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Influence of limestone addition on calcium leaching mechanisms in cement-based materials

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Abstract

In order to investigate the mechanisms of calcium leaching and their implications on the long-term durability of cement-based materials, four different systems (C_3S, $C_3S + C_3A + CaSO_4{\cdot}2H_2O$, $C_3S + C_4AF + CaSO_4{\cdot}2H_2O$, and Portland cement) were prepared, mixed with water, and cured for several weeks. Four percentages of calcium carbonate addition (0%, 5%, 10%, and 20%) were used in the preparation of these systems. In all cases, the water/solid ratio was fixed at 0.5. At the end of the curing period, 1-mm thick samples were cut and immersed in distilled water. The kinetics of degradation was assessed by thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis after 10, 20, 40, and 90 days of immersion. The volumetric stability was also followed by length-change measurements. Test results clearly indicate that the mechanisms of leaching are directly affected by the mineralogical composition of the system, in particular by the calcium carbonate content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium leaching; $CaCO_3$; Durability; Volume stability; Chemical composition

1. Introduction

The term fillers refers to rock particles (added to a binder) obtained by fine milling or crushing. In certain countries, limestone additions have been used for decades as partial cement replacement. Limestone fillers are generally added directly at the cement production plant. Research on the influence of limestone additions on the properties of hydrated cement-based materials indicates that their action is primarily physical in nature [1]. However, evidence of reaction with the aluminate-bearing phases usually found in cement systems has been reported [2]. Calcite fines have also been used as a replacement for gypsum in Portland cement [3]. It has been shown that limestone additions can accelerate the hydration of the calcium silicate components of cement [4].

The use of limestone fines results in products that have acceptable mechanical properties [1,5]. These additions also have beneficial rheological effects [1]. The positive effects of limestone addition can explain why regulations worldwide have permitted its addition to cement. However, depending on the country, the amount permitted varies from 0% to 35%. Debate on acceptable amounts of limestone addition to cement continues.

The wide variety of practical cases of contact where concrete structures are directly in contact with chemically aggressive salt solutions and the expensive maintenance and repair of damaged structures account for the global interest in the durability of cement-based materials. The contact with softer waters (as in nuclear waste storage situations) is also of interest. In general, when the chemical attack of cement paste occurs, it is often accompanied by a decalcification of the matrix. The mechanisms of decalcification generally involve the dissolution of calcium hydroxide ($Ca(OH)_2$) crystals and the partial dissolution of C-S-H (the binding phase) [6–10].

The mechanisms of calcium hydroxide dissolution and C-S-H decalcification have recently been the subject of extensive research [6–10]. This is the basis for numerous projects involving the study of the material behavior in contact with distilled water. Distilled water is the simplest solution (no chloride or sulfate ions) inducing decalcification of the matrix. In order to investigate the effects of decalcification on the properties of cement systems, var-

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Table 1
Chemical analysis and phase composition of the cement

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	C_3S	C_2S	C_3A	C_4AF
20.68	4.15	2.98	62.38	2.4	3.33	0.21	0.87	2.69	55.17	17.68	5.94	9.07

ious techniques have been developed to accelerate the kinetics of degradation [6,10–12]. Most data clearly emphasize the very detrimental influence of decalcification on the mechanical and transport properties of cement-based materials [6–14].

The specific case of limestone addition and its effect on durability has not been widely investigated. Research is needed to support regulation. Evaluating the detrimental or beneficial impact of the addition of calcium carbonate (the main constituent of limestone addition) on the calcium leaching and discussion of the various phenomena that can occur should improve understanding of the influence of a chemical attack on these systems.

The main results of an investigation of the influence of limestone fillers on calcium leaching mechanisms in hydrated cement systems are presented. Four different systems (C_3S, $C_3S + C_3A + CaSO_4{\cdot}2H_2O$, $C_3S + C_4AF + CaSO_4{\cdot}2H_2O$, and Portland cement) prepared with various amounts of calcium carbonate addition (0%, 5%, 10%, and 20%) were hydrated and tested. This test program was carried out as part of a comprehensive study of the durability of cement-based materials exposed to various salt solutions.

2. Experimental

2.1. Materials and preparation of the various mixtures

The C_3S, C_3A, C_4AF, and $CaCO_3$ used in this study had specific surface area values of 3000, 3010, 3060, and 4600 cm^2/g, respectively. The calcium carbonate utilized contained more than 99% $CaCO_3$. The composition of the ordinary Portland cement (type 10 according to the Canadian standard) is given in Table 1.

Table 2 presents the characteristics of the 16 different paste mixtures tested in this investigation. The pastes were prepared at a water/solid ratio of 0.5. Distilled water was used in the preparation of all mixtures. Hydration was carried out in tightly sealed Plexiglas containers rotated continuously during the first 24 h. After demolding, slices (approximately 1-mm thick) were sawn and placed in saturated lime solution for a several weeks. Mixtures of the first three systems (C_3S, $C_3S + C_3A + CaSO_4{\cdot}2H_2O$, and Portland cement) with water were cured for a minimal period of 6 months. Mixtures prepared with the fourth system ($C_3S + C_4AF + CaSO_4{\cdot}2H_2O$) were kept in the lime solution for 4 weeks.

2.2. Characterization of the initial state of the samples

The microstructural properties of the various mixtures were determined at the end of the curing period. Thermogravimetric analysis (TGA) measurements using a Du Pont 951 thermogravimetric analyzer were conducted between 20°C and 1000°C, at a heating rate of 10°C/min in order to estimate the non-evaporable water content per unit mass of initial solid (other than calcium carbonate). About 25 mg of ground vacuum dried (at 105°C for 3 h) material were used.

TGA test results are summarized in Table 3. Approximate values for the degree of hydration, calculated assuming that 25 g of water is necessary for complete the hydration of each system, are given in the right column of Table 3. The value for the C_3S paste with 10% $CaCO_3$ was not obtained. The lower values obtained for the pastes containing C_4AF can be explained by the reduced curing period of these mixtures.

X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analysis were also conducted in order to characterize the initial state of the various mixtures. The thermal analyses were conducted on a Du Pont Thermal Analysis System using a 10°C/min heating rate in a N_2 atmosphere and about 20 mg of material. Samples were dried under vacuum at 105°C and ground before analysis. The final temperature was 600°C. XRD analyses were conducted using a Rigaku Geigerflux apparatus and Cu Kα radiation. The scan speed was 5θ/min. The specimens

Table 2
Composition per unit of mass of the various components of the solid part of the various pastes containing x% of calcium carbonate

	C_3S	C_3A	C_4AF	Gypsum	Cement	$CaCO_3$
C_3S	$100 - x$	0	0	0	0	x
$C_3S + C_3A$ + gypsum	80	20	0	5	0	$105x/100$
Cement	0	0	0	0	$100 - x$	x
$C_3S + C_4AF$ + gypsum	80	0	20	5	0	$105x/100$

Table 3
Non-evaporable water content of the various pastes and corresponding degree of hydration α for each type of pastes

	0% $CaCO_3$	5% $CaCO_3$	10% $CaCO_3$	20% $CaCO_3$	α in %
C_3S	0.20	0.21		0.21	80/85
$C_3S + C_3A$ + gypsum	0.23	0.22	0.24	0.24	90/95
Cement	0.19	0.20	0.20	0.19	75/80
$C_3S + C_4AF$ + gypsum	0.12	0.11	0.11	0.12	40/50

Table 4
Composition of the various pastes from DSC and XRD analysis where A is $Ca_4Al_2O_3(CO_3)_{0.5}(OH)\cdot 11.5H_2O$ and B is $Ca_4Al_2O_6CO_3\cdot 11H_2O$

	Composition
$C_3S + C_3A$ + gypsum + 0% $CaCO_3$	$Ca(OH)_2$ – AFm – A – $CaCO_3$
$C_3S + C_3A$ + gypsum + 5% $CaCO_3$	$Ca(OH)_2$ – B – A – $CaCO_3$
$C_3S + C_3A$ + gypsum + 10% $CaCO_3$	$Ca(OH)_2$ – B – A – $CaCO_3$ – AFt
$C_3S + C_3A$ + gypsum + 20% $CaCO_3$	$Ca(OH)_2$ – B – A – $CaCO_3$ – AFt
Cement + 0% $CaCO_3$	$Ca(OH)_2$ – $CaCO_3$ – AFt
Cement + 5% $CaCO_3$	$Ca(OH)_2$ – $CaCO_3$ – AFt – B
Cement + 10% $CaCO_3$	$Ca(OH)_2$ – $CaCO_3$ – AFt – B
Cement + 20% $CaCO_3$	$Ca(OH)_2$ – $CaCO_3$ – AFt – B
$C_3S + C_4AF$ + gypsum + 0% $CaCO_3$	$Ca(OH)_2$ – C_4AF – AFt – $CaCO_3$
$C_3S + C_4AF$ + gypsum + 5% $CaCO_3$	$Ca(OH)_2$ – C_4AF – AFt – $CaCO_3$
$C_3S + C_4AF$ + gypsum + 10% $CaCO_3$	$Ca(OH)_2$ – C_4AF – AFt – $CaCO_3$
$C_3S + C_4AF$ + gypsum + 20% $CaCO_3$	$Ca(OH)_2$ – C_4AF – AFt – $CaCO_3$

were taken directly from the solution and ground in a mortar with just sufficient distilled water to allow easy grinding. Excess evaporation on the glass slide and carbonation were minimized. Table 4 presents the composition of the various mixtures as established on the basis of the TGA, DSC, and XRD test results.

A mercury porosimeter (American Instruments) was used to obtain the pore size distributions of the various mixtures. Measurements were conducted pressures up to 387 MPa. The samples were vacuum dried at 105°C for 3 h before measurement. The total porosity values and percentage of pores with diameters less than 50 nm for the 16 different pastes are presented in Table 5. The addition of calcium carbonate contributed to the increase of the total porosity, mainly due to pores with diameter greater than 50 nm.

2.3. The immersion in distilled water

At the end of the curing period, 1-mm thick samples were cut and immersed in distilled water. 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 the solution to sample volume was sufficiently large to minimize error.

2.4. Experimental procedures

The kinetics of degradation was assessed after 10, 20, 40, and 90 days of immersion using various experimental techniques. XRD and DSC analysis were conducted in order to determine any change in composition due to dissolution of solids or the appearance of complexes or well-crystallized compounds.

The length-change measurements were made on small sliced pieces (about $5 \times 25.4 \times 1$ mm) of paste, with no apparent edge effect. A Tuckerman optical extensometer was used to measure length change with a 2×10^{-6} mm/mm accuracy [14].

A few observations of the microstructure were made on 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 before coating with gold.

3. Test results

3.1. Dissolution of calcium hydroxide

Fig. 1 presents the percentage (obtained from TGA) of calcium hydroxide initially present in each paste. For a given composition of material, the calcium hydroxide content depends in part on the degree of hydration of the material (see Table 3). The differences in moles of calcium in the various pastes for an equal mass of the initial materials (solid plus distilled water) can also explain the differences between the various mixtures.

The rate of the dissolution of portlandite in the C_3S-based pastes is not highly dependent on the calcium carbonate content (Fig. 2). This is true for the entire period of immersion before consumption of portlandite is complete. The rate of dissolution of portlandite in the pastes containing C_3A, C_3S, and gypsum is enhanced by the presence of calcium carbonate. The distinction between the pastes with and without addition is clear after 10 days of immersion. The initial rate of dissolution (i.e., between 10 and 40 days of immersion) is similar for the samples containing 20% and 5% of $CaCO_3$. After a 40-day period of immersion, the use of 20% addition had accelerated the rate of dissolution significantly.

The pastes prepared with the ordinary Portland cement undergo a significantly lower rate of dissolution of the portlandite. During the first 10 days of immersion, the presence of calcium carbonate on the rate of dissolution has little or no influence. After this period, the use of calcium carbonate increases slightly the dissolution rate.

Table 5
Total volume in percent of pores with diameter higher than 4 nm or lower than 50 nm

	0% $CaCO_3$		5% $CaCO_3$		10% $CaCO_3$		20% $CaCO_3$	
	Total	< 50 nm	Total	< 50 nm	Total	< 50 nm	Total	< 50 nm
C_3S	28.9	17.8	30.2	17.3	33.2	15.7	32.8	13.4
$C_3S + C_3A$ + gypsum	29.4	14.5	30.9	14.6	32.4	13.4	33.4	13.0
Cement	31.7	19.3	36.9	22.9	38.4	21.2	37.1	19.9
$C_3S + C_4AF$ + gypsum	42.1	7.5	41	6.6	43.3	6.8	43.1	6.4

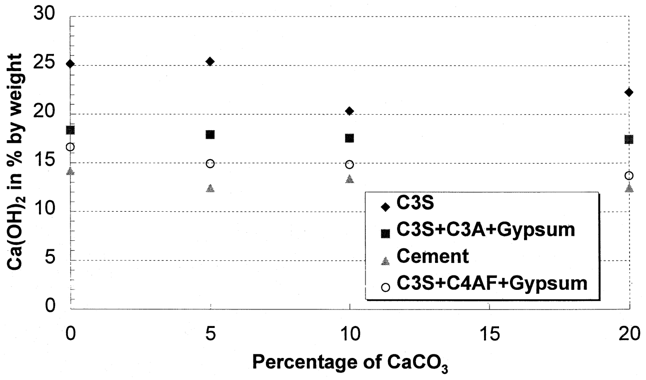

Fig. 1. Initial portlandite content of the 16 different pastes.

The total dissolution is achieved before 20 days of immersion for the pastes prepared with the fourth system ($C_3S + C_4AF + CaSO_4{\cdot}2H_2O$). Unfortunately, the number of analyses on specimens of these pastes was limited. However, some XRD analyses of the pastes revealed that the total dissolution of the calcium hydroxide occurred within 20 days of immersion. This corresponds to a very significant rate of dissolution. This can also be due to the higher porosity of these mixtures and a faster diffusion rate of ions through the material.

The rate of dissolution during the first 10 days of immersion in distilled water for a given percentage of calcium carbonate increases in the following order: cement paste, $C_3S + C_3A +$ gypsum paste, C_3S paste, and $C_4AF + C_3S +$ gypsum paste.

3.2. Additional calcite formation

The calcite content was estimated qualitatively from the XRD analyses. Precise quantitative estimations are not possible with this method. However, the large number of analyses provides an approximate idea of the content of well-crystallized calcite.

The XRD analysis initially conducted on the pastes indicated the largest increase in the calcite peak intensity for the C_3S pastes containing calcium carbonate. The calcite peak intensity of the pastes with 0%, 5%, and 10% carbonate addition for the other systems remained in a same range. This is due to the fact that the $C_3S-CaCO_3$ pastes do not contain any aluminate, which can react directly with the added calcium carbonate.

The C_3S-based pastes undergo the formation of the largest amount of new calcite during the immersion in distilled water. This new calcite appears mainly during the first 20 days of immersion in distilled water. This system provides the largest source of calcium hydroxide that can react with the atmospheric CO_2 to form calcite. The increase in the calcite content is not highly dependent on the initial carbonate addition.

For all the other pastes, the formation of new calcite seems to be enhanced by an increase in the calcium carbonate content of the material. The difference is particularly important between the pastes with and without 5% carbonate addition.

For the cement–$CaCO_3$ and $C_3S + C_3A +$ gypsum–$CaCO_3$ pastes, the formation of calcite occurs during the entire immersion period. For the pastes containing $C_3S + C_4AF +$ gypsum–$CaCO_3$, the formation occurs predominately between the first 20 days of immersion. The rates of dissolution of calcium hydroxide and formation of calcite may eventually be linked for the pastes with carbonate addition. For the pastes without addition, the presence of aluminates in the material may explain the recorded differences.

3.3. AFm and AFt phases

Independent of the carbonate content, the pastes containing C_3S, C_3A, gypsum, and $CaCO_3$ contain about 2.5 more moles of aluminate than sulfate (on the basis of the same total mass of unhydrated powder and water). The same approximate characteristic exists for the corresponding pastes with C_4AF. However, the difference between the aluminate and sulfate contents is lower (about 1.8 times). In the cement-based pastes, the molar content of sulfate ion is greater than the molar content of aluminate ion (about 1.1 times). The AFm (monosulfoaluminate) phase has a higher molar ratio of aluminate/sulfate than the corresponding AFt (ettringite) phase.

The notations A and B in Figs. 3 and 4 refer, as in Table 4, to hydrated calcium hemicarboaluminate and monocarboaluminate, respectively. XRD analyses for the $C_3S + C_3A +$ gypsum pastes with 10% and 20% carbonate addition were very similar. The same remark is valid for the cement pastes with 5% or 10% $CaCO_3$.

The AFm phase was not detected initially in the pastes made with C_3A, C_3S, and gypsum in the presence of calcium carbonate. It is replaced by AFt, hemicarboaluminate (to a limited extent), and monocarboaluminate. Specimens of the paste without initial carbonate addition

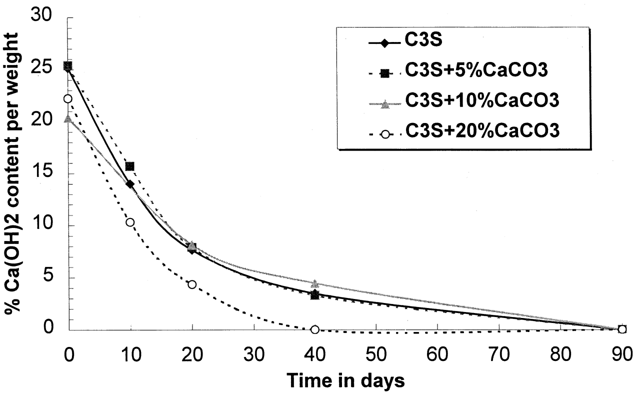

Fig. 2. Portlandite content of $C_3S-CaCO_3$ pastes versus time of immersion in distilled water.

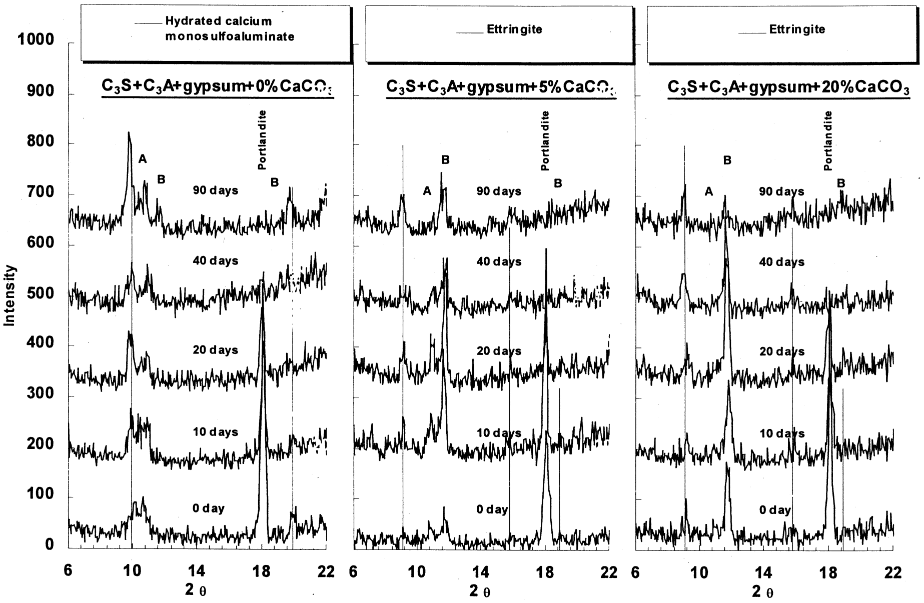

Fig. 3. XRD analysis on $C_3S + C_3A +$ gypsum–$CaCO_3$ pastes immersed in distilled water for various periods.

underwent carbonation (the XRD peak of calcite increases) when immersed in distilled water. The AFm phase remained AFm. The formation of both hemicarboaluminate and monocarboaluminate and an increase in AFm content was observed. This suggests that the phenomena occurring upon immersion of the specimens in distilled water favor the formation of more aluminate. This can be due to a change in solubility of aluminate-based products due in part to a decrease of calcium concentration in the solution. In presence of AFm the formation of hemicarboaluminate seems preferred to the formation of monocarboaluminate. The opposite occurs when AFt instead of AFm is present (see Table 4).

The Portland cement–$CaCO_3$ pastes do not exhibit significant formation of monocarboaluminate. The AFt content may increase slightly with immersion in distilled water.

The $C_3S + C_4AF +$ gypsum–$CaCO_3$ pastes contain (to a limited extent) some AFt. With immersion in distilled water its content does not change significantly. However, even if the molar ratio of aluminate/sulfate is large, a large quantity of unhydrated C_4AF remains (XRD analyses) due to the limited degree of hydration of those pastes. The

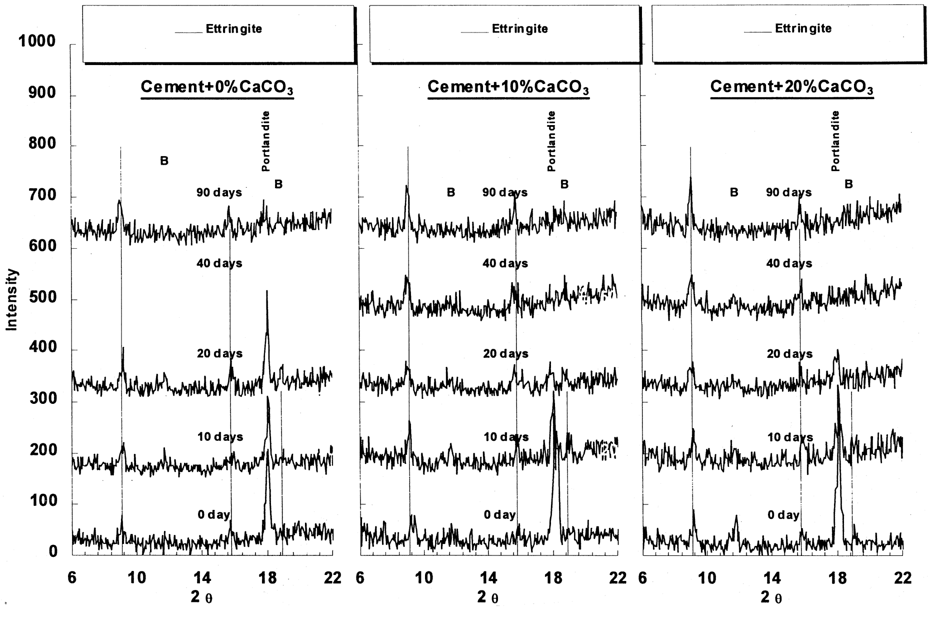

Fig. 4. XRD analysis on cement–$CaCO_3$ pastes immersed in distilled water for various periods.

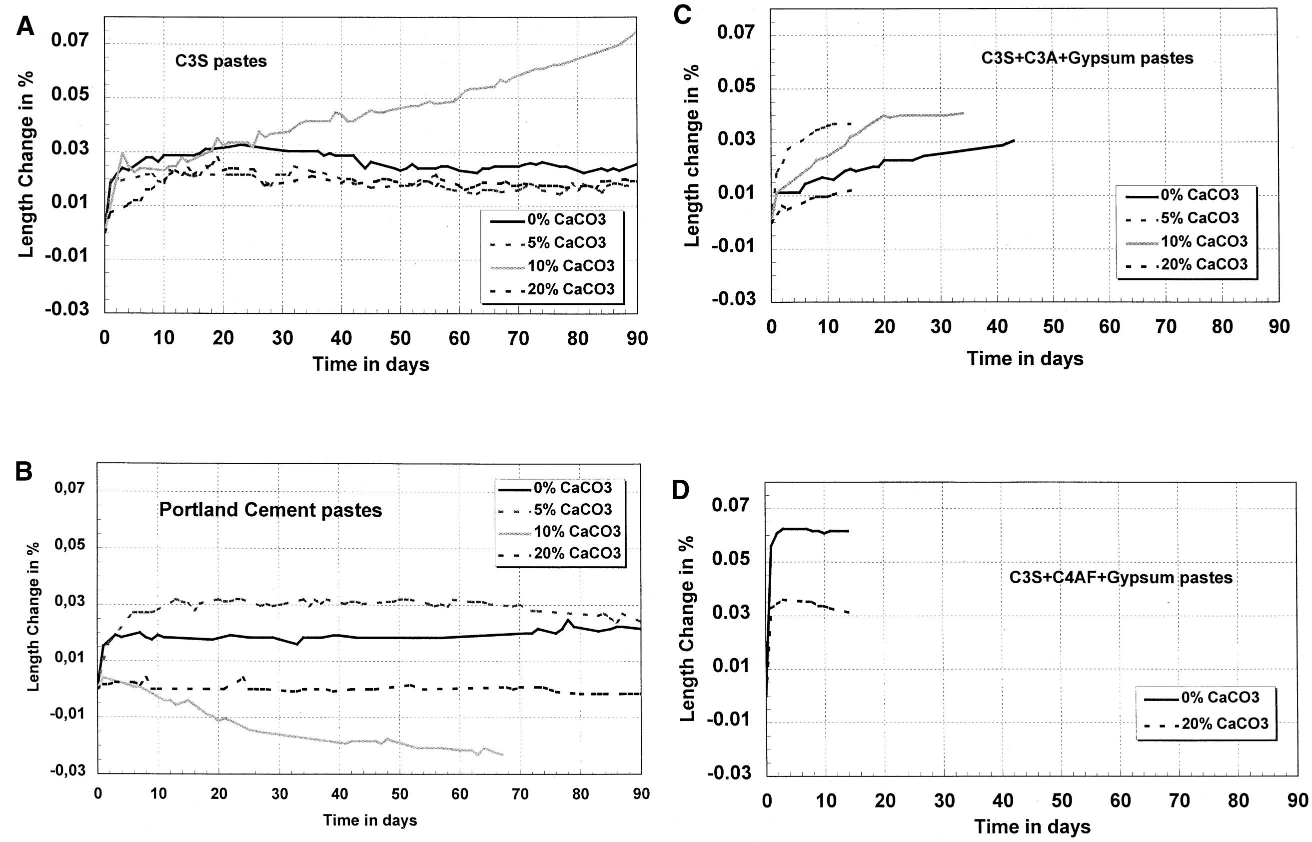

Fig. 5. (A) Influence of calcium carbonate on length change of the C_3S pastes. (B) Influence of calcium carbonate on length change of the cement pastes. (C) Influence of calcium carbonate on length change of the C_3S+C_3A+gypsum pastes. (D) Influence of calcium carbonate on length change of the C_3S+C_4AF+gypsum pastes.

hydration of C_4AF is slower than the hydration of C_3A. Instead of the total aluminate/sulfate molar ratio, the available aluminate/sulfate molar ratio may be more relevant for understanding behavior.

The presence of calcium carbonate prevents the conversion of AFt into AFm because of the formation of carboaluminates [15]. However, this might only apply for an aluminate/sulfate molar ratio in a given range of values. Both the carboaluminate and AFm content increase when the paste is immersed in distilled water. However, the aluminate and sulfate contents remain quite similar with increasing carbonate addition. It appears that both the molar ratio of these two ionic species, the nature, and the time of addition of the calcium carbonate to the system are important.

The form of carbonate occurring when a cement-based material undergoes carbonation depends on the time from the beginning of carbonation, the extent of carbonation and the presence or absence of some portlandite [16]. If portlandite is not present in the paste, then monocarboaluminate and calcite are formed successively. If the material contains some portlandite, the hemicarboaluminate forms before the monocarboaluminate. The hemicarboaluminate may become unstable when the calcium concentration decreases.

This provides an explanation why some monocarboaluminate only appeared in the paste containing C_3S, C_3A, and gypsum (without carbonate addition) when the calcium hydroxide had totally disappeared (Fig. 3). In the case of carbonate addition, the monocarboaluminate (and hemicarboaluminate for 5% $CaCO_3$) content increased and then decreased as soon as all the calcium hydroxide disappeared. The same phenomenon seems to exist for the cement paste containing 20% calcium carbonate (Fig. 4). In those cases, where AFt is not clearly formed in large amounts, some aluminate might be released. The dissolution of carboaluminate can correspond to the formation of new calcite (produced not from a reaction involving atmospheric CO_2 but as a result of the initial carbonate addition). This can explain the observation that even if the rate of the carbonation process is similar for all the pastes, the increase in calcite content is enhanced with carbonate addition.

3.4. Length-change measurements

The length changes observed for the various pastes immersed in distilled water are presented in Fig. 5. Fig. 5 illustrates, for a given type of paste, the influence of calcium carbonate addition. Fig. 5A demonstrates that the superposition of calcium leaching and carbonation leads to a global expansion for the C_3S–$CaCO_3$ pastes. The carbonation process has not previously been associated with an expansion mechanism. The leaching of calcium from the calcium hydroxide and C-S-H may however result in expansion. Except for the paste with a 10% carbonate addition, the expansion is quickly stabilized after 12 days. The final value of expansion decreases slightly with an addition of some $CaCO_3$.

The Portland cement–$CaCO_3$ pastes (except for 10% calcium carbonate addition) exhibit the same type of behavior (Fig. 5B). However, the ultimate length changes are highly dependent on the calcium carbonate content. Length changes were not recorded for a long period of immersion for the $C_3S + C_3A$ or C_4AF + gypsum–$CaCO_3$ pastes. However, the rate of expansion after 40 days of immersion in distilled water is still significant for the paste containing C_3A (without carbonate addition).

Comparison of the continuous gray curves in Fig. 5A–C, corresponding to 10% $CaCO_3$ addition, reveals a special behavior. The rate of expansion remains quite significant with time. Curves for the other percentages of $CaCO_3$ addition do not demonstrate the same systematic behavior. The S.E.M. observations did not reveal the presence of an expansive phase, either hydrated calcium sulfoaluminate or carboaluminate.

In the $C_3S + C_3A$ + gypsum–$CaCO_3$ pastes, it appears that adding 5% $CaCO_3$ initiates another phenomenon leading to an increase in the expansion compared to the paste without carbonate addition. Further addition of $CaCO_3$ leads to a decrease in the expansion. The percentage of $CaCO_3$ addition required to reduce expansion compared to that for the paste without addition is probably between 10% and 20%.

The presence of the AFm or AFt phases does not appear to provide a singular explanation for the recorded behavior. However, the expansion of the paste containing $C_3S + C_4AF$ + gypsum is quite large compared to the other pastes. The presence of C_4AF might provide a significantly different behavior. The release of energy from the dissolution of solid phases and the disturbance (leaching effects) of the C-S-H phase may play an important role regarding the volume stability of pastes.

S.E.M. observations of selected specimens showed that immersion in distilled water resulted in porosity increase; the C-S-H microstructure changed. The different initial porosities of the pastes (Table 5) contribute to different initial mechanical properties. A decrease in values of those mechanical properties is likely with the immersion in distilled water. Matrix strength undoubtedly contributes to the recorded differences in length changes. A larger expansion may not directly correspond to the generation of higher internal stresses. However, the particular behavior for pastes containing 10% $CaCO_3$ is noted, even if the porosity characteristics are not systematically different. It is suggested that the difference in mechanical properties due to the presence of $CaCO_3$ is not necessarily the a priori source of length change. It is obviously difficult to separate chemical and mechanical effects (often interdependent) when seeking causative relations.

4. Conclusions

The available aluminate/sulfate molar ratio introduced in the paste appears to have an important role in determining the nature of the sulfoaluminate product formed. Hemicarboaluminate or monocarboaluminate are present in the paste depending on the preferential formation of the AFm or AFt phase, respectively.

The rate of dissolution of calcium hydroxide is highly dependent on the composition of the paste and on the transfer properties, linked in part to the porosity characteristics. For pastes containing aluminates, the rate of dissolution of these phases influences the rate of formation of carbonate-based compounds. It appears that the hydrated monocarboaluminate can even be reconverted to calcite without the formation of additional calcium sulfoaluminate. During the immersion in distilled water, eventually some of the aluminate is released into solution.

The length change induced by calcium leaching and carbonation processes depends on the composition of the material. Twelve of the fourteen length change–time curves indicate expansion. This expansion is highly dependent on the calcium carbonate percentage used. The use of C_4AF appears to induce larger expansions. However, due to a difference in the degree of hydration of these pastes, the matrix strength was less well developed. The three other types of pastes experienced length changes of the same order of magnitude. The complexity of the influence of the $CaCO_3$ content on the length change of Portland cement-based paste would suggest that the volume stability of these systems immersed in distilled water is likely to be the result of a superposition of various phenomena. The behavior of the C-S-H phase in this process may be significant. An apparently unique behavior was recorded for the C_3S, $C_3S + C_3A$ + gypsum and cement pastes when 10% $CaCO_3$ was used. The possible incorporation of $CaCO_3$ into the hydrated silicate phases and the degree of reversibility of this process offers a possible explanation for the influence of $CaCO_3$ addition on volume stability.

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