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Dimensional stability under wet curing of mortars containing high amounts of nitrates and phosphates

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ABSTRACT

Investigations were carried out in order to solidify in cement some aqueous streams resulting from nuclear decommissioning processes and characterized by a high salinity (300 g/L), as well as important concentrations of nitrate (150–210 g/L) and phosphate ions (0–50 g/L). Special attention was paid to the influence of these compounds on the dimensional variations under wet curing of simulated solidified waste forms. The length changes of mortars containing nitrate salts only (KNO_3, $NaNO_3$) were shown to be governed by a concentration effect which involved osmosis: the higher their concentration in the mixing solution, the higher the swelling. The expansion of mortars containing high amounts of phosphates (≥30 g/L in the mixing solution) was preceded by a shrinkage which increased with the phosphate concentration, and which could be suppressed by seeding the cement used with hydroxyapatite crystals. This transitory shrinkage was attributed to the conversion into hydroxyapatite of a precursor readily precipitated in the cement paste after mixing.

1. Introduction

Cementation is a widely applied technique for the conditioning of aqueous low-level radioactive wastes generated by nuclear power plants, fuel reprocessing facilities or nuclear research centres [1,2]. Compared with other solidification techniques, the process is relatively simple and inexpensive. Moreover, water from the wastes is used up for cement hydration, properly set compositions exhibit a good self-shielding and a high compressive strength, and many radionuclides readily precipitate in the high pH environment of cement. Difficulties can however be encountered when some components of the wastes chemically react with cement phases or mixing water, thus affecting the rate of hydration and/or reducing the quality of the product [3,4]. For instance, some streams resulting from decommissioning processes using nitric and phosphoric acids are characterized by a high salinity (300 g/L), and important concentrations of nitrate (150–210 g/L) and orthophosphate ions (0–50 g/L). The influence of nitrates on cement hydration remains moderate: slight acceleration for concentrations below 1 to 2 mol/L depending on the counter-ion, and slight retardation for higher concentrations [5,6]. The effect of phosphates is however much more severe. These ions are known to be retarders of cement hydration [7–10]. Setting time can be strongly delayed while hardening can be greatly lowered, at least at early age. A comprehensive study of the hydration of cement pastes in phosphate-rich solutions has shown however that the delay increases with the phosphate concentration up to *ca.* 25 g/L, but then decreases at higher concentrations [11]. Rheological investigations carried out on cement pastes containing increasing amounts of phosphates have also revealed the occurrence of a discontinuity for a similar phosphate concentration (*ca.* 25 g/L). These results have been explained by assuming two competing processes: adsorption of phosphates on the silicate phases of cement, which delay their hydration, and, at high phosphate concentrations, precipitation of a calcium phosphate compound which does not [12]. This work has then been supplemented by investigating the dimensional variations under water of mortars prepared with phosphate- and/or nitrate-rich solutions. Expansion under wet curing is indeed an important parameter to assess the quality of a waste-embedding material since, according to a potential accidental scenario, water could flow into the disposal facility where the solidified waste form is eventually stored. This article presents the results obtained and tries to identify the mechanisms involved.

2. Experimental

Aqueous solutions simulating wastes containing nitrates, phosphates or a mixture of the two were prepared by dissolving sodium and potassium salts ($NaNO_3$, $Na_3PO_4{\cdot}12H_2O$, KNO_3, or K_3PO_4 of analytical grade) into demineralised water (Table 1). Salinity (which represents the total weight of anhydrous salts dissolved in water) was

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Table 1
Chemical composition of mixing solutions

Reference no.	Composition		
I (reference)	Demineralised water		
II	$NaNO_3$ 300.0 g/L	Na^+ 81.2 g/L	Na^+ 3.53 mol/L
		NO_3^- 218.8 g/L	NO_3^- 3.53 mol/L
III	KNO_3 300.0 g/L	K^+ 116.0 g/L	K^+ 2.97 mol/L
		NO_3^- 184.0 g/L	NO_3^- 2.97 mol/L
IV	$NaNO_3$ 170.0 g/L	Na^+ 46.0 g/L	Na^+ 2.00 mol/L
		NO_3^- 124.0 g/L	NO_3^- 2.00 mol/L
V	KNO_3 202.2 g/L	K^+ 78.2 g/L	K^+ 2.00 mol/L
		NO_3^- 124.0 g/L	NO_3^- 2.00 mol/L
VI	K_3PO_4 111.7 g/L	K^+ 61.7 g/L	K^+ 1.59 mol/L
		PO_4^{3-} 50.0 g/L	PO_4^{3-} 0.53 mol/L
VII	$Na_3PO_4 \times 12H_2O$ 200.0 g/L	Na^+ 94.1 g/L	Na^+ 4.09 mol/L
	$NaNO_3$ 213.7 g/L	NO_3^- 155.9 g/L	NO_3^- 2.51 mol/L
		PO_4^{3-} 50.0 g/L	PO_4^{3-} 0.53 mol/L
VIII	K_3PO_4 111.7 g/L	K^+ 134.5 g/L	K^+ 3.44 mol/L
	KNO_3 188.3 g/L	NO_3^- 115.5 g/L	NO_3^- 1.86 mol/L
		PO_4^{3-} 50.0 g/L	PO_4^{3-} 0.53 mol/L
IX	K_3PO_4 67.0 g/L	K^+ 127.1 g/L	K^+ 3.25 mol/L
	KNO_3 233.0 g/L	NO_3^- 142.9 g/L	NO_3^- 2.30 mol/L
		PO_4^{3-} 30.0 g/L	PO_4^{3-} 0.32 mol/L
X	K_3PO_4 178.8 g/L	K^+ 145.7 g/L	K^+ 3.73 mol/L
	KNO_3 121.2 g/L	NO_3^- 74.3 g/L	NO_3^- 1.20 mol/L
		PO_4^{3-} 80.0 g/L	PO_4^{3-} 0.84 mol/L
XI	$Na_3PO_4 \times 12H_2O$ 160.0 g/L	Na^+ 62.5 g/L	Na^+ 3.98 mol/L
	$NaNO_3$ 230.9 g/L	NO_3^- 168.5 g/L	NO_3^- 2.72 mol/L
		PO_4^{3-} 40.0 g/L	PO_4^{3-} 0.42 mol/L

maintained constant at 300 g/L in most solutions (nos. II, III, VII to XI). Mortars were prepared by mixing the solutions with sulphate-resistant Portland cement (CEM I 52.5) and sand, the properties of which are given in Table 2. The selected mix design (1000 g of cement, 374 g of sand, 350 g of solution) was derived from a cement-waste formula used in a conditioning plant treating aqueous effluents from nuclear research centres. Mixing was performed with a normalized (European standard EN 196-1) mortar mixer according to the following sequence: (1) introduction of solution, (2) mixing at low speed, (3) addition of premixed cement and sand while maintaining slow stirring for 1 min, (4) mixing at high speed for 3 min. The grout was then cast into 4×4×16 cm moulds and cured for 3 days at 20±1 °C and 95±5% R.H.. The curing period before demoulding had to be extended up to 3 days because of the retarded hydration of mortars containing phosphates. After the specimens were demoulded, they were weighed, measured, and placed into cells filled with 700 mL of demineralised water at room temperature. Length changes of the samples were measured with displacement gauges consisting of LVDTs (linear variable differential transducers — measurement range±1 mm, resolution 1 µm) as shown in Fig. 1. External signal conditioning was performed using a multi-channel modular 600 system from RDP with a data logger/computer interface. Data collection was controlled using Labview software. Measurements were recorded every 30 min over an approximately 90-day period. This experimental set-up allowed the recording of rapid and unexpected length variations which could have been missed with manual measurements (for instance according to French standard NF P 15-433). The first experiments (with solution nos. IV and V) were performed in a non-thermostated room and the signals were noisy. In the other runs, the temperature was regulated at 20 °C±1 °C, which greatly improved the signal to noise ratio. Three experiments (with solution nos. I, II and VIII) were doubled in order to check the repeatability of the results. 5-mL aliquots of the curing solutions were sampled after 3, 14, 42 and 68 days and analyzed for sodium and potassium using I.C.P. optical emission spectrometry. At the end of a run, the relevant specimen was weighed and measured in order to check that the length change was consistent with the measurement provided by the LVDT. Its porosity was then determined using mercury intrusion porosimetry (Micromeritics Autopore III 9420, pressure varying from 0.005 to 365 MPa).

Additional experiments aiming at investigating the hydration of phosphate-containing cement pastes were carried out using isothermal microcalorimetry. Samples of about 1 g were placed shortly after mixing in a nacelle specially designed so as to avoid any heat production due to friction during the introduction in the calorimetric chamber. The experimental set-up and protocol have already been described [11]. The mixing solution to cement ratio was fixed to 0.3 and the mixing solution was either demineralised water (reference — solution no. I of Table 1) or a $Na_3PO_4/NaNO_3$ solution with a salinity of 300 g/L and a phosphate concentration of 40 (solution no. XI) or 50 g/L (solution no. VII).

3. Results and discussion

3.1. Mortars prepared with solutions of alkaline nitrates (KNO_3, $NaNO_3$)

Fig. 2 presents the length variations of five different specimens: mortar I was prepared with pure water and thus constituted a reference; mortars II and III were elaborated with 300-g/L $NaNO_3$ or KNO_3 solutions which simulated simplified evaporator concentrates, and mortars IV and V were prepared with $NaNO_3$ or KNO_3 solutions having different salinities, but the same molar concentration (2 mol/L). In all cases, the samples exhibited expansion which at first was rapid (swelling reached 80 µm/m in a few hours), and then slowed down to an extent which strongly depended on the nature of mixing solution. Equilibrium was however not reached at the end of the experiments. Swelling increased with the concentration of nitrates in the mixing solution, whatever the associated cation (Na^+ or K^+). Moreover, identical molar concentrations of sodium and potassium nitrate in the mixing solution led to similar swelling of the cementitious materials (see mortars IV and V). These results suggest that expansion was controlled by a concentration effect rather than by a specific influence of sodium or potassium. At least two processes may be involved: *(i)* diffusion and *(ii)* osmosis. *(i)* After immersion of the specimens under pure water, ions of the pore solution would diffuse into the curing solution so as to reduce the concentrations gradients between the two solutions. This explains the progressive increase of the leached concentrations of Na^+ and K^+ with time (Fig. 3). *(ii)* Water would tend to diffuse from the less concentrated (curing solution) to the more concentrated (interstitial) solution to equilibrate the chemical potentials and would cause swelling of the sample. The system would reach equilibrium when the mechanical pressure induced by swelling equals the osmotic pressure resulting from the differences in

Table 2
Chemical and mineralogical composition of sulphate-resistant Portland cement and siliceous sand

Reference	Cement		Sand	
	CEM I 52.5 PM ES CP2		Sifraco NE34	
	Lafarge Le Teil		Granulometry 0–400 µm	
Oxides (% weight)	SiO_2	19.9		
	Al_2O_3	5.4		
	Fe_2O_3	2.6	SiO_2	>99.6
	CaO	65.0	Fe_2O_3	<0.024
	MgO	1.4	Al_2O_3	<0.098
	K_2O	0.9	TiO_2	<0.031
	Na_2O	0.1	CrO	<0.022
	SO_3	3.4	K_2O	<0.029
	S^{2-}	<0.01		
	Loss of ignition	1.0		
Minerals (% weight)	C_3S	65.6	Quartz	
	C_2S	16.0		
	C_3A	4.0		
	C_4AF	5.6		
	Gypsum	4.8		
	Carbonate	2.8		

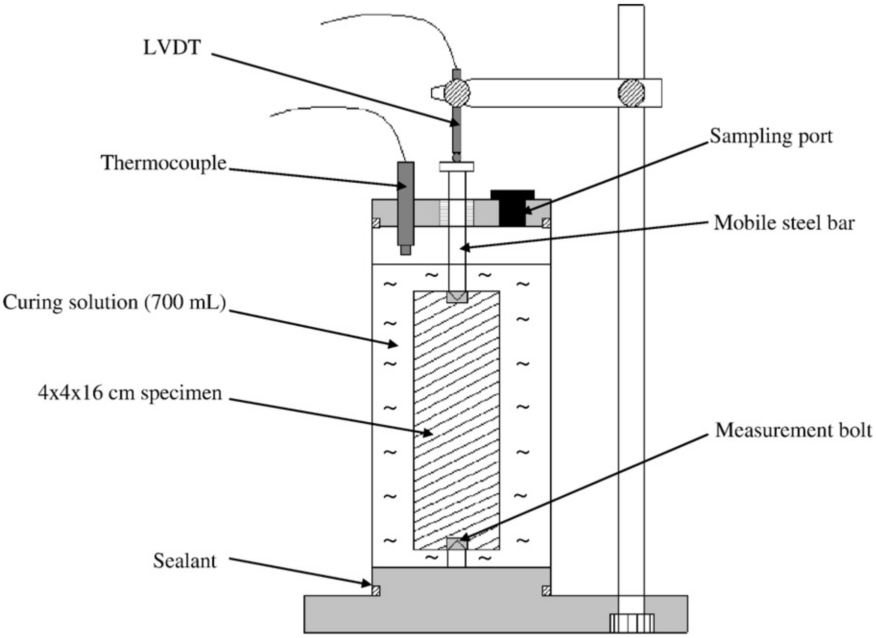


Fig. 1. Experimental device to monitor length variations of specimens cured under water.

concentrations (Eq. (1)).

$$\Delta\Pi = \Pi_{\text{pore solution}} - \Pi_{\text{curing solution}} = G \cdot \gamma \tag{1}$$

with

$\Delta\Pi$	osmotic pressure (Pa)
G	Young modulus (Pa), and
γ	length change (m/m)

In order to check this assumption, the relationship between osmotic pressure and length change at the end of the experiments was investigated. In a first approximation, the solutions were considered as behaving ideally and their pressure was calculated using the Van't Hoff equation (Eq. (2)).

$$\Pi = C_{\text{solutes}} \cdot R \cdot T = 2C_{\text{alkalis}} \cdot R \cdot T \tag{2}$$

with

C_{solutes}	concentration of the solutes (cations and anions) (mol/m^3),
C_{alkalis}	concentration of Na$^+$ or K$^+$ (mol/m^3),
R	gas constant (8.314 J K^{-1} mol^{-1}),
T	temperature (K)

By measuring the porosity of the mortars at the end of the experiments and analyzing the Na$^+$ and K$^+$ concentrations in the curing solutions, it was possible to estimate the corresponding

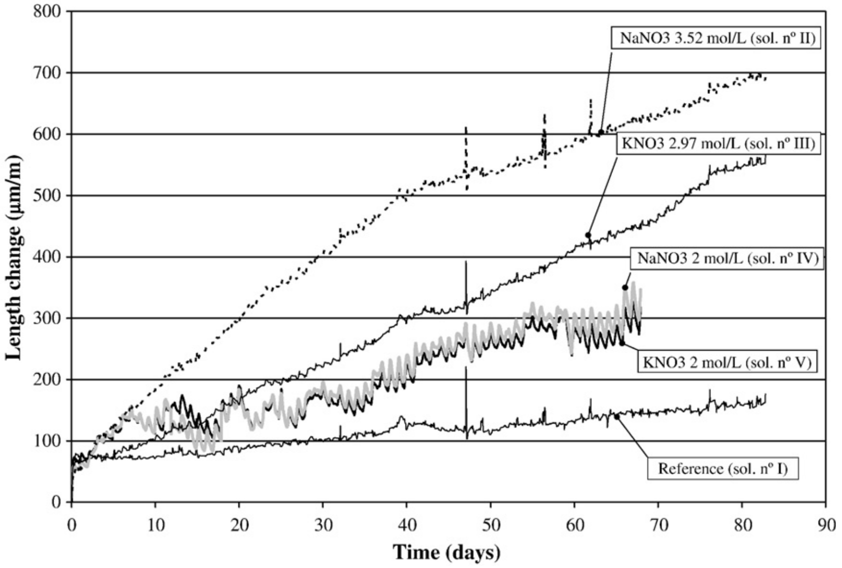


Fig. 2. Length changes of nitrate-containing mortars under wet curing.

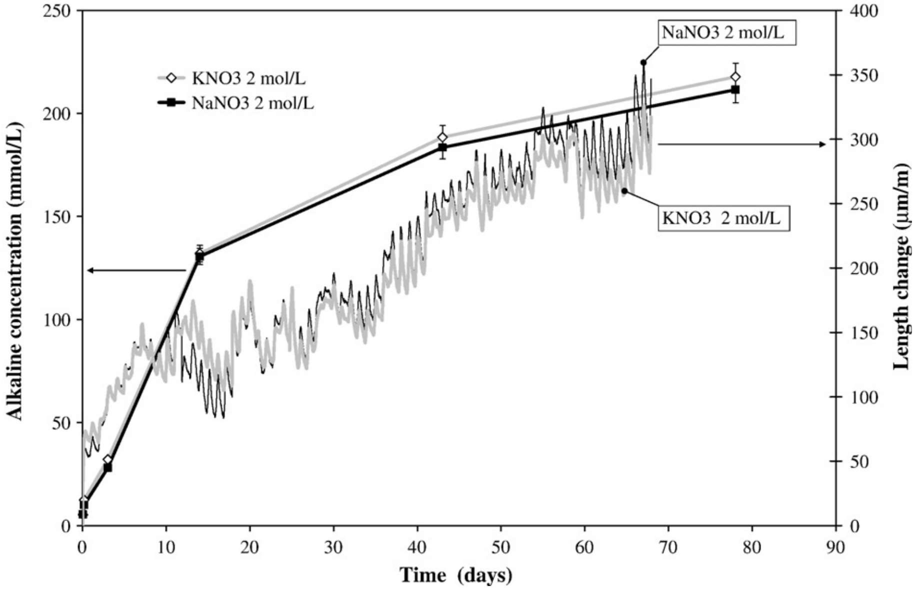


Fig. 3. Comparison of mortars IV and V properties: expansion under water, and evolution of the alkali concentrations in the curing solution.

concentrations in the pore solutions (Table 3), and thus to calculate the resulting osmotic pressure. This parameter was shown to be strongly correlated with the length change of the specimen, as shown in Fig. 4. The inverse of the slope of the fitted straight line provided a rough estimation for the Young modulus of the samples. The resulting value of 23 GPa was plausible for such cementitious materials. This result thus supports the hypothesis according to which osmotic effects play an important part in swelling under the investigated conditions.

Osmosis depends on the existence of a semipermeable membrane, that is a membrane which restricts the passage of solutes while the solvent is not restricted. Solute rejection is usually caused by particle size and/or electrical effects. In the case of clay, it has been shown that the compacted material can exhibit semipermeable properties which are caused by the negative charge of the clay platelets [13–15]. When a solution strives to pass through the pores, anions tend to be repelled by the negative charge of the clay platelets. Movement of cations is also restricted since they tend to remain with their anionic counterpart to maintain electrical neutrality in the external solution. Water, by contrast, can move across the structure. Ideal membranes completely prevent the passage of solutes. Natural semipermeable membranes such as clays are non-ideal since they allow restricted diffusion of ions through the membrane. Cement-based materials may present some analogies with clay materials. The particles of C–S–H are nanocrystalline materials with a lamellar structure. A typical cement paste has a very high pH, and the C–S–H particles become highly negatively charged due to the titration of the silanol groups. This negative surface charge is counterbalanced mainly by divalent calcium counter-ions in the solution [16]. An electrical double layer thus exists in the vicinity of the walls of pores. Fig. 5 shows the pore distribution of mortar II (prepared with a 300-g/L $NaNO_3$ solution) after 85 days of wet curing, which is typical of the results obtained with the other materials under our experimental conditions. The porosity was mainly in the mesoporous (<50 nm) and microporous (<2 nm) ranges. Restricted movement of anions and cations due to electrostatic repulsion by the electrostatic fields associated with the diffuse double layers thus seems conceivable in the smaller pores of the mortars. In the field of diffusion, it is nowadays well accepted that ionic diffusion rates in hydrated cement pastes are greatly affected by the existence of this surface charge and double-layer region of the aqueous pore liquid phase [17,18].

Table 3
Osmotic pressure estimation at the end of the experiments

Mortar	I	IV	V	III	II
	Water	$NaNO_3$	KNO_3	KNO_3	$NaNO_3$
		2 mol/L	2 mol/L	2.97 mol/L	3.53 mol/L
Alkali mol number initially in the specimen[a]	0.028	0.233	0.234	0.354	0.413
Alkali mol number in the curing solution[b]	0.008	0.148	0.152	0.131	0.133
Alkali mol number in the pore solution[c]	0.020	0.085	0.082	0.223	0.280
Porosity of the specimen[d]	18.6%	27.4%	24.1%	21.0%	19.1%
Alkali concentration in the curing solution (mol/m^3)	11.4	211.4	217.1	187.1	190.0
Alkali concentration in the pore solution (mol/m^3)	420.0	1211.8	1329.1	4334.1	5660.1
Osmotic pressure $\Delta\Pi$ (Pa)[e]	1.99×10^6	4.87×10^6	5.42×10^6	20.20×10^6	26.65×10^6
Mass variation of the specimen (%)	1.51	1.22	1.23	0.71	0.61
Length change (µm/m)	165	346	317	560	700

[a] Including alkalis from cement.
[b] Analyzed by ion chromatography.
[c] Calculated by mass balance.
[d] Measured by mercury intrusion porosimetry.
[e] Calculated using Eq. (2).

From a more global point of view, the restrictive passage of ions as compared to water in a cement-based material is also shown by the differences in the diffusion coefficients of these species. In particular, it is well known that the effective diffusion coefficient of tritiated water in a Portland cement paste is higher than that of caesium by a factor 2 at high W/C ratio, and by one order of magnitude or more at low W/C ratio [19]. This result may be extended to the case of sodium and potassium, since these ions have a higher hydrated radius than caesium and should thus be even less mobile.

All samples exhibited a mass increase at the end of the experiments (Table 3). It was maximal for the reference, and decreased when the nitrate salt concentration in the mixing solution of the mortars increased. Thus, surprisingly, mass gain and swelling varied inversely. Different assumptions were considered to explain these results. *(i) Mass gain was due to osmosis*. Water uptake due to osmotic effects should theoretically increase with the ionic concentration of the mixing solution. It should thus have been maximum for mortar II ($NaNO_3$ 3.52 mol/L), and minimum for mortar I (water), which was contradicted by the results. *(ii) Mass gain resulted from two antagonist processes: water penetration in the mortar due to osmosis, and diffusion of the salts from the pore solution to the curing solution, causing a weight*

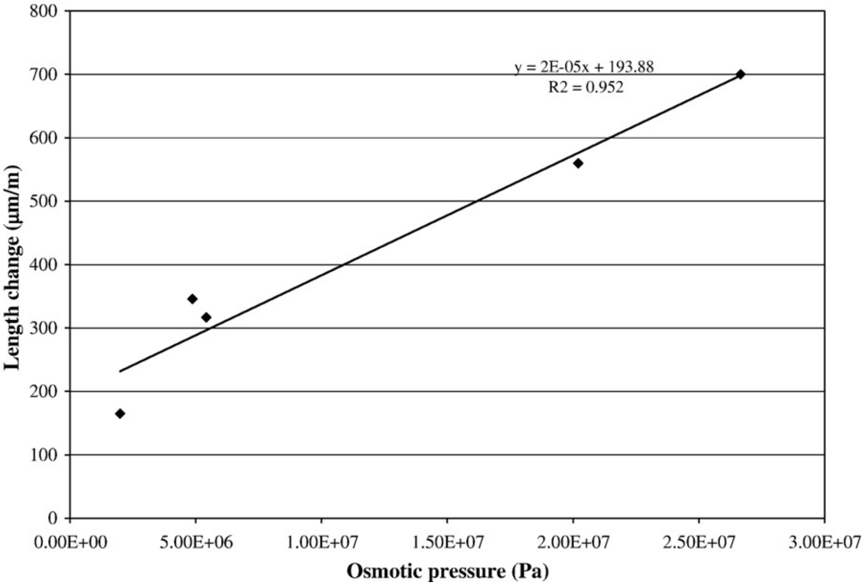


Fig. 4. Dependence of length change on the osmotic pressure resulting from differences in concentration between the curing and the pore solution.

loss. The analyses carried out on the leachates (Table 3) showed that leaching was maximum for mortars IV ($NaNO_3$ 2 mol/L) and V (KNO_3 2 mol/L), and minimum for mortar I (water). The maximum mass gain for mortar I could be explained by assuming that leaching prevailed on osmotic water uptake, but in that case, the mass gain of mortars IV and V should have been lower than that of mortars II and III, which was not in agreement with the experiments. *(iii) Mass gain was mainly controlled by water uptake due to capillary suction to compensate for water depletion by hydration*. Nitrate ions are known to be retarders of cement hydration at high concentration [20], the delay increasing with the nitrate concentration. Fig. 6 shows for instance that, over a 30-day period, the portlandite content of a cement paste prepared with a sodium nitrate solution (3.53 mol/L) remained much lower than that of the reference prepared with pure water. The hydration degrees of the mortars should thus have decreased in the following order: mortar I (reference) > mortars IV and V ($[NO_3^-]=2$ mol/L) > mortar III ($[NO_3^-]=2.97$ mol/L) > mortar II ($[NO_3^-]=3.53$ mol/L). The lower the hydration degree, the lower the water uptake. This third assumption seemed to be consistent with the results.

3.2. Mortars containing phosphates

The length changes under wet curing of mortars containing phosphates or a mixture of phosphates and nitrates were recorded over an 80-day period. The counter-ions were either sodium or potassium. Fig. 7 presents the results obtained for a 50-g/L phosphate concentration. Swelling strongly increased with the ionic concentration (IC) of the mixing solution. Indeed, at the end of the monitoring, values of 100 µm/m, 400 µm/m and 800 µm/m were respectively measured for mortars VI (IC=2.12 mol/L), VIII (IC=5.83 mol/L) and VII (IC=7.13 mol/L). This result is consistent with the previously reported observations dealing with nitrate salts only. A difference could be noticed however: after a rapid expansion at the very beginning of the experiment, the samples containing phosphates transitorily exhibited a shrinkage which seemed to be greater when the mixing solution contained potassium.

The influence of the phosphate concentration in the mixing solution was then investigated (Fig. 8). Shrinkage at early age was still observed and increased with the phosphate concentration. At later age, swelling was predominant and seemed once again to be mainly governed by the ionic concentration of the mixing solution (respectively 5.77, 5.83 and 5.87 mol/L for mortars X, VIII and IX): the higher the concentration, the more important the length change.

The interstitial solution of mortars is characterized by a high calcium concentration and a high pH. In such conditions, the presence

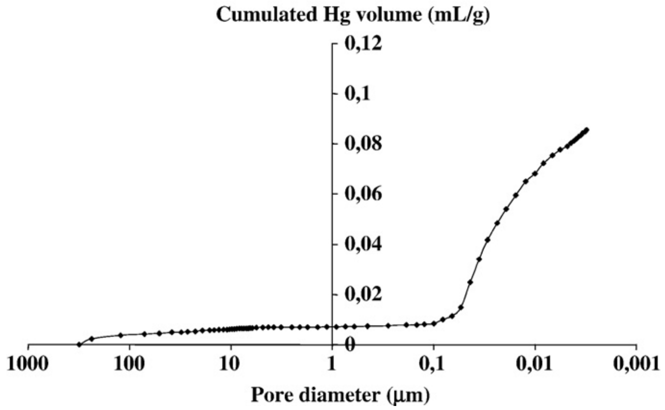


Fig. 5. Pore size distribution of mortar II ($NaNO_3$ 300 g/L) after 87 days of wet curing.

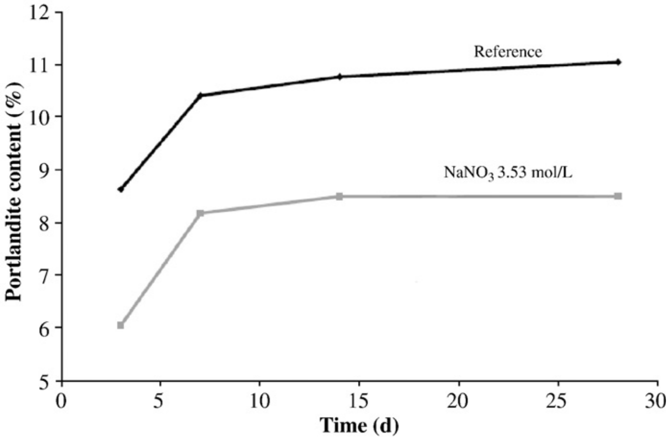


Fig. 6. Evolution with time of the portlandite content of two cement pastes (W/C=0.3) prepared with pure water (reference) or a $NaNO_3$ solution (3.53 mol/L) (wet curing in a lime-saturated solution) [20].

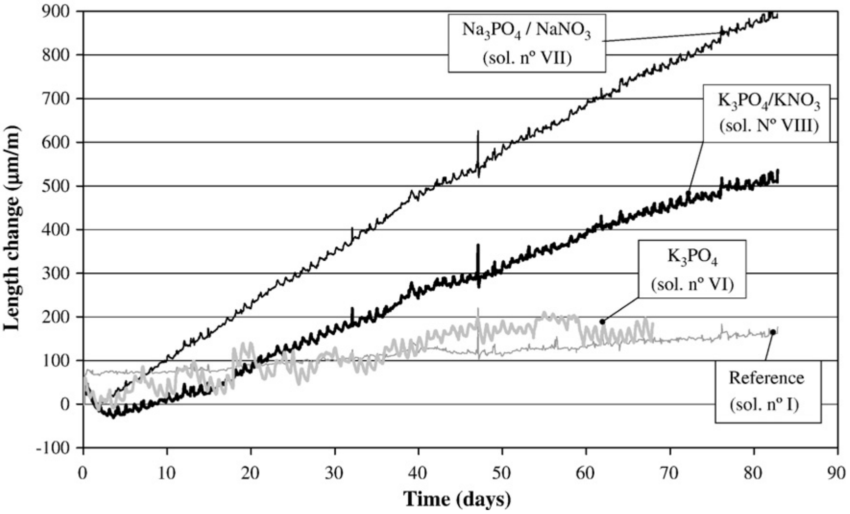


Fig. 7. Length changes of phosphate-containing mortars under wet curing ($[PO_4^{3-}] = 50$ g/L in the mixing solution).

of phosphates should lead to the formation of hydroxyapatite, as shown by thermodynamical calculations using PHREEQC software [21]. Although the activity coefficients were not accurately computed in such high ionic strengths, results indicated that, in all investigated cases, the system was very supersaturated with respect to this phase (Fig. 9). The formation of hydroxyapatite in aqueous solution has been extensively studied since this phase is considered to be the model compound for tooth and bone mineral [22,23]. In the presence of high concentrations of calcium and phosphate ($>10^{-2}$ mol/L), and at pH values higher than 6.8, the precipitation of hydroxyapatite always seemed to be preceded by the precipitation of one or more precursor phases [24,25]. Studies of Feenstra [26] at pH 7.4 and 8.5 at medium or high supersaturation showed for instance that heterogeneous formation of amorphous calcium phosphate (a compound with a Ca/P molar ratio within the range 1.18–1.50 and glass-like properties) was followed by subsequent precipitation of octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \times 5H_2O$), which finally served as a template for hydroxyapatite precipitation. At lower pH, the formation of hydroxyapatite rather seemed to be preceded by octacalcium phosphate and/or dicalcium phosphate dihydrate ($CaHPO_4 \times 2H_2O$) [27]. Relying on these results, it is possible to propose an explanation to the shrinkage of phosphate-containing samples at early age. Shortly after mixing, a precursor of hydroxyapatite would precipitate into the cement paste. It would be later converted into hydroxyapatite. This reaction, which would be much slower and promoted by the presence of water, would occur once the samples immerged under water, and it would generate chemical shrinkage. This assumption is supported by the four following remarks.

1/ Isothermal microcalorimetry was performed on cement pastes prepared with solutions containing increasing concentrations of sodium phosphate and a 300-g/L salinity adjusted with sodium nitrate. Fig. 10 shows the heat evolution rate at the beginning of hydration. After an initial increase due to pure cement dissolution of cement, the thermal flow dropped down. For phosphate concentrations of 40 or 50 g/L, an exothermic signal was clearly observed approximately 200 min after mixing. It might result from the precipitation of an hydroxyapatite precursor. The attempts to identify the compound formed by classical methods

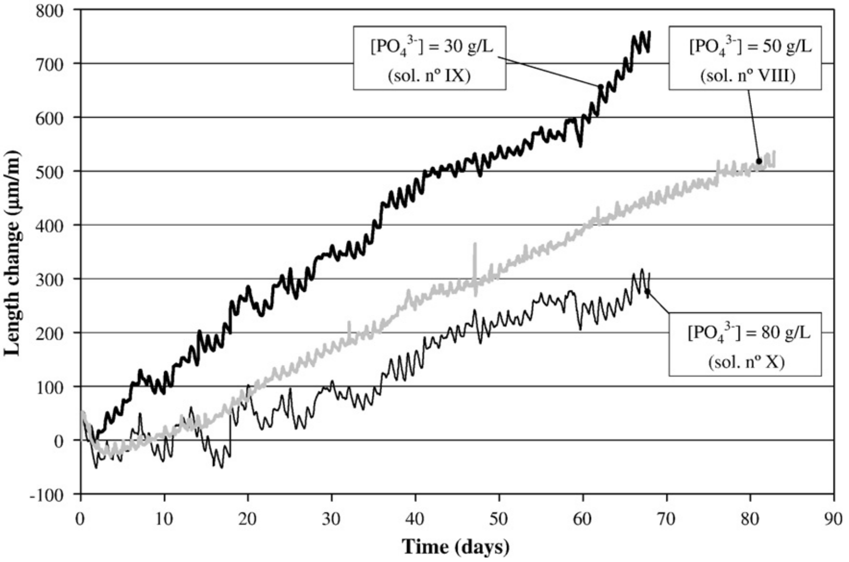
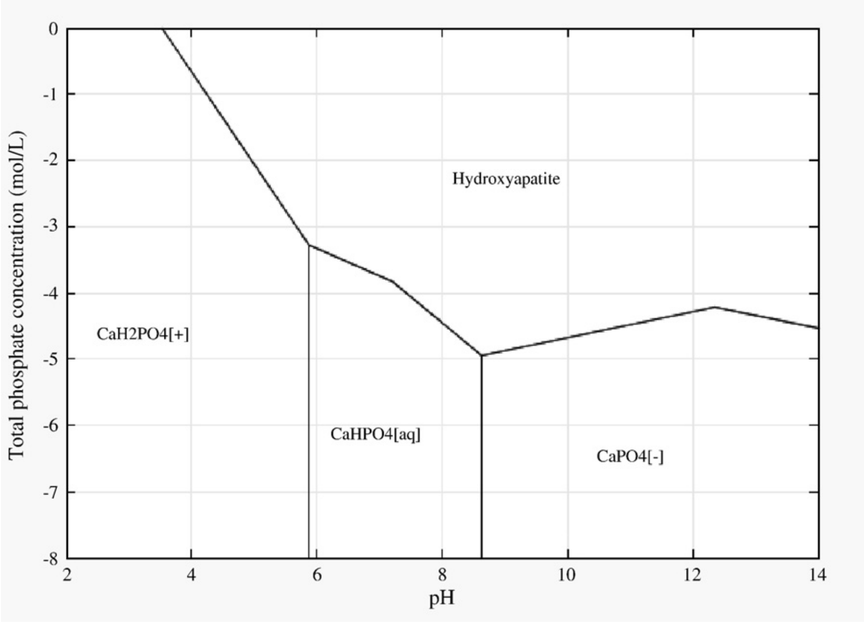


Fig. 8. Influence of the phosphate concentration in the mixing solutions on the length variations of mortars under wet curing (mixing solutions prepared with KNO_3 and K_3PO_4 salts, constant salinity of 300 g/L).



Solubility constants used for the calculations:

$Ca_5(PO_4)_3OH = 5\ Ca^{2+} + 3\ PO_4^{3-} + OH^-$ log K = 40.459 at 25ºC

$CaH_2PO_4^+ = Ca^{2+} + PO_4^{3-} + 2\ H^+$ log K = 20.961 at 25ºC

$CaHPO_4 = Ca^{2+} + PO_4^{3-} + H^+$ log K = 15.085 at 25ºC

$CaPO_4^- = Ca^{2+} + PO_4^{3-}$ log K = 6.459 at 25ºC

Fig. 9. Phosphates speciation as a function of pH and calcium concentration ($[PO_4^{3-}]_{tot} = 50$ g/L).

(XRD or SEM/EDS) failed because of its too low concentration (which represented less than 2% of the solid mass in the best case), and probably poor crystallinity. However, complementary investigations [11] carried out by dynamical rheometry showed an early rigidification of cement pastes prepared with a 50-g/L phosphate solution which could also be explained by the rapid precipitation of an hydroxyapatite precursor.

2/ Additional experiments were carried out by seeding the mortars with hydroxyapatite crystals. The objective was to try to suppress the formation of a precursor before precipitating hydroxyapatite. Indeed, it is well known that appropriate crystal seeding can strongly accelerate the hydration process of calcium phosphate cements forming hydroxyapatite as a final product [28–31]. The seeds, the structure of which must be similar to that

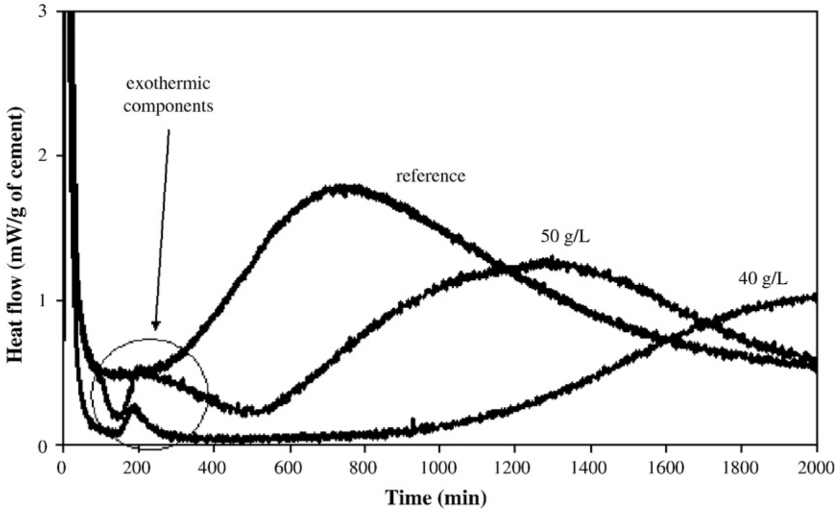


Fig. 10. Evolution of heat flow during hydration of cement pastes elaborated with demineralised water or $NaNO_3/Na_3PO_4$ solutions (constant salinity of 300 g/L, phosphate concentration of 40 or 50 g/L).

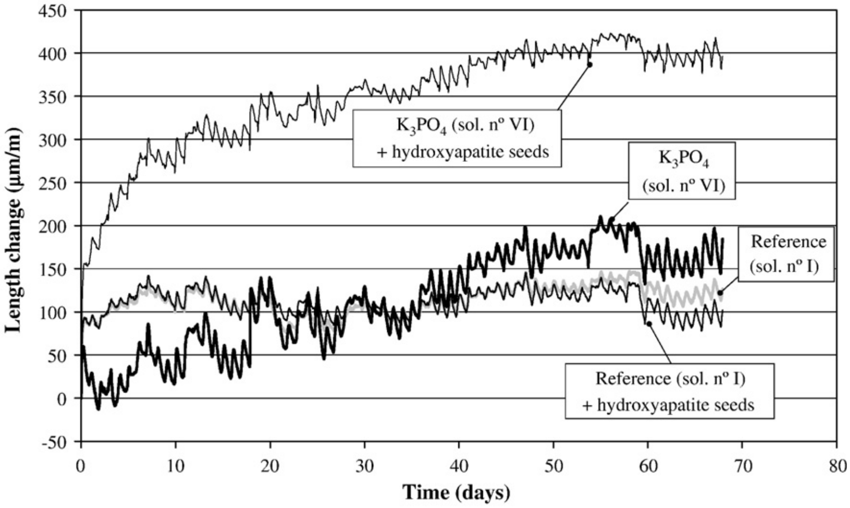


Fig. 11. Influence of the addition of hydroxyapatite seeds to cement on the length changes of mortars under wet curing (mixing solutions: water or K_3PO_4 solution with a phosphate concentration of 50 g/L).

of the product, constitute substrates for heterogeneous nucleation. Furthermore, Moreno et al. [32] have shown that there is no evidence for the formation of a precursor when hydroxyapatite is precipitated by seeding dilute supersaturated solutions with well characterized hydroxyapatite crystals. Their observations are consistent with the occurrence of a simple growth process of hydroxyapatite on the seeds. The amount of hydroxyapatite added in our experiments (30.86 g for 1000 g of cement) corresponded to the one which should be formed in mortars prepared with a 50-g/L phosphate solution and a 0.35 W/C ratio by assuming total precipitation of phosphates into hydroxyapatite. It was first checked that adding hydroxyapatite to the mortar prepared with pure water (reference) had no influence on its further swelling under wet curing (Fig. 11). Hydroxyapatite was then introduced in a mortar elaborated with a 50-g/L phosphate solution. The specimens did not exhibit shrinkage any more (Fig. 11) but a swelling slightly more important than the reference. This result thus gives support to the assumption according to which the chemical shrinkage observed in the absence of seeds would result from the transformation of a precursor into hydroxyapatite.
3/ The conversion of octacalcium phosphate, a possible precursor according to literature, into hydroxyapatite results in a reduction of the volume fraction of the solid phase by a factor 1.4, as calculated from the densities of the phosphate compounds.

$$5Ca_8(HPO_4)_2(PO_4)_4.5H_2O \rightarrow 4Ca_{10}(PO_4)_6(OH)_2 + 6H_3PO_4 + 17H_2O$$

Similar calculations could not be performed for amorphous calcium phosphate, the other likely transitory product on the route to hydroxyapatite, through lack of data.
4/ The rate of formation of microcrystalline hydroxyapatite from amorphous calcium phosphate has been studied within the pH range 6.8–10 [33]. The time required for the reaction to reach completion strongly increased with pH. Furthermore, water was necessary for the reaction to take place. The increase in the rate of conversion with increased water to solid ratio up to 400:1 supported the view of a solution-mediated mechanism. Supposing the early precipitation of amorphous calcium phosphate in our experiments, these results would suggest that the further conversion into hydroxyapatite would be slow because of the high pH (*ca.* 13) imposed by cement, and that wet curing of the material would have a favourable effect for the transformation to occur.

4. Conclusion

The purpose of this article was to investigate the dimensional variations of mortars containing high concentrations of nitrate and phosphate salts under wet curing. The main conclusions can be summarized as follows.

1. Mortars prepared with solutions of KNO_3 or $NaNO_3$ exhibited expansion which increased with the nitrate concentration in the mixing solution, whatever the associated cations. Swelling was controlled by a concentration effect which involved diffusion and osmosis: diffusion of the ions of the pore solution into the less concentrated curing solution, and water uptake by the material due to the osmotic pressure gradient between the pore and curing solutions.
2. Mortars containing phosphates or a mixture of phosphates and nitrates exhibited shrinkage at early age, which increased with the phosphate concentration. At later age, swelling was predominant and, as previously, increased with the ionic concentration of the mixing solution. The transitory shrinkage might result from the conversion into hydroxyapatite of a precursor (possibly amorphous calcium phosphate or octacalcium phosphate) readily precipitated into the cement paste after mixing.

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