silica in solution

Fig. 1 shows the evolution of the concentrations of calcium and silica during the 25 first minutes of hydration of pure tricalcium silicate at a w/c ratio equal to 200. Three expected periods, as described by Barret and Ménetrier [8], could be defined: the first one, which shows a rapid increase of the calcium and silicate concentrations, corresponds to the pure congruent dissolution of the tricalcium silicate. During this period, calculations with PHREEQC speciation software [9] of saturation index according to equilibrium (1), showed that C–S–H precipitation is unlikely (Fig. 1).

Table 2
Average of the different phases calculated from Bogue formula

Phases	C_3S	C_2S	C_3A	C_4AF	Gypsum
Average	73.6	10.6	3.94	5.78	1.9

Table 3
Wavelengths used to determine the concentrations of the different species

Elements	Wavelengths/nm
Calcium	443.496 and 445.478
Silica	288.158
Phosphorus	214.914 and 253.399
Sodium	568.821 and 589.492
Potassium	766.491 and 769.897

Depending on the concentrations and the composition of the solutions to analyse, several wavelengths can be used.

$$Ca_{1.1}SiO_{6.4}H_{6.3} + 2.2H^{+} = 1.1Ca^{+2} + H_4SiO_4 + 2.3H_2O \quad (1)$$

$$Ks = 10^{-16.82}.$$

During the second period, the calcium concentration and the silicate concentration do not increase, the solution reached a critical supersaturation with respect to C–S–H, C–S–H started to precipitate. The third period was characterized by an increase in the calcium concentration together with a decrease in the silicate concentration; the C–S–H precipitation is accelerating.

Our work focused on the process of the dissolution of tricalcium silicate, i.e. on the first period in order to avoid the occurrence of simultaneous phenomena, i.e. dissolution of Ca_3SiO_5 and precipitation of C–S–H. The rates of production of calcium and silicate ions in the suspension were determined from the slopes at the origin of the curves showing the evolution of the concentrations versus time (Fig. 1). In normal conditions, i. e. in water, the rate of production of calcium ions is three times the rate of appearance of silicate ions as C_3S dissolution is congruent [8].

The monitoring follow-up of the calcium and silicate ion concentrations during our dissolution experiments was performed with different water-to-anhydrous ratios (50 and 200) and with either sodium or potassium orthophosphates. The different orthophosphate concentrations we used depended on the water-to-anhydrous ratio as shown in Table 4.

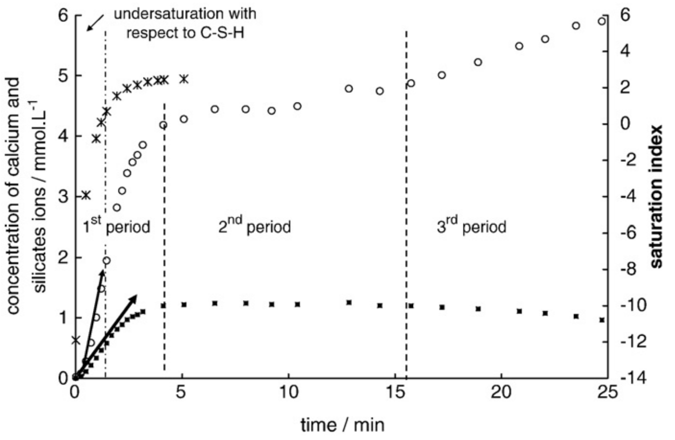

Fig. 1. Evolution of the calcium (○) and silica (■) concentrations and the saturation index (ж) with respect to C–S–H during the hydration of tricalcium silica with a w/c = 200. Thermodynamically, no C–S–H is likely to precipitate before 1.2 min. The appearance rates in solution of the calcium and silicate ions are inferred from the slopes of the concentration curves.

Table 4
Initial concentration of orthophosphate ions used to perform dissolution experiments in diluted suspensions as well as concentration of orthophosphate ions used by Bénard and al. to perform hydration of cement pastes (w/c=0.3)

Mol of orthophosphate ions per gram of anhydrous	Initial concentration of orthophosphate ions in solution/ mol L^{-1}	Initial concentration of orthophosphate ions in solution/ µmol L^{-1}	Initial concentration of orthophosphate ions in solution/ µmol L^{-1}
	(l/s=0.3)	(l/s=50)	(l/s=200)
$3.1.10^{-5}$	0.105	631	155
$6.3.10^{-5}$	0.210	1260	315
$9.4.10^{-5}$	0.315	1880	470
$12.6.10^{-5}$	0.420	2520	630
$18.9.10^{-5}$	0.630	3780	945
$25.2.10^{-5}$	0.840		1260

3.3. Calorimetric monitoring

Hydration of cement pastes can be followed by recording the evolution of the thermal flow which is released during the first hours after mixing. This method was used to compare the heat evolution rates of cement pastes containing increasing orthophosphate concentrations. The experiments were performed with a high sensitivity (0.1 µW) isothermal Tian-Calvet type microcalorimeter. The temperature of the apparatus was set at 25 °C. Each experiment was performed along the following procedure: about 1 g of cement was mixed with an orthophosphate solution for 1 min, then the paste was placed in a cell which was pushed down to the microcalorimetric chamber without friction to prevent undesirable extra heating.

In order to compare the delay induced by different orthophosphate concentrations, a characteristic time was defined to evaluate the time when the cement hydration began to accelerate, as shown in Fig. 2. The time when hydration begins to accelerate which corresponds to the acceleration of C_3S hydration [10], was chosen as the *x*-intercept of a line matching the slope of the accelerating portion of the reaction.

4. Results and discussion

Fig. 3 shows a typical example of the dissolution of tricalcium silicate in the presence of orthophosphate ions. Without orthophosphate ions, a fast increase in the calcium and silicate ion concentrations was always observed during the first period, as defined earlier. On the contrary, orthophosphate ion concentration decreased very quickly to reach a value close to zero. Over the same period, the alkaline concentration remained approximately constant.

The rate of appearance of calcium and silicate ions, calculated from the slope of plots similar to that shown in Fig. 3 for the different concentrations of orthophosphates, was plotted versus the initial orthophosphate concentration for different phosphate salts (Figs. 4, 6: potassium; Fig. 5: sodium) and a water-to-C_3S ratio (Figs. 4 and 5: 200; Fig. 6: 50). In each graph, we also added calculated rates corresponding to the three times values of rates of appearance of silicates ions, in order to compare calcium and silicate rates of appearance according to the congruent dissolution of C_3S.

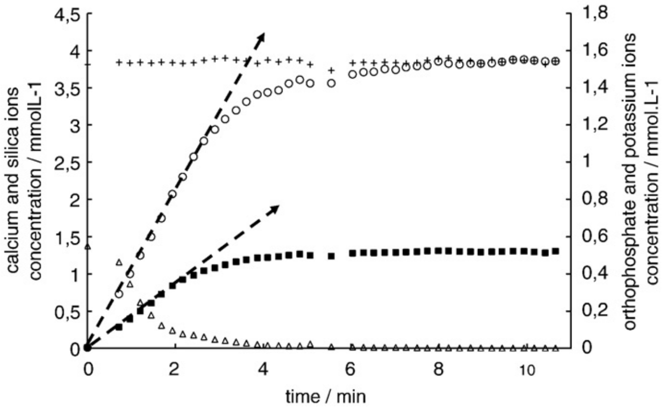

Fig. 3. Evolution of concentrations of the calcium (○), silicate (■), orthophosphate (△) and potassium (+) ions in the suspension during the first 15 min of hydration of tricalcium silicate (initial potassium orthophosphate concentration: 630 µmol L^{-1}, water/anhydrous=200).

All these results showed that the higher the initial orthophosphate concentration, the lower the production rate of calcium and silicate ions in the suspension. However, in each case a discontinuity was observed for a phosphate concentration depending on the water-to-C_3S ratio: 470 to 630 µmol L^{-1} for a water-to-C_3S of 200 (Fig. 4) and 630 to 800 µmol L^{-1} for a water-to-C_3S ratio of 50 (Fig. 6). As a very similar evolution was observed in the three studied cases (Figs. 4, 5 and 6), the existence of a non-monotonous evolution of the rate of ion appearance was clearly revealed.

4.1. Evolution before the discontinuity

Whatever the water-to-C_3S ratio of the diluted suspension (50 or 200), and observed for orthophosphate concentrations ranging from 0 to the concentration corresponding to the discontinuity, we observed a decrease in the rates of appearance of calcium and silicate ions when orthophosphate concentration increases (Figs. 4, 5 and 6). This phenomenon was accompanied (as we can see in Fig. 3) by a rapid depletion in the first 2 min of the orthophosphate ions initially

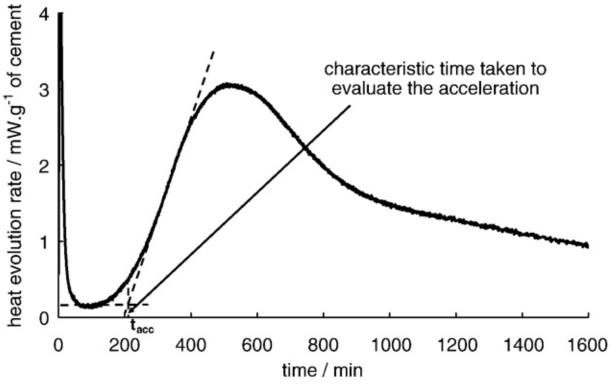

Fig. 2. Example of heat evolution rate during the hydration of cement pastes versus time. This figure defines how we determined an arbitrary criterion giving the time when the hydration reaction accelerates.

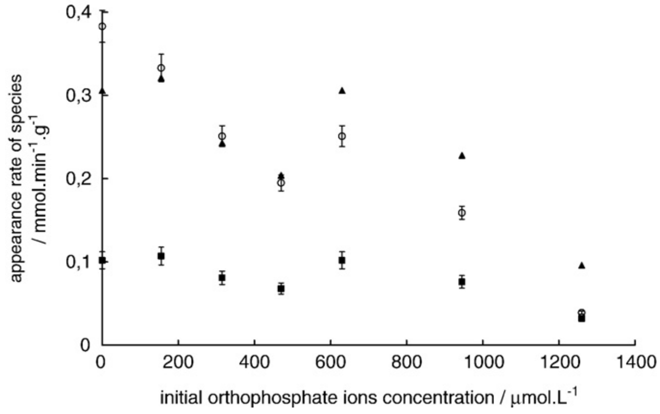

Fig. 4. Evolution of the production rate of calcium (○) and silicate (■) ions in the diluted suspension versus the initial potassium orthophosphate concentration (water/anhydrous=200). The three times values for silicates ions values are also represented (▲).

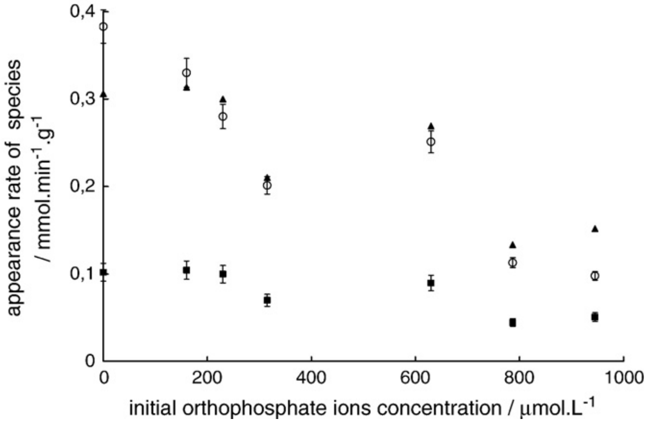

Fig. 5. Evolution of the appearance rate of calcium (○) and silicate (■) ions in the diluted suspension versus the initial sodium orthophosphate concentration (water/anhydrous = 200). The three times values for silicates ions values are also represented (▲).

present in the suspension. These observations show that the dissolution of tricalcium silicate is slowed down by orthophosphate ions. Since the rate of production of calcium ions was always three times that of silicate, as observed during the congruent dissolution of C_3S, it is reasonable to think that no calcium-phosphate compound precipitated during this period. Hence, the results could not be explained otherwise than by considering an adsorption of orthophosphate ions on the surface of the tricalcium silicate particles. Also, this adsorption is increased with the initial orthophosphate concentration. It might have occurred on preferential dissolution sites of C_3S, leading to a slowing down of the dissolution of the anhydrous phase proportional to the number of sites which were blocked. This would explain the linear decrease in the rate of appearance of calcium and silicate ions in the suspension as well as the total depletion of orthophosphate ions.

In some experiments, especially with a water/C_3S ratio of 50 and 200 with absence of phosphates, the Ca/Si ratio was slightly greater than 3/1. This difference which indicates a lack of silicate ions with respect to calcium ions has been interpreted by Barret et al. [11] as being due to local supersaturation with respect to the C–S–H which exists in the very close surrounding of the tricalcium silicate particles in suspension. Indeed, the local ionic environment of particles which are dissolving can slightly differ from that of the solution. Thus, it is possible, under certain conditions, to observe local supersaturation responsible for the precipitation of C–S–H, which would explain the small difference of stoichiometry which is measured in the bulk, especially when the concentrations increase rapidly.

Table 5
Comparison of the amount of mol of orthophosphate ions per gram of tricalcium silicate (deduced from the discontinuity concentrations for the different dissolution series) to the amount of mol of orthophosphate ions per gram (deduced from the cement hydration series)

Water-to-anhydrous ratio	Range of initial concentrations of orthophosphate ions for which the discontinuity occurs	Range of numbers of mol of orthophosphate per gram of anhydrous
0.3 (cement)	210,000–315,000 µ mol L^1	$6.3.10^5$–$9.4.10^5$
50	630–800 µ mol L^1	$3.1.10^5$–4.10^5
200	470–630 µ mol L^1	$9.4.10^5$–$12.6.10^5$

4.2. Discontinuity

In all cases (Figs. 4, 5 and 6), we observed a discontinuity in the decrease of the production rate of calcium and silicate ions. After the discontinuity, there was a significant lack of calcium ions during the pure dissolution period. This was shown by comparing the rate of calcium ion appearance to the theoretical rate assuming a congruent dissolution of C_3S, and calculated as three times that of the silicate ions appearance. It means that one or several calcium-phosphate compounds, which are known to have a very low solubility, precipitated. In such experimental conditions, the presence of phosphates should lead to the precipitation of precursors of hydroxyapatite phase [12–15]. Indeed, this precipitation would lead to a consumption of calcium ions and would explain the 'excess' of silicate ions.

We have already suggested this hypothesis about cement pastes in our previous paper [5] to explain, the non-monotonous evolution of the delay of tricalcium silicate hydration as a function of the initial phosphate concentration, as well as the early rigidification of the cement paste for phosphate concentrations exceeding a limit value. A pessimum of delay of hydration was emphasized for a phosphate concentration close to 0.25 mol L^{-1}. Moreover, rheological investigation of the cement pastes with increasing amount of phosphates also showed a change of behaviour for a similar phosphate concentration. This phosphate concentration was about four hundred times greater than values obtained for diluted suspensions (Table 5). However, comparing the amounts of phosphates per gram of an anhydrous solid for which changes in behaviour occurred, it appeared that C_3S suspensions and cement pastes led to similar results (Table 5). This observation suggests that the phenomenon induced by the orthophosphate ions does not depend on the concentration but would be rather a surface effect. Therefore, we suggest that the precipitation of a calcium-phosphate compound is only possible after the saturation of a fixed number of dissolution sites of the silicate phases by adsorption of orthophosphate ions. Unfortunately, because of the very small amount

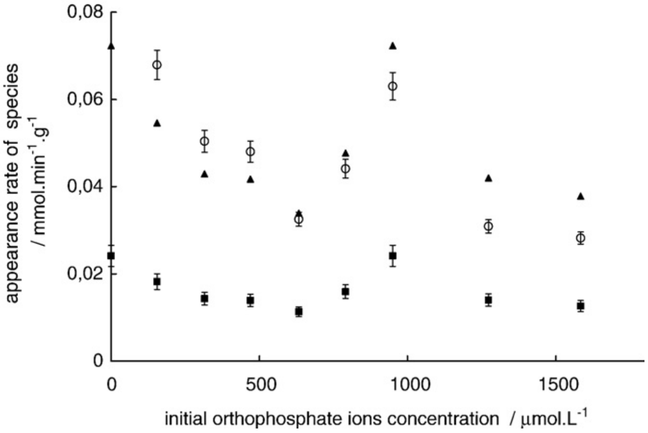

Fig. 6. Evolution of the appearance rate of calcium (○) and silicate (■) ions in the diluted suspension versus the initial potassium orthophosphate concentration (water/anhydrous = 50). The three times values for silicates ions values are also represented (▲).

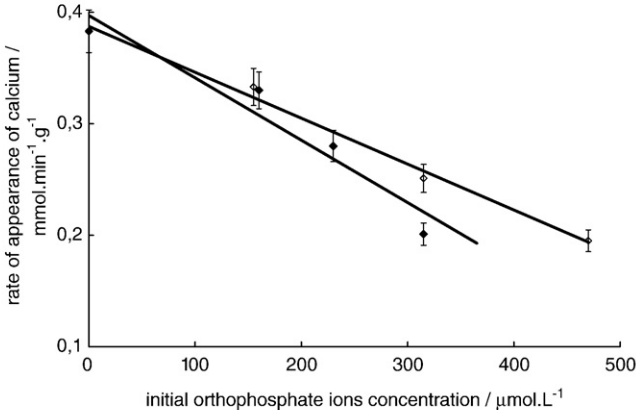

Fig. 7. Comparison of the rates of appearance of the calcium ions in suspension during the pure dissolution period for the hydration of tricalcium silicate with solutions of sodium orthophosphate (◆) and potassium orthophosphate (◊).

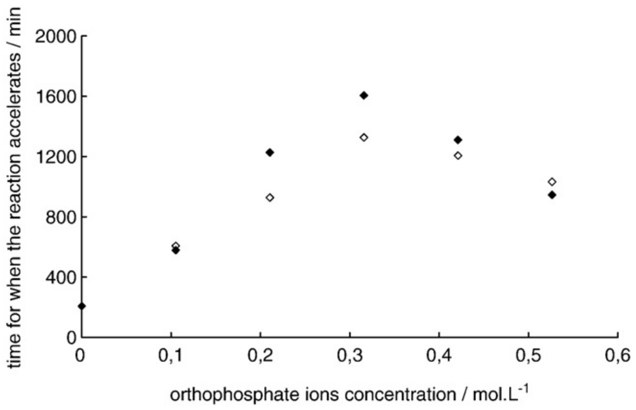

Fig. 8. Time from calorimetric measurements when the hydration accelerates (t_{acc} as defined in Fig. 2) for cement pastes hydrated with solutions containing increasing sodium (◆) or potassium orthophosphate (◊) concentrations (w/c = 0.3).

of calcium-phosphate compound precipitating (it represented less than 2% of the solid mass at best) its identification remained unsuccessful.

4.3. Influence of counter ions on dissolution rate of tricalcium silicate

In order to compare the influence of the counter ion (sodium and potassium) before the discontinuity, some experiments with either sodium or potassium orthophosphate were carried out. Fig. 7 shows the evolution of the dissolution rate of tricalcium silicate in solutions of either sodium or potassium orthophosphate for a water-to-C_3S ratio of 200. The dissolution seemed to occur less rapidly with sodium orthophosphate than with potassium orthophosphate. These observations are consistent with results obtained from calorimetric experiments on cement pastes (w/c = 0.3) with the same ratio of orthophosphate to anhydrous phase; in cement paste the retardation of tricalcium silicate acceleration hydration acceleration was shown to be higher with sodium orthophosphate than with potassium orthophosphate (Fig. 8).

Two parameters could be calculated: (i) the ratio between the slopes of the two lines describing the slowing down of tricalcium silicate dissolution as a function of sodium orthophosphate and potassium orthophosphate concentrations (Fig. 7) and (ii) the ratio between the slopes corresponding to the retardation of tricalcium silicate hydration in the same solutions (Fig. 8). These two ratios were rather similar with values of 1.36 and 1.31. This similarity tends to prove that the counter ion associated to phosphate influences the evolution of both systems (cement paste and C_3S suspension) in the same way. Furthermore, the retardation of acceleration of tricalcium silicate in cement paste can also be linked to its reduced dissolution.

5. Conclusion

The continuous titration of the calcium and silica concentrations, resulting from Ca_3SiO_5 dissolution in concentrated phosphate solutions, shows that the higher the initial orthophosphate concentration, the lower the production rate of calcium and silicate ions in the suspension. In each case a discontinuity is however observed. Before this discontinuity the dissolution of tricalcium silicate is slowed down by orthophosphate ions adsorption on preferential dissolution sites of C_3S and this process seems to be influenced by the nature of the counter ions. After the discontinuity, it is assumed that some calcium-phosphate compounds precipitate. Comparison with paste experiments shows that this phenomenon would be a surface effect with possible precipitation after the saturation of a fixed number of dissolution sites of tricalcium silicate by adsorption of orthophosphate ions.

Acknowledgments

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