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Catinaud, S.; Beaudoin, J. J.; Marchand, J.

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Volume stability of hydrated C_3S systems in various salt solutions

S. Catinaud¹, J. J. Beaudoin² and J. Marchand¹

(1) CRIB-Department of Civil Engineering, Laval University, Quebec, Canada, G1K 7P4.

(2) Institute for Research in Construction, NRC, Ottawa, Canada, K1A 0R6.

ABSTRACT

The volume stability of well-hydrated C_3S samples immersed in various salt solutions was investigated. Test variables included type of solution (sodium chloride, calcium chloride, magnesium chloride and magnesium sulfate) and salt concentration (from 0 to 180 g/l). All samples were prepared at a water/solid ratio of 0.5 and hydrated for several months in a lime-saturated solution. At the end of the curing period, one-mm thick samples were cut and immersed in salt solutions. The kinetics of degradation was assessed by thermal and X-ray diffraction analysis after 10, 20, 40 and 90 days of immersion. The volumetric stability was also followed by length change measurements. All samples were found to expand during immersion. In some cases, expansion was associated to the formation of new products. However, in most instances, length changes appeared to be induced by the progressive dissolution of the hydrated phases initially present in the material. These results tend to support the hypothesis that dissolution mechanisms can inflate expansion.

1. INTRODUCTION

Chemical reactions that alter the cement paste microstructure are among the primary causes of concrete degradation. Hydrated cement systems exposed to aggressive environments such as aqueous chloride or sulfate solutions often sustain damage as a result of excessive volume change. Actual degradation theories have focused on mechanisms occurring at the micrometer scale. The deleterious expansions are attributed to pressures originating from the formation of crystalline phases such as ettringite and gypsum [1, 2].

A universal theory of expansion developed by Litvan [3] attributes the solid dissolution process itself to the source of expansion. This idea has been partially con-

firmed by a recent series of experiment [4] in which dissolution of calcium hydroxide was found to induce marked expansions. Results also suggested that a significant portion of the volume instability of hydrated cement systems is linked to the interaction of the C-S-H gel with aggressive ions such as chloride and sulfate. These results corroborate the argument of Thorvaldson that decalcification of the C-S-H gel may be expansive [5], which could have a significant effect on the service life prediction of concrete.

A comprehensive investigation of the volume stability of hydrated cement systems was recently completed. The main results of the first part of this study are summarized in the following section. This initial part of the project was devoted to the behavior of well-hydrated C_3S pastes immersed in chloride and sulfate solutions prepared at various concentrations. The kinetics of degradation was assessed by thermal and X-ray diffraction analysis after 10, 20, 40 and 90 days of immersion. The volumetric stability was also followed by length change measurements.

2. MATERIALS

The C_3S used in this study had a specific surface area 3000 cm^2/g . The paste was prepared at a water/solid ratio of 0.5. Distilled water was used in the preparation of all samples. Hydration was carried out in a tightly covered plexiglass container, which was rotated continuously during the first 24 hours. Thin slices (approximately 1-mm thick) were sawn after demolding and immersed in saturated lime solution for few months.

3. TEST SOLUTIONS

At the end of the curing period, samples were immersed in distilled water, chloride and sulfate solutions. Reagent grade NaCl, CaCl₂, MgCl₂ and MgSO₄ were used in the preparation of the various salt solutions. The chloride solutions were prepared at three different concentrations: 20, 60 and 180 g/L. The magnesium concentration of the MgSO₄ solution was fixed at 41 g/l (*i.e.* equal to that in MgCl₂ solution prepared at 60g/l of chloride). As can be seen in Table 1, the pH of these solutions ranges from 4.5 to 9.8.

During the immersion experiments, special care was taken to use relatively large volumes of solution compared to the mass of the immersed sample. The solutions were not renewed as it was felt that the solution to sample volume was sufficiently large to maintain the boundary conditions fairly constant throughout the test.

4. EXPERIMENTAL PROCEDURES

TGA analyses were performed on the reference (virgin) sample. Measurements were carried out in a nitrogen atmosphere using a Du Pont 951 thermogravimetric analyzer. All analyses were conducted from 20 and 1000°C, at a heating rate of 10°C/min. About 25 mg of ground material (first dried at 105°C for three hours) were used for each analysis.

The pore size distribution of the reference sample was determined using a mercury intrusion porosimeter (American Instruments Company). The instrument was capable of a minimum intruding pressure of 14 kPa and a maximum of 387 MPa. Samples were in the form of small pieces and had a dried mass of approximately 0.3 grams. Prior to testing, all samples were vacuum dried at 105°C for three hours prior to testing. Calculations were made assuming a contact angle of 130°.

Differential Scanning Calorimetry (DSC) analyses were performed after 0, 10, 20, 40 and 90 days of immersion. The analyses were conducted using a Du Pont Thermal Analysis System. The heating rate was fixed at 10°C/min and all experiments were carried out in a N₂ atmosphere. Approximately 20 mg of crushed material was used for each analysis. Experiments were conducted between 20°C and 600°C.

X-ray diffraction (XRD) analyses were conducted using a Rigaku Geigerflux apparatus and copper K α radiation. The scan speed was fixed at 5 θ /min. The diameter of the majority of the particles was in the ranges 3 and 6 μ m or 6 and 12 μ m. The specimens were taken directly from the solution and ground with a small amount of distilled water (to allow

Table 1 – The pH values of the various test solutions

Solution	Ph value
NaCl 20 g/l	5.9
NaCl 60 g/l	6
NaCl 180 g/l	6.4
CaCl ₂ 20 g/l	7.1
CaCl ₂ 60 g/l	8.5
CaCl ₂ 180 g/l	9.8
MgCl ₂ 20 g/l	5.5
MgCl ₂ 60 g/l	5.1
MgCl ₂ 180 g/l	4.5
MgSO ₄	6.7

easy grinding). Special care was taken to minimize excess evaporation and carbonation during the experiment. The analyses were performed after 0, 10, 20, 40 and 90 days of immersion.

The length change measurements were made on small sliced pieces (about 5 × 25.4 × 1 mm) of C₃S paste, with no apparent edge effects. A Tuckerman optical extensometer was used to measure length change with a 2.10-6in/in accuracy [6]. Measurements were made at regular intervals.

Microhardness (Hv) measurements were carried out with a Leitz testing machine equipped with a Vickers indenter. Measurements were performed after 90 days of immersion. The size of the indentation resulting from the application of a standard mass is used to calculate the hardness value [7]. An average of 5 measurements was taken on the wet surface. A linear relation between the macroscopic strength and the microhardness of Portland cement paste has been reported [7]. It is assumed that such a relationship also exists for C₃S pastes.

A few observations of the microstructure were made using a Cambridge Stereoscan S250 scanning electron microscope equipped with an energy dispersive X-ray analyzer. The specimens were vacuum dried at about 60°C for a few hours and coated with gold prior to analysis.

5. TEST RESULTS

5.1 Characteristics of the reference material

TGA analyses indicate that the non-evaporable water content was about 0.20 gram per unit mass of C₃S. Assuming that approximately 0.25 g of water is required to fully hydrate a gram of C₃S, the degree of hydration of the paste used in this study was thus about 80%. TGA test results also indicate that the initial percentage of calcium hydroxide in the C₃S paste was about 25.1% (by mass). This value was deduced from the mass of water lost at about 440°C. The paste is thus a composite containing calcium

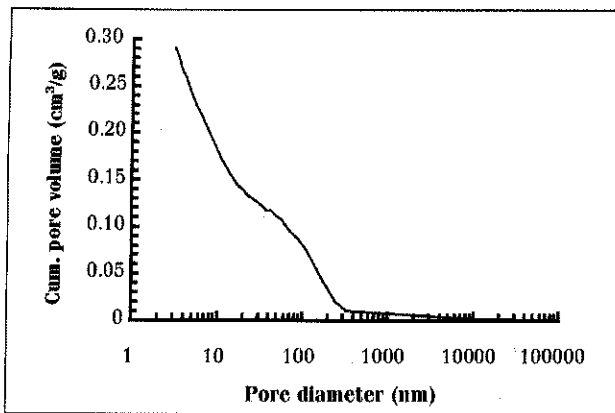


Fig. 1 – Pore size distribution ($\pm 0.5\%$) of the hydrated C_3S paste mixture.

hydroxide, hydrated calcium silicate and residual unhydrated tricalcium silicate.

The pore size distribution of the reference sample is given in Fig. 1. Mercury intrusion porosimetry test data indicate that the total porosity of the mixture is equal to 28.9%. As can be seen, the threshold diameter is approximately 350 nm.

5.2 DSC and XRD analyses

The hydrated C_3S paste is a porous solid and salts are obviously dissolved in the material pore solution. The presence of these salts can influence the results of the DSC analyses. A first series of DSC analyses was therefore performed on the dehydrated salts themselves. The thermograms are presented in Fig. 2. As can be seen, sodium chlo-

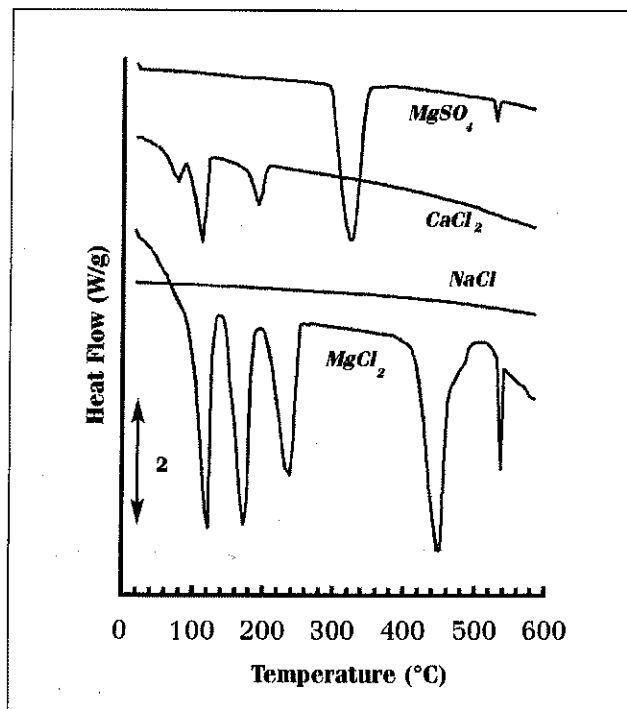


Fig. 2 – Thermograms of the hydrated salts.

Solution	Time (days)
NaCl 20 g/l	20
NaCl 60 g/l	20
NaCl 180 g/l	Some remains after 90 days
CaCl ₂ 20 g/l	20
CaCl ₂ 60 g/l	10
CaCl ₂ 180 g/l	40
MgCl ₂ 20 g/l	10
MgCl ₂ 60 g/l	10
MgCl ₂ 180 g/l	10
MgSO ₄	Some remains after 90 days
Distilled water	90

ride does not exhibit any peaks when heated. Calcium chloride and magnesium chloride exhibit peaks at 80, 115, 195°C and 125, 175, 240, 450, 540°C respectively. Peaks were observed at 330 and 535°C for magnesium sulfate.

The results of the DSC analyses performed on the various samples after 90 days of immersion are summarized in Figs. 3 to 6 and Table 2. The trend which appears at low temperature is not significant of any species because the specimens were dried before analysis. The peak at about 440°C indicates the presence of calcium hydroxide. As can be seen, calcium hydroxide was found to be totally leached out of most samples after 90 days of immersion. Residual amounts of $Ca(OH)_2$ could only be detected in the samples immersed in the magnesium sulfate and the 180 g/L sodium chloride solutions. The evolution of calcium hydroxide content with time of immersion is also shown in Fig. 7 for selected solutions. The portlandite content was calculated from the area under the peak at 440°C on the DSC curves.

For the samples immersed in the sodium chloride solutions, a broad peak could be detected at low temperatures. This peak corresponds to the dehydration of the calcium silicate hydrates. In a few cases, the peak appears to become sharper as the immersion period is increased. XRD analyses also tend to indicate the presence of rustumite

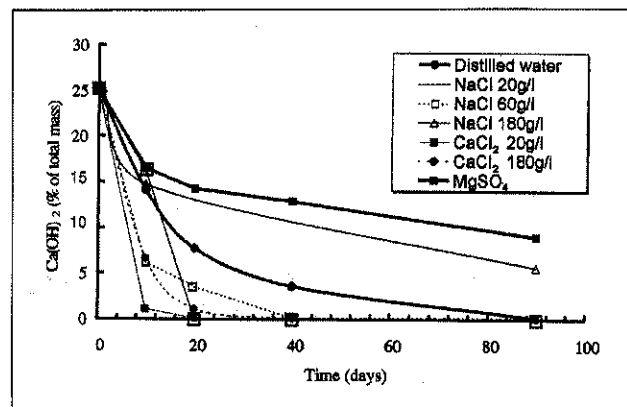


Fig. 7 – Evolution of the $Ca(OH)_2$ content of the specimens during immersion.

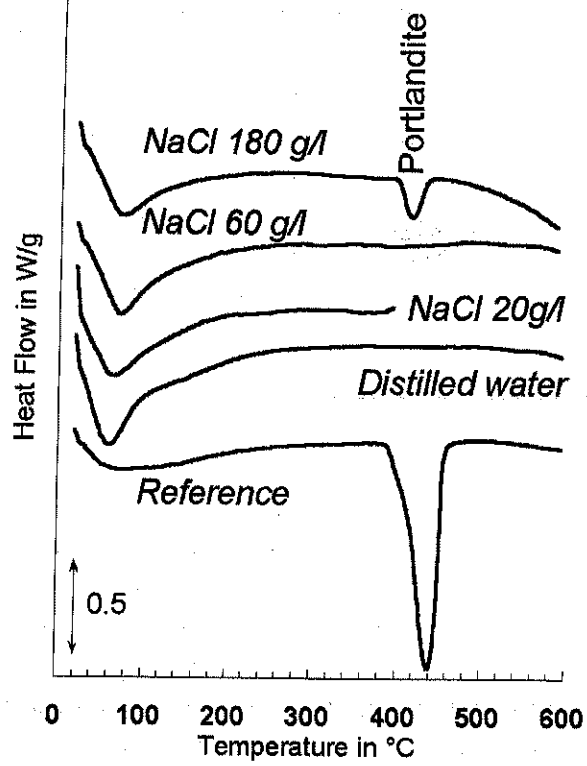


Fig. 3

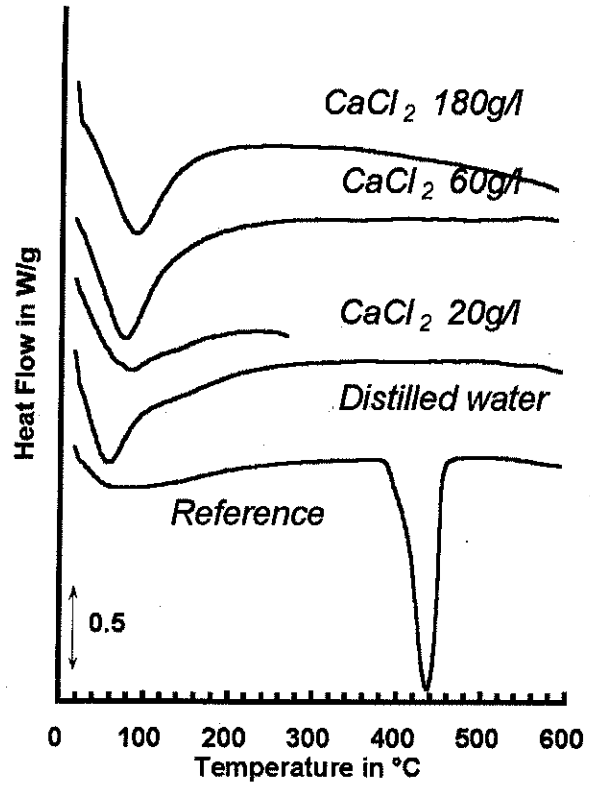


Fig. 4

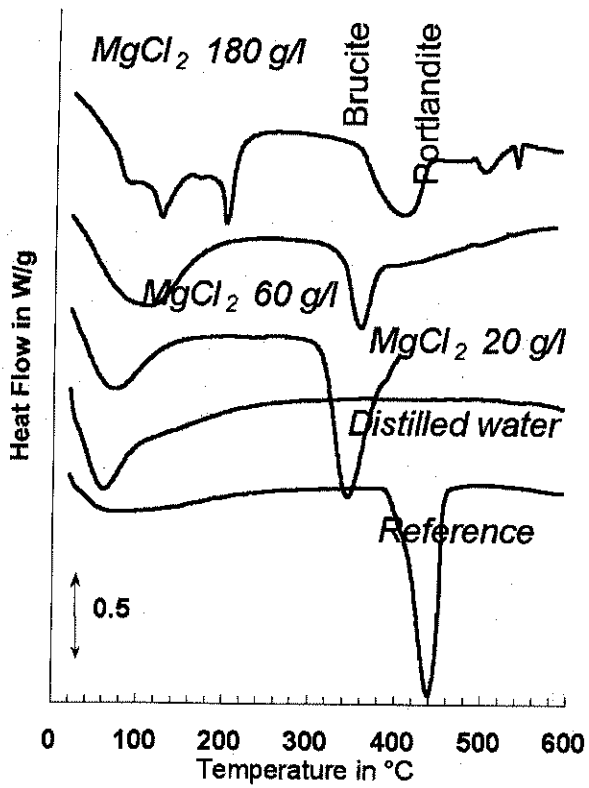


Fig. 5

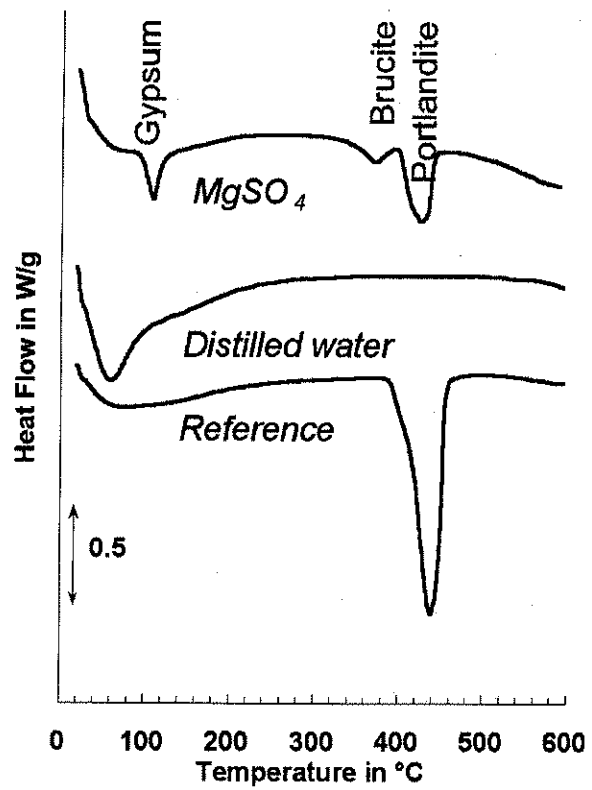


Fig. 6

Figs. 3 to 6 - DSC thermograms of the hydrated C_3S pastes - Immersion time = 90 days.

$(Ca_{10}(SiO_7)2SiO_4Cl_2(OH)_2)$ in the samples immersed in the most concentrated solution.

Similar observations can be made for the specimens immersed in the calcium chloride solutions (see Fig. 4). The analyses do not indicate the formation of calcium oxychlorides in any of the samples tested. This is in apparent contradiction with the observations of Ramachandran [8], Chatterji [9] and Regourd [10] who have reported the formation of at least one form of calcium oxychloride in cement systems in contact with highly concentrated calcium chloride solutions. It should however be emphasized that in Ramachandran's study, calcium chloride was dissolved in the mixing water.

The peaks (for specimens immersed in magnesium chloride solutions) at a temperature of about 380°C are due to the presence of $Mg(OH)_2$ or brucite. The peak for the most concentrated solution is broader and not so clear. Both the DSC and XRD analyses tend to indicate a reduction in the amount of brucite as the concentration of the solution is increased. For the samples immersed in the 20 and 60g/l chloride solutions, a second peak, corresponding the calcium silicate hydrates, could be detected. That was not the case in the samples immersed in the 180 g/l $MgCl_2$ solution. Additional peaks at 85, 125, 170, 200, 400 and about 430°C were observed for the samples immersed in the most concentrated solution. The presence of salt precipitated from the solution can certainly explain the peaks at 125, 170 and 430°C. The peak at about 190/200°C needs explanation. XRD analyses indicate the possible formation $Mg_3Si_2O_5(OH)_4$, $Mg_2Cl(OH)_3 \cdot 4H_2O$ and $MgClOH$. The presence of these compounds could not be confirmed by the thermal analyses.

The specimens immersed in the magnesium sulfate solution exhibit peaks at 110, 375 and 430°C. The latter is due to the decomposition of calcium hydroxide. The 110°C peak corresponds to the presence of gypsum in the sample. According to the XRD analyses, the quantity appears to increase with the period of immersion. The peak at 375°C may be due to presence of magnesium hydroxide.

5.3 Scanning electronic microscopy

C-S-H, unhydrated tricalcium silicate and calcium hydroxide are the principal constituents of the reference C_3S paste. As can be seen in Fig. 8, $Ca(OH)_2$ exists as large crystals well integrated into the core of the C-S-H. Undamaged C-S-H appear to be quite dense and slightly fibrous.

The immersion in distilled water initiates damage of the paste. After 90 days of immersion, C-S-H particles seem to have a more open feature (Fig. 9). SEM observations

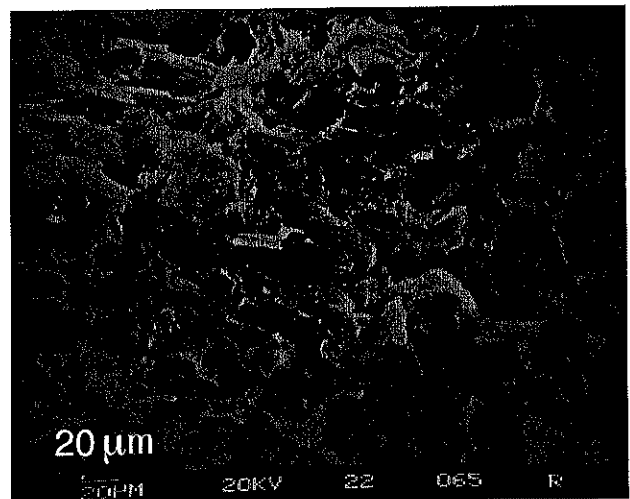


Fig. 8 – C_3S paste – reference state.

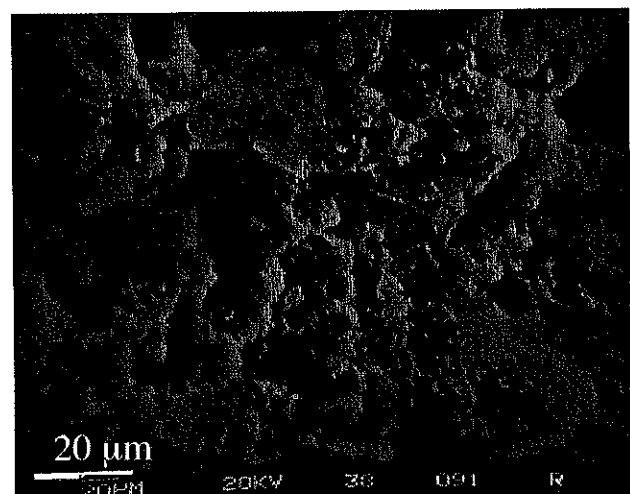


Fig. 9 – C_3S paste immersed for 90 days in distilled water.

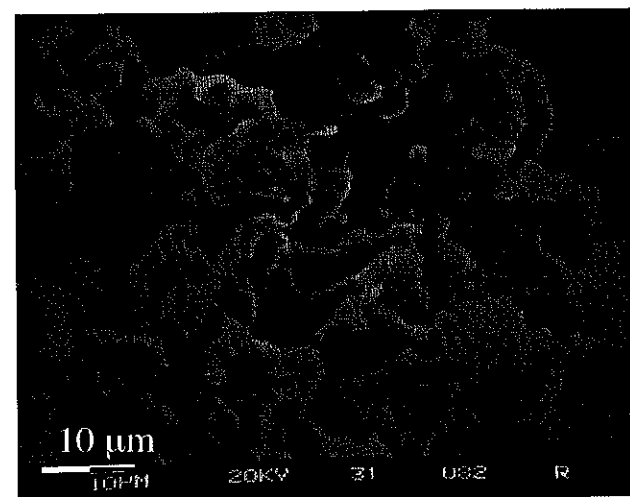


Fig. 10 – C_3S paste immersed for 90 days in the NaCl solution (60 g/l of chloride).

clearly indicated an increase in porosity for these samples. No calcium hydroxide crystals could be detected during the observations.

Significant damage could also be observed for the samples immersed for 90 days in the sodium chloride solutions (see for instance Fig. 10). SEM observations revealed a

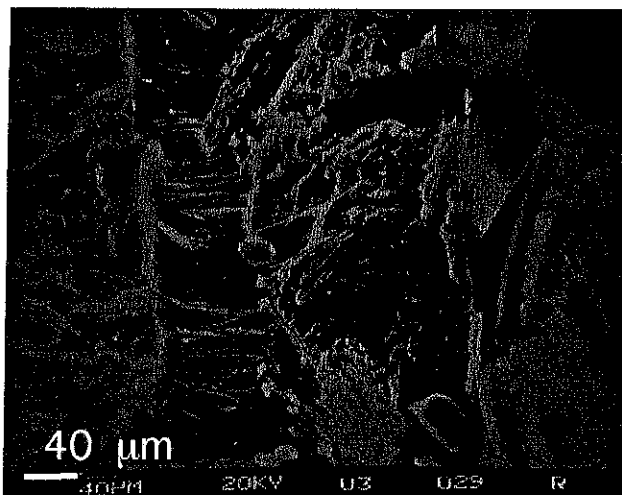


Fig. 11 – C₃S paste immersed for 90 days in the MgSO₄ solution.

marked increase in porosity for these samples similar to what had been observed for the prisms immersed in distilled water. No Ca(OH)₂ crystals could be detected. SEM observations and energy dispersive x-ray analyses also revealed signs of C-S-H decalcification.

The specimen immersed for 90 days in the MgCl₂ solution (at 60g/l) was heavily degraded. A white coating was visible on the surface of the sample. Magnesium, silicon, chlorine and calcium were detected by energy dispersive x-ray analysis, in the core of the paste. Those four components were present at each spot analysis.

SEM observations of the samples immersed for 90 days in the magnesium sulfate solution clearly indicated that the chemical attack progresses from the external surfaces towards the core of the material. A view of the microstructure of the material near one of the external surfaces is given in Fig. 11. The different features along the external surface suggest that an aggressive chemical attack has occurred. Gypsum was observed either as isolated crystals (well integrated in the C-S-H) in the core of the specimen, or as a layer not far from the external surface. It was also present blended with brucite at the vicinity of the external surface. In certain locations, magnesium, silicon and small amounts of calcium could be detected in the samples. This supports the opinion that C-S-H can incorporate magnesium and transform to Ca-Mg-Si-H and then Mg-Si-H. The replacement of calcium by magnesium has begun to take place after 90 days of immersion even if the quantity of well-crystallized product is not significant (see XRD and DSC analysis). The core of the sample appeared quite well preserved in terms of its texture.

5.4 Microhardness measurements

Microhardness test data obtained on the samples immersed for 90 days in the various solutions are summa-

Solution	Loss of HV in %
NaCl 20 g/l	80
NaCl 60 g/l	50
NaCl 180 g/l	65
CaCl ₂ 20 g/l	70
CaCl ₂ 60 g/l	70
CaCl ₂ 180 g/l	-
MgCl ₂ 20 g/l	90
MgCl ₂ 60 g/l	70
MgCl ₂ 180 g/l	80
MgSO ₄	60
Distilled water	70

rized in Table 3. Results are expressed in terms of the approximate loss in microhardness (calculated as a percentage of the initial (reference) value). It should be emphasized that measurements were very difficult to perform. The white color of the degraded samples required a treatment of the surface, which might have affected the results. Test data should also be considered with caution since (as previously mentioned) the degradation of some mixtures was not uniform throughout the thickness of the samples. For instance, the microhardness values obtained for the samples immersed in the magnesium solutions is certainly not a reliable indicator of the mechanical properties of the core of the samples.

As can be seen, the percentage loss in microhardness observed for the specimens immersed in distilled water or in the calcium chloride solutions (containing 20 and 60g/l of chloride) is similar. The loss varies substantially in sodium chloride and magnesium chloride solutions. Immersion in a concentrated solution does not always produce a greater decrease in microhardness. In fact, immersion in the solutions of NaCl and MgCl₂ at 20g/l has clearly accentuated the loss in microhardness.

5.5 Length-change measurements

Selected results are presented in Figs. 12 to 18. As can be seen in Fig. 12, immersion in distilled water leads to marked expansion after only a few hours of test. The expansion peaks after approximately 20 days of immersion. Then, the material undergoes shrinkage. The deformation stabilizes after 40 days of immersion.

The behavior of the samples immersed in the sodium chloride solution tends to differ from that observed for the samples exposed to distilled water. As can be seen in Fig. 12, all samples were found to expand markedly after only a few hours of immersion. In most cases, the rate of deformation levels off after approximately 20 days of immersion for all samples but one. For the sample

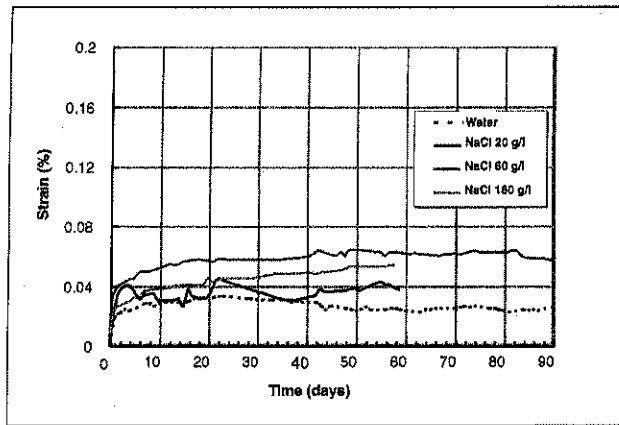


Fig. 12 - Length change of the C_3S paste in distilled water and NaCl solutions.

immersed in the 180g/l NaCl solution, expansion still increases after 60 days of immersion. Contrary to the sample immersed in distilled water, no subsequent shrinkage phase can be seen for the specimens tested in the chloride solutions. It should be emphasized that most of the initial expansion (measured only after a first few hours of immersion) seems to establish the order of magnitude of the final length change.

As can be seen in Fig. 13, the initial length change of the samples immersed in the calcium chloride solutions tends to increase with an increase in concentration. However, contrary to what could be observed for the previous series of samples, the specimen placed in the 20 g/L calcium chloride solution undergoes shrinkage after a few days of immersion. Very significant deformation is observed for the sample immersed in the most concentrated solution.

The strains measured in the magnesium chloride solutions (always expansive) are much larger than those measured for the sample immersed in distilled water (Fig. 14 - note the change in the scale of the y axis). In less than 20 days of immersion, the specimen in the most concentrated

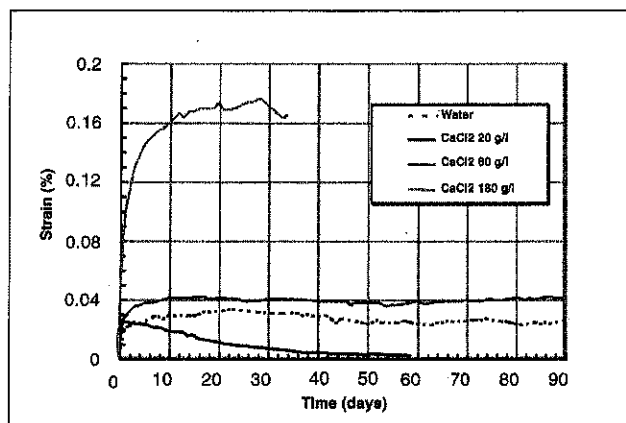


Fig. 13 - Length change of the C_3S paste in distilled water and $CaCl_2$ solutions.

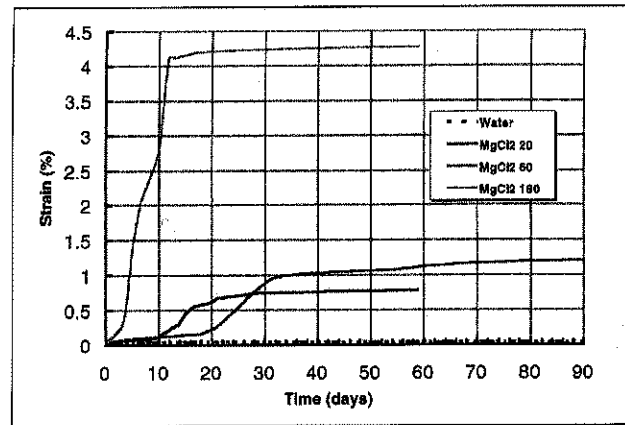


Fig. 14 - Length change of the C_3S paste in distilled water and $MgCl_2$ solutions.

solution is very significantly damaged. The large deleterious expansion occurs after only two days of immersion. The samples in the 20g/l solution and the 60 g/l chloride solution undergo a significant increase in the rate of expansion at 10 and 21 days of immersion. The expansion then decreases quickly after 24 and 33 days respectively. The thin coating of brucite observed on the surface of both samples was very smooth and almost detached from the specimen. It is therefore unlikely that the presence of brucite has totally impeded the transport of ions (in and out of the samples). The formation of brucite could however explain the delayed expansion observed for both samples.

As can be seen in Fig. 15, the C_3S paste specimen immersed in magnesium sulfate solution exhibited constant expansion from the beginning of the immersion up until the end of the test (*i.e.* approximately 140 days). The rate of expansion was about 0.004% per day. This behavior is markedly different from that of the previous series of samples for which most of the expansion was achieved after only a few days of immersion. This expansion was attributed to the formation of gypsum [10].

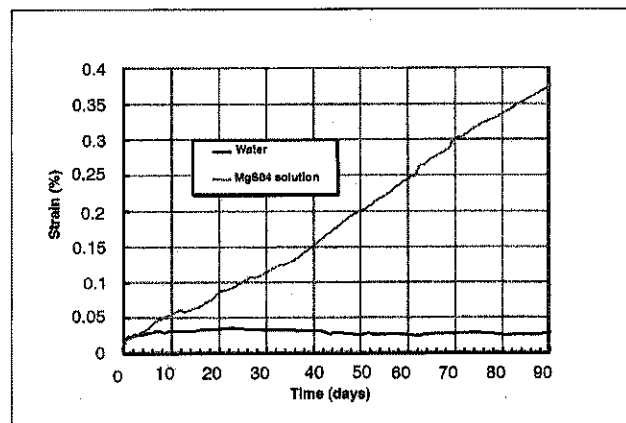


Fig. 15 - Length change of the C_3S paste in distilled water and $MgSO_4$ solutions.

6. DISCUSSION

Test results clearly indicate that the immersion of hydrated C_3S samples in salt solutions can lead to substantial expansion after only a few hours of exposure. It should be emphasized that a positive strain of 0.1% corresponds (for these samples) to a linear deformation of $1000 \mu\text{m/m}$. As can be seen in Figs. 12 to 15, strains well over 0.04% ($400 \mu\text{m/m}$) were observed for most samples after 60 days of immersion in the salt solutions.

The volume instability of the hydrated C_3S samples is apparently linked to microstructural damage induced by the exposure to the various salt solutions. All samples were initially fully saturated with the lime saturated solution. It is therefore unlikely that swelling could have been induced by the absorption of water. Furthermore, trial tests conducted prior to this investigation have clearly showed that the immersion in lime saturated solution does not result to significant length change. This underlines the fact that the test does not induce any artefact.

In that respect, results obtained for the samples immersed in distilled water and in the sodium and calcium chloride solutions are particularly interesting. In all cases but two (samples immersed in the 180 g/l solutions), immersion has only contributed to dissolve existing phases without promoting the precipitation of any new compounds. These results tend to confirm previous observations that dissolution mechanisms can lead to swelling [3, 4, 11, 12].

Feldman and Ramachandran [12] explained the volume instability of hydrated cement paste samples immersed in distilled water by the superposition of two (competing) phenomena: the dissolution of $\text{Ca}(\text{OH})_2$ and the removal of calcium (decalcification) from the C-S-H structure. The authors associated the initial expansion of the hydrated cement paste samples to the dissolution of portlandite. The subsequent shrinkage of the material (noticed after roughly 20 days of immersion in distilled water) was attributed C-S-H decalcification.

As can be seen in Fig. 16, the model proposed by Feldman and Ramachandran [12] is supported by the results obtained in this study for the sample immersed in distilled water. The initial expansion corresponds to a marked depletion in $\text{Ca}(\text{OH})_2$. These data are also in good agreement with the results of a previous investigation where the immersion of compacts of calcium hydroxide in distilled water was found to lead to significant expansion [4].

The effect of portlandite dissolution on the volume stability of hydrated cement system is hard to explain. As suggested by Litvan [3, 11], changes occurring on the surface of the porous solid, whether sorption of inert ions or disso-

lution of either a constituent of a non-homogeneous matrix or a portion of the entire solid, may result in significant expansion.

The selective dissolution of portlandite may also contribute to expansion through a strain-relief mechanism. This assumption was first raised by Feldman and Ramachandran [12] to explain the early expansion of their samples upon immersion in distilled water. Evidence that $\text{Ca}(\text{OH})_2$ crystals embedded in a C-S-H matrix are under strain has been reported in the literature [13-15]. This mechanism could also explain why compacts of $\text{Ca}(\text{OH})_2$ expand during immersion in water [4].

The assumption that $\text{Ca}(\text{OH})_2$ directly contributes to the initial volume change of hydrated C_3S is also supported by the results obtained for the samples immersed in the sodium chloride solutions. As can be see in Fig. 12, the immersion in these solutions contributes to increase the early expansion of the specimens. It should be emphasized that exposure to the 20 g/l and 60 g/l sodium chloride solutions did not lead to the precipitation of any new compound but was found to accelerate the dissolution rate of calcium hydroxide (see Table 2 and Fig. 7).

As can be seen in Table 4, the detrimental influence of sodium chloride is probably linked to its effect on the solubility of $\text{Ca}(\text{OH})_2$. The solubility data summarized in the table was obtained using a geochemical code (called SIMUL) developed at the University of Waterloo [16]. The code accounts for chemical activity effects (using the Pitzer equations) and considers the thermodynamic stability of numerous solid phases. Numerical data clearly indicate that the presence of sodium chloride in solution (at least for the 20 g/l to 60 g/l concentration range) contributes to increase the solubility of portlandite. This phenomenon probably favors the rapid dissolution of the calcium hydroxide crystals and the initial increase in deformation. The large expansion measured for the sample immersed in the 180 g/l sodium chloride solution is likely associated to the formation of rustumite ($\text{Ca}_{10}(\text{SiO}_7)_2\text{SiO}_4\text{Cl}_2(\text{OH})_2$).

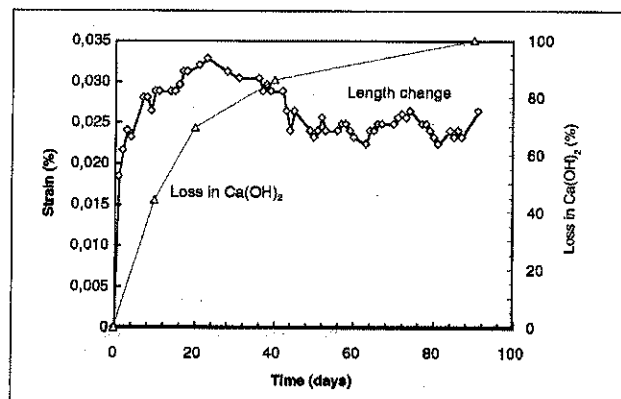


Fig. 16 - Kinetics of deformation and $\text{Ca}(\text{OH})_2$ dissolution for the C_3S sample immersed in distilled water.

Table 4 - Solubility of Ca(OH)₂ in various salt solutions

Solution	Solubility Ca(OH) ₂ (mol/l)	Calcium-bearing phase formed in the system
NaCl 20 g/l	0.0288	
NaCl 60 g/l	0.0293	
NaCl 180 g/l	0.0193	
CaCl ₂ 20 g/l	0.0176	
CaCl ₂ 60 g/l	0.0225	
CaCl ₂ 180 g/l	4.2239	*
MgCl ₂ 20 g/l	0.2995	
MgCl ₂ 60 g/l	0.8683	
MgCl ₂ 180 g/l	7.3400	*
MgSO ₄	0.8657	*
Distilled water	0.0212	

The results obtained for the samples immersed in the calcium chloride solutions are somewhat contradictory. According to the data appearing in Table 4, relatively low concentrations (20 g/L and 60 g/l) of calcium chloride in solution tend to reduce or slightly the solubility of Ca(OH)₂ (when compared to distilled water). This is in good agreement with the length change results appearing in Fig. 13 where the immersion in the 20 g/L and 60 g/L solutions was not found to increase the early expansion of the samples. However, the test data appearing in Table 4 and Table 2 clearly demonstrate that the presence of more calcium chloride (180g/L) increases the solubility of Ca(OH)₂ but not the rate of calcium hydroxide depletion. The very significant early deformation of the sample immersed in the 180 g/l solution is also difficult to explain considering that no new phase could be detected by the XRD and DSC analyses.

The results obtained for the samples immersed in the calcium chloride solutions could indicate that the interaction of ions with the material pore surface plays an important role in the mechanisms of expansion. ³⁷Cl and ³⁵Cl nuclear magnetic resonance (NMR) data indicate that the affinity of chloride for the C-S-H surface varies strongly with the nature of the counter-ion present [17]. Test results also show that the ability of the cation to penetrate the C-S-H interlayer differs significantly from one species to another. This could explain the detrimental influence of sodium chloride at low concentrations.

The character of the curves appearing in Fig. 16 also tends to confirm the assumption made by Feldman and Ramachandran [12] that Ca(OH)₂ is not the only phenomenon affecting the volume instability of hydrated cement systems. As can be seen, after 20 days of immersion, the sample starts to shrink as Ca(OH)₂ continues to be leached out of the material. It should be noted that the shrinkage phase has been observed in a previous study for hydrated C₃S samples (containing various amounts of limestone fillers) immersed in distilled water [18]. These

results suggest that, as proposed by Feldman and Ramachandran [12], C-S-H decalcification may have a significant influence on the behavior of the porous solid. SEM observations performed in this study have indicated that C-S-H was affected by the immersion in distilled water. The aggressive nature of distilled water has also been emphasized by a number of recent studies [19-22].

Length-change data obtained for the samples immersed in the MgCl₂ and MgSO₄ solutions emphasize the complexity of the degradation mechanisms in magnesium solutions, which involve a series of dissolution/precipitation processes. The length change of the C₃S paste in MgCl₂ and MgSO₄ solutions may be due in part to the dissolution of calcium hydroxide. At the beginning of the immersion in MgSO₄ solution some calcium may be removed from the portlandite (but not all of it is dissolved). Calcium is also probably removed from the C-S-H to form gypsum.

As previously discussed, the formation of a layer of brucite on the surface of the samples has most probably affected the transport of ions in and out of the material. Magnesium may also replace calcium in the C-S-H [23, 24]. The fact that the rate of expansion observed after 30 days for the sample immersed in the MgCl₂ solution is similar to that of the specimen immersed in the MgSO₄ solution suggest that gypsum formation has a minor role on the expansion process. This needs to be confirmed. Other phenomenon may be operative upon immersion in MgCl₂ solutions. This may involve the interaction of chloride with C-S-H.

It is now well established that the decalcification of C-S-H results in a major reduction in the mechanical strength of the material [25]. The end product of the dissolution reaction is a silica-rich phase (often called silica "gel") with little, if any, binding properties [19, 20, 25]. Microhardness test results tend to indicate that the dissolution of Ca(OH)₂ also contributes significantly to the alteration of the mechanical properties of concrete.

7. CONCLUSION

Test results indicate that the immersion of hydrated C₃S samples in salt solutions can lead to substantial expansion after only a few hours of exposure. Significant strains (well over 0.04% or 400 μm/m) were observed for most samples after 60 days of immersion in the salt solutions.

The volume instability of the hydrated C₃S samples is apparently linked to microstructural damage induced by the exposure to the various salt solutions. All samples

were initially fully saturated. It is therefore unlikely that swelling could have been induced by water absorption.

The volume instability of hydrated C_3S samples immersed in salt solutions appears to be induced by the superposition of two phenomena: the dissolution of $Ca(OH)_2$ and the decalcification of C-S-H. In many instances, swelling was associated to the dissolution of portlandite, which was not accompanied by the precipitation of any new compounds.

Test results indicate that the presence of salts in solution tends to modify the mechanisms of volume change. The influence of these salts on the volume instability of hydrated C_3S is not necessarily linked to the formation of new phases.

Length-change data obtained for the samples immersed in the $MgCl_2$ and $MgSO_4$ solutions emphasize the complexity of the degradation mechanisms in magnesium solutions, which involve a series of dissolution/precipitation processes.

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