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Pessimum effect of externally applied chlorides on expansion due to delayed ettringite formation: Proposed mechanism

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Abstract

Mortars and concretes were subjected to a heat treatment cycle consisting of a pre-set period of 4 h at 23 °C followed by accelerated curing at 95 °C prior to storage at room temperature in water or limewater, 0.5 M, 2.8 M sodium chloride solutions. It was found that the specimens stored in 0.5 M sodium chloride solution gave a much greater expansion than those stored in limewater or 2.8 M sodium chloride solution. This pessimum influence of chlorides on expansion due to delayed ettringite formation deviates from the commonly held view that chlorides mitigate sulphate attack in concretes. The mechanism of the pessimum effect of chlorides on expansion due to delayed ettringite formation, and the final products of the associated phase transformations have been proposed. X-ray diffraction and differential thermal analysis techniques were used to follow phase transformations.

Keywords: Delayed ettringite formation; Chlorides; Steam curing; Monosulphates; Friedel's salt

1. Introduction

1.1. Interaction between chlorides and ettringite

The influence of chlorides on cement hydration has been widely investigated as reported in the literature. Skalny and Odler [1] found that calcium chlorides did not prevent the formation of ettringite but reacted with $Ca(OH)_2$ and C_3A forming calcium aluminate chloride hydrates at later stages of hydration. Other authors [2,3] have advanced that calcium aluminate chloride hydrate formation is possible only when calcium sulphate is absent, implying that the gypsum in the hydrating system must first be totally consumed before the hydrates can form.

Some studies have shown that there is an active chemical interaction between ettringite and chlorides. It has been reported that the primary ettringite formed during hydration is less stable in the presence of chlorides [4]. Marks and Dubberke [5] while studying cracking deterioration in a three-year old pavement concrete concluded that the ettringite in air voids initially swelled before subsequently dissolving when kept in sodium chloride brine. Buck [6] mentions of their study showing that ettringite was preferentially replaced by chloroaluminate (Friedel's salt) in grouts mixed with admixed chlorides. Recently Zibara [7] examined hydration products formed in cement pastes exposed to externally applied chlorides at normal temperatures. There were some findings to the effect that at high salt concentrations (>2.0 M) ettringite was partially consumed and replaced by Friedel's salt ($C_3A\cdot CaCl_2\cdot 10H_20$). It has also been shown that the presence of chlorides in cementitious systems kept under low temperature conditions favour the formation of ettringite and Friedel's salt at the expense of monosulphate [8]. Others disagree with the view that ettringite is influenced by chlorides. Midgley and Illston [9] reported that ettringite was not attacked by chlorides when pastes were exposed to chloride penetration. Chloride concentrations of 30 g/l and 150 g/l NaCl were used in that study.

Some incidental results from our concrete laboratories revealed some interesting findings. A set of concrete core

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Fig. 1. Severely cracked core of 0.45 w/c Portland cement concrete heat cured at 95 °C, stored outdoors for 28 days and ponded in 2.8 M NaCl for 90 days. It was removed from NaCl and kept in −18 °C freezer when it cracked after about 6 months of storage.

specimens prepared for bulk diffusion test showed unusually severe cracking while being kept in a freezer (awaiting profile grinding) following a 90-day ponding in 2.8 M NaCl. A photograph of one of these specimens is shown in Fig. 1. The Portland cement concrete was of 0.45 w/c and 7% air, heat cured at 95 °C and stored outdoors for 28 days before cores were taken for a bulk diffusion test. After spending about 6 months in a freezer, the cracks formed were so wide that the specimens were only held together by the epoxy coating previously applied on the curved surfaces and one flat surface of the specimens.

1.2. Mechanism of chloride attack on ettringite

In the literature, different scenarios have to be distinguished when assessing the influence of chlorides: the case of externally applied chlorides, and chlorides that are admixed during concrete production. Midgley and Illston [10] argued that for concretes incorporating chloride admixtures, the sulphates and chlorides in the system compete for reaction with C_3A resulting in a direct conversion of C_3A to ettringite and chloroaluminate [6]. In the case of externally applied chlorides (such as deicer salt penetration or storage in chloride solution), there is no such competition between Cl^- and SO_4^{2-} for C_3A, instead the free chlorides entering concrete have a preferential reaction with any unreacted C_3A or its hydrates rather than with existing ettringite, leaving the latter unaffected. Only after the unreacted C_3A hydrates are consumed will the chlorides attack ettringite.

Attempts have also been made to explain the mechanism by which chlorides influence ettringite crystallization. Kalousek and Benton [11] studied cement pastes of 0.3 and 0.5 water–cement ratios cured at 23 °C and suggested that the expansion observed in the paste bars, 25×25×290 mm, exposed to seawater could have been a result of the adsorbed sulphate, C–(S,Ŝ)–H reacting with the chloroaluminate already formed, precipitating ettringite deep in the paste and allowing the Cl^- ions to penetrate into the C–S–H structure. Another mechanism postulated is much like the mechanism by which carbonation breaks up monosulphate. In such a case, chlorides partially replace the sulphate ions in monosulphate, forming monochloride (Friedel's salt) and releasing sulphate ions. The latter combines with the remaining monosulphate, forming ettringite [12].

The postulated mechanisms discussed above were mainly based on moist-cured cementitious systems and have not been validated with deliberate experimental investigations in the context of modern application of heat curing methods, where the occurrence of delayed ettringite formation is possible. This paper reports new findings showing that externally applied chlorides do exhibit a pessimum influence on expansion due to delayed ettringite formation (DEF). Expansions of specimens along with phase transformations were monitored. X-ray diffraction (XRD) and differential thermal analysis (DTA) techniques were used to evaluate the development of ettringite and other phase changes in heat-cured mortars.

2. Experimental

2.1. Mixtures

CSA Type 30 high-early strength Portland cement was used in the investigation to generate DEF in heat treated mortars or concretes. Table 1 shows the composition of the cement used. Mortar bars, 25×25×285 mm were prepared and either moist-cured at 23 °C or steam-cured at 95 °C. Mortar mixtures consisting of 1 : 2.25 : 0.47 cement to sand to water were made using 20–30 standard sand (quartz).

Concrete mixtures of 0.45 water–cement ratio were made and used to cast 75×75×285 mm prisms. Glacial sand and 10 mm crushed dolomitic limestone were used for aggregates. No air entrainment or admixtures were used in the mortar or concrete mixtures.

2.2. Curing and storage

Concrete prisms and mortar bars were cast in steel moulds and heat-cured at 95 °C. Steam curing of mortars and concretes was carried out by sealing the moulds in plastic bags containing a small quantity of water and heating the assembly in a programmable environmental chamber. The cycle applied consisted of 4 h delay (pre-set) period, temperature rising at 20 K/hour, then the maximum temperature of 95 °C was maintained for 9 or 12 h for concretes or mortars, respectively, followed by cooling back to 23 °C. The specimens were demoulded after heat treatment and stored at room temperature

Table 1
Composition of CSA type 30 Portland cement

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	Na_2O	Na_2Oe	LOI	Blaine *(cm^2/g)*
CSA Type 30	20.38	5.45	2.06	63.41	4.82	1.21	0.10	0.90	0.91	5490

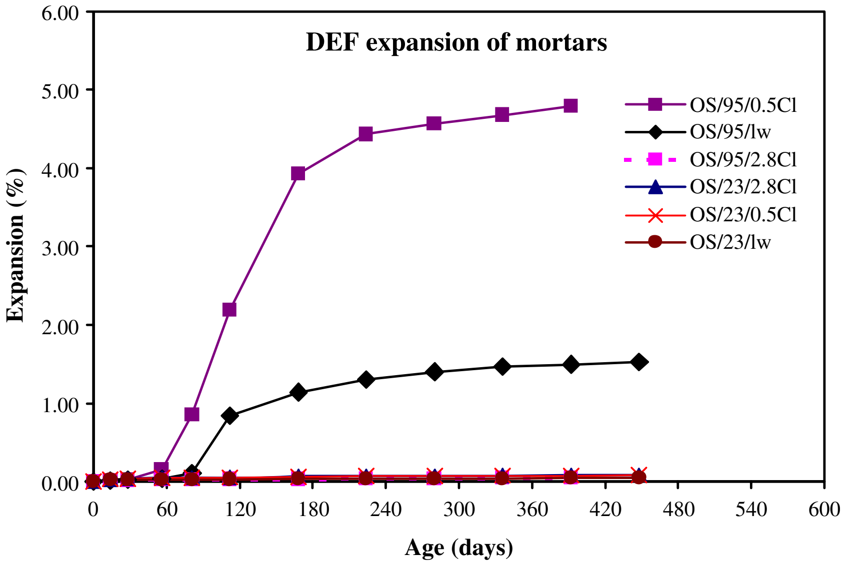


Fig. 2. Expansion of mortars heat-cured at 95 °C and stored in limewater, 0.5 M or 2.8 M sodium chloride solution (OS=Ottawa sand, lw=limewater, Cl=chlorides).

in water or limewater, 0.5 M NaCl, or 2.8 M NaCl. Mortars and concretes were also prepared without heat curing for storage in the same solutions.

The conventional 18-h curing cycle applied in this investigation is typically used in the industry for steam curing of precast concretes [13]. The extreme maximum curing temperature of 95 °C and Portland cement of high sulphate content (Type 30) were deliberately selected to ensure that DEF could be generated for investigation of the phenomenon. It is now generally accepted that subjection of concretes at early ages to temperatures in excess of 70 °C is a necessary condition for DEF [14]. It has also been found that concretes can generate temperatures exceeding 85 °C even without external application of heat especially for large concrete sections made with high cement contents [15,16].

In this study, water was used as control storage solution for concrete prisms while saturated limewater was used as control solution for mortar bars. The pH of limewater used was determined to be 12.5. It is known that high alkalinity in pore solution (Na^+, K^+, OH^-) retards ettringite formation [17–20]. But due to highly solubility of the alkalis, they quickly leach out upon immersion of mortar bars into storage solution [21]. It is therefore unlikely in this study that pore solution alkalis could significantly influence ettringite formation. This is confirmed by results seen in Figs. 2 and 3 showing that mortars stored in limewater solution and concretes stored in water showed similar expansion behaviours relative to the respective specimens stored in salt solutions.

2.3. Methods

The tests carried out included expansion measurements, XRD, and DTA analysis. Mortar specimens were used for XRD analyses. The specimens were gently ground into fine powder. Sand particles were removed from the fine powder by passing the latter through 90 μm sieve. The fine powder was then back loaded into sample holders and analyzed using Philips PW 1820 Automatic Powder X-ray diffractometer. A silicate-free cement,

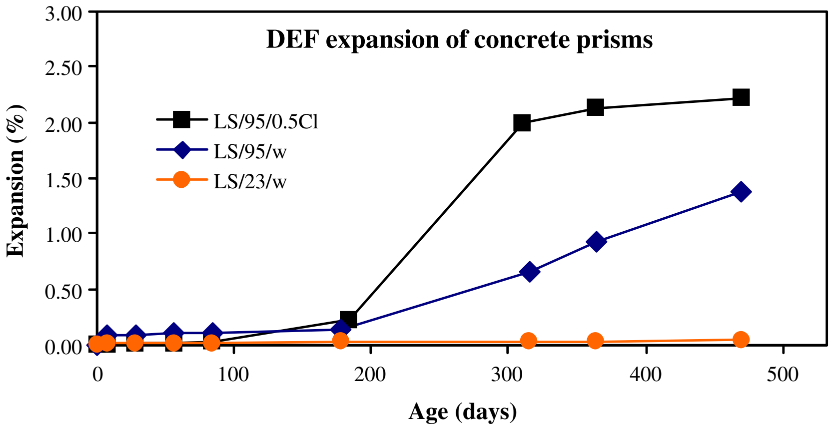


Fig. 3. Expansion of concretes heat-cured at 95 °C and stored in water, 0.5 M or 2.8 M sodium chloride solution (LS=limestone, w=water, Cl=chlorides).

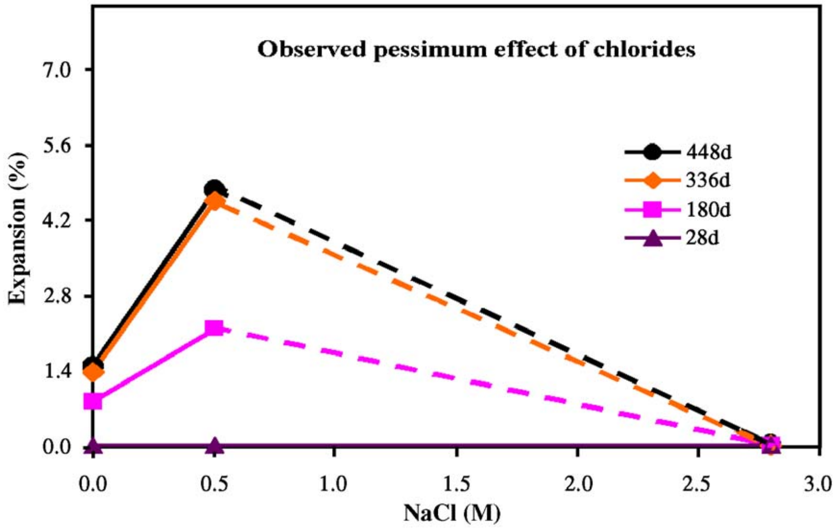


Fig. 4. Pessimum influence of chlorides on DEF expansion of mortars observed at 0, 0.5 and 2.8 M sodium chloride concentrations.

prepared as described in 3.2.1, was used to make 25 mm paste cubes for DTA.

3. Results

3.1. Expansion measurements

The expansions due to delayed ettringite formation were monitored in the heat-cured mortar and concrete specimens during storage in water or limewater, 0.5 M NaCl, and 2.8 M NaCl. Fig. 2 shows that the expansions observed were significantly influenced by the concentration of sodium chloride solution. The specimens kept in limewater, that is at 0 M NaCl, showed an expansion of 1.5% after one year but storage in 0.5 M NaCl led to a corresponding three-fold increase in expansion to about 4.6% over the same period. These mortar bars soon broke into pieces due to the excessive continued expansion in the chloride solution. Interestingly, the mortars stored in the higher salt concentration of 2.8 M NaCl showed no expansion whatsoever at all ages. The specimens that were not heat cured did not expand regardless of the storage condition. The expansion studies undertaken using concrete prisms are given in Fig. 3. Again the prisms stored in 0.5 M NaCl solution gave the greatest expansion at all later ages. These results show the catalyzing influence of the seawater level of salt concentration on delayed ettringite formation as given in Figs. 4 and 5.

The observations from these expansion studies carried out using mortars and concretes depict a pessimum influence of chlorides on expansion due to delayed ettringite formation. However, since only a limited number of salt concentrations were used, better pessimum curve(s) (in Fig. 4) of the observed data could not be plotted.

3.2. Phase transformations and mechanism

3.2.1. The final phase products

An XRD investigation of the phases formed under different storage environments revealed the final products affecting expansion in heat-cured mortars and concretes. Fig. 6 comprises XRD patterns of heat-cured mortars analyzed at the ages of one day and 448 days. It can be seen as expected

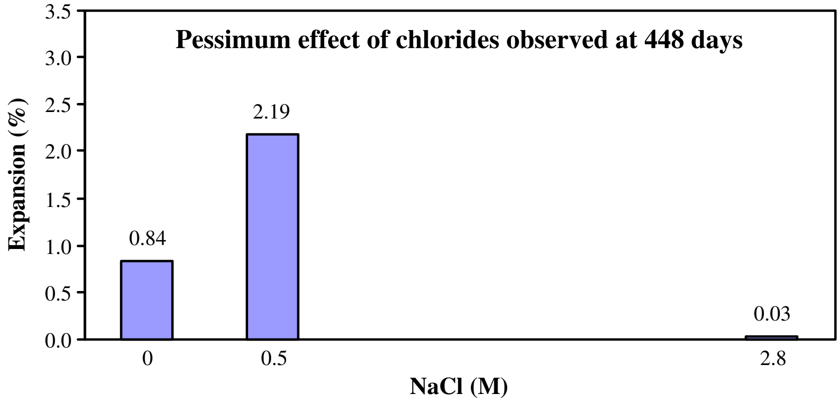


Fig. 5. Pessimum DEF expansion of mortars after 448 days of storage in varied concentrations of sodium chloride solution.

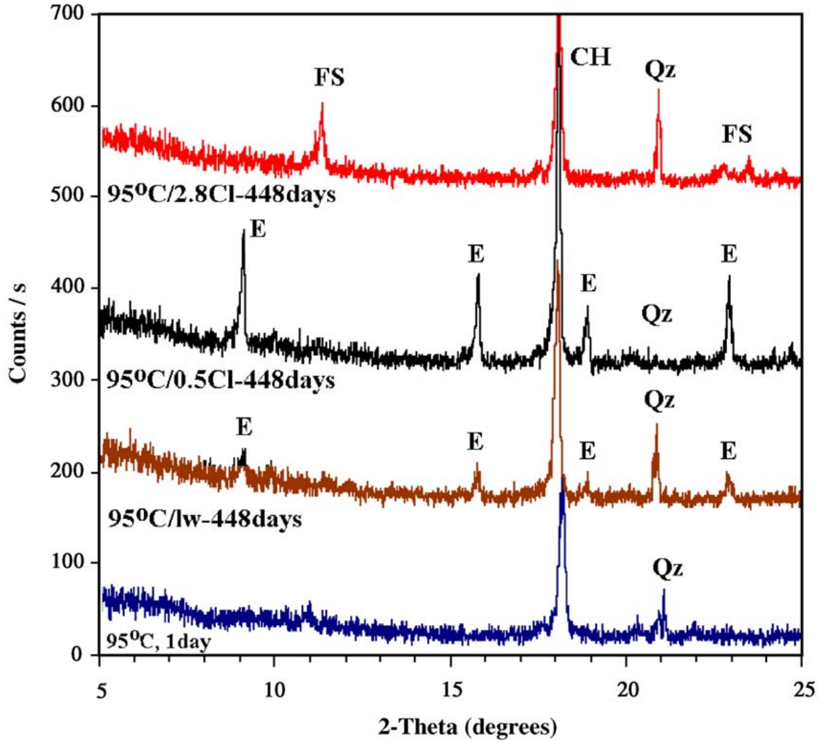


Fig. 6. XRD patterns of heat-cured mortars: Qz-quartz (Ottawa sand), E—ettringite, FS—Friedel's salt, CH—calcium hydroxide (lw=limewater, 0.5 Cl = 0.5 M NaCl, 2.8 Cl = 2.8 M NaCl).

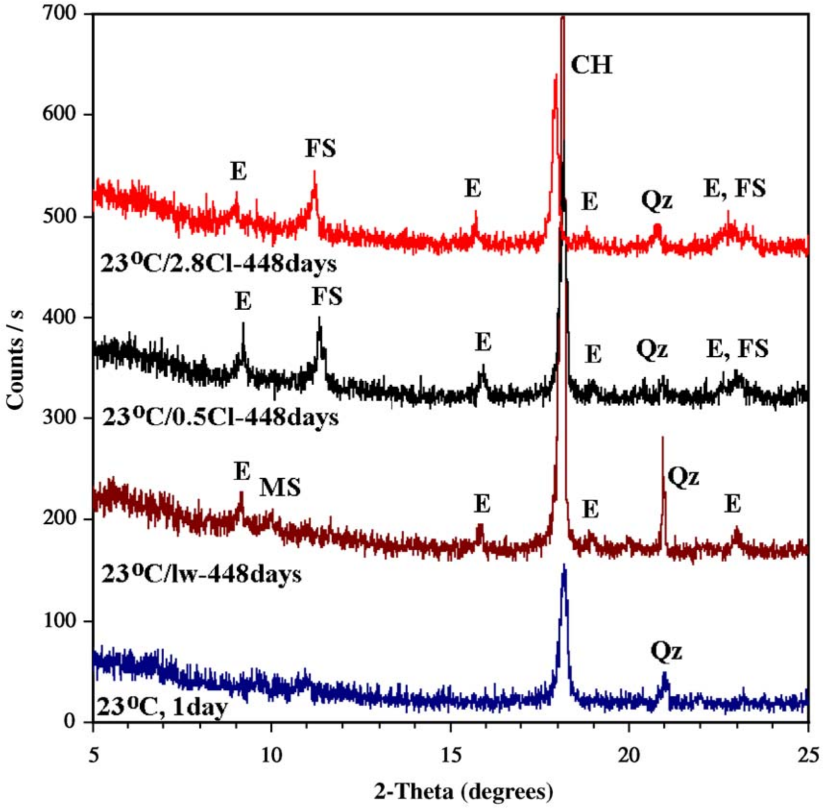


Fig. 7. XRD patterns of moist-cured mortars: Qz-quartz (Ottawa sand), E—ettringite, MS—monosulphate, FS—Friedel's salt, CH—calcium hydroxide (lw=limewater, 0.5 Cl = 0.5 M NaCl, 2.8 Cl = 2.8 M NaCl).

that no ettringite formation was observed at one day following heat treatment. The heat-cured specimens stored in limewater showed massive development of ettringite ($3CaO\cdot Al_2O_3 3CaSO_2\cdot 32H_2\ O$) at the later age of 448 days. This late growth in ettringite was responsible for the high expansion observed in the limewater specimens. But even a greater ettringite formation can be seen in those specimens stored in 0.5 M sodium chloride solution as characterized by the stronger ettringite peaks. This explains why the expansion of the specimens stored in 0.5 M NaCl solution was three times greater than the expansion observed in limewater specimens as earlier discussed (see Section 3.1 and Fig. 2). In contrast to 0.5 M NaCl and limewater storage, the XRD pattern as given in Fig. 6 revealed that storage of specimens in 2.8 M NaCl solution exhibited a significant transformation of phases, forming Friedel's salt ($CaO\cdot Al_2O_3.CaCl_2\cdot 10H_2O$) as the main final product. Consequently, no expansion was observed in these specimens.

There is an important distinction in the role played by externally applied chlorides in situations involving moist-cured and heat-cured cementitious systems. In moist-cured systems, normal ettringite formation occurs during early cement hydration and some of it transforms into monosulphate once all gypsum is consumed. Therefore the ingress of chlorides into moist-cured cementitious systems during storage will encounter the presence of monosulphate ($3CaO\cdot Al_2O_3\cdot CaSO_2\cdot 12H_2O$) and ettringite in the system. In Fig. 7, the XRD patterns revealed that chlorides attacked both ettringite and monosulphate forming Friedel's salt. By comparing the strengths of Friedel's salt and ettringite peaks during storage in chloride solutions, it can be seen in the XRD patterns that more Friedel's salt was formed at the expense of ettringite under 2.8 M NaCl storage compared to the products formed under 0.5 M NaCl storage.

Further details of phase transformations in heat-cured cementitious systems under the different storage solutions were observed using differential thermal analysis. The problem usually faced in using the DTA technique is that ettringite and C–S–H peaks overlap [22]. In addition, sulphates are usually adsorbed on C–S–H during hydration [23,20]. To overcome this problem, C_3S and C_2S phases were extracted from the Type 30 Portland cement to form a C_3A-rich cement free of silicates. The extraction was done with 15% salicylic acid–methanol (SAM) solution. Fig. 8 shows the XRD patterns of the Portland cement before and after extraction of silicate phases.

The silicate-free cement was used to make 12.5 mm paste cubes of 1.60 water–cement ratio. These were heat-cured at 95 °C then stored in the different storage solutions. The phase transformations were followed by DTA for ages up to 28 days as given in Fig. 9. Unfortunately, the heat-cured paste cubes simply disintegrated upon placement in storage solutions.

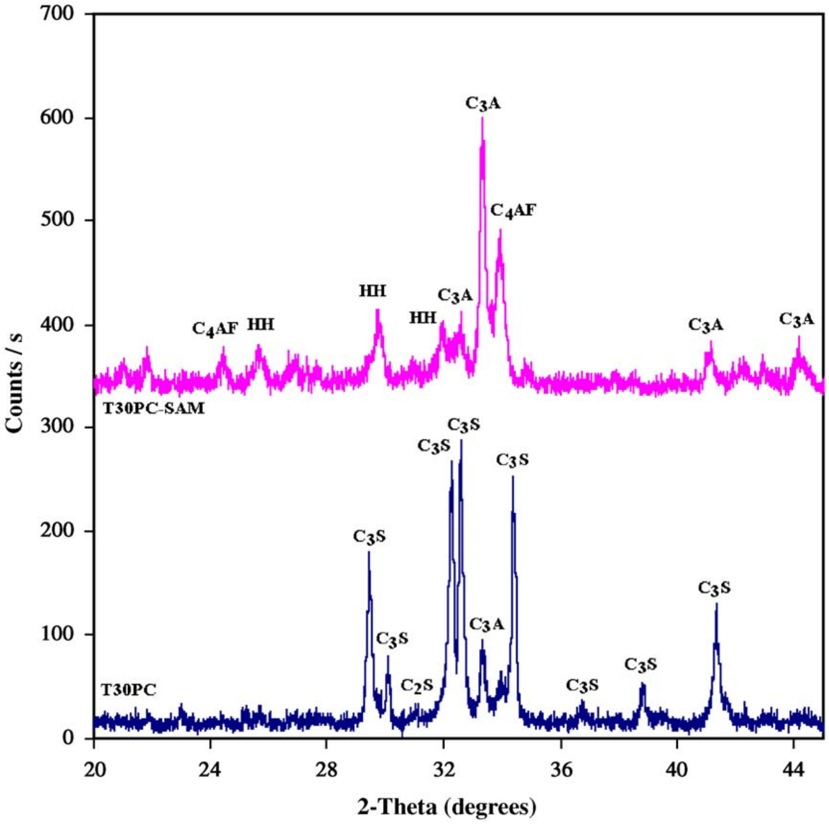


Fig. 8. XRD patterns of Type 30 Portland cement before and after extraction of silicate phases (T30PC=Type 30 Portland cement, T30PC-SAM=Type 30 Portland cement after extraction using 15% salicylic acid–methanol solution (SAM), HH=hemi-hydrate).

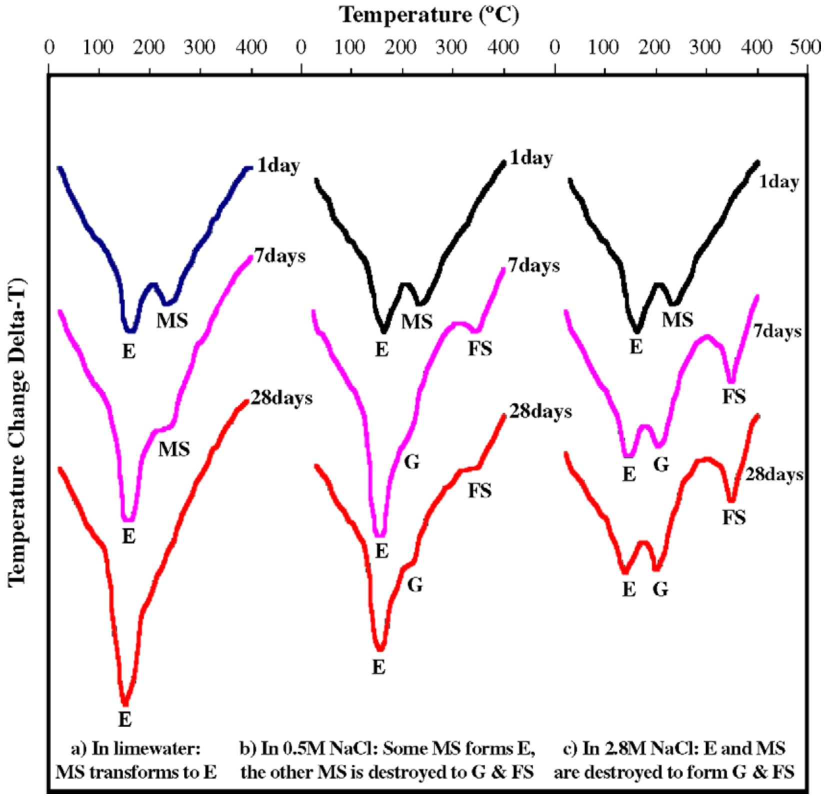


Fig. 9. DTA curves showing phase transformations in silicate-free cement pastes, heat-cured at 95 °C and stored in limewater, 0.5 M NaCl or 2.8 M NaCl (E=ettringite, MS=monosulphate, G=gypsum, FS=Friedel's salt). Please note that because of the small specimen size (12.5 mm) and the disintegration of cube pastes upon storage in the solutions, the expected relatively larger formation of ettringite phases during storage in 0.5 M NaCl could not be well observed in the DTA but its stability in this chloride concentration is nevertheless confirmed.

However, the phase changes observed confirm the XRD results discussed above. In addition, the DTA also gave more detailed observations of phases transformations, some of which could not be easily detected by XRD. This is because XRD has higher detection limits such that minor phase changes may not be easily seen in the patterns.

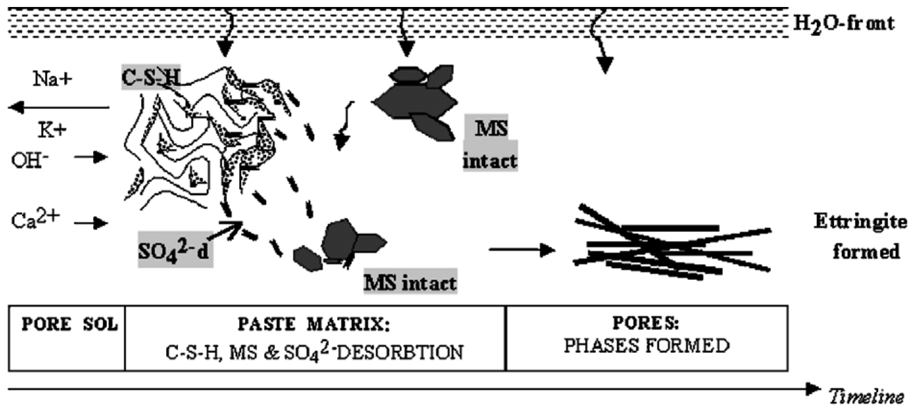
3.2.2. Mechanism of chloride influence on delayed ettringite formation

The phase changes occurring in heat-cured cementitious systems are a dynamic interaction of ions until more stable products are finally formed, that may or may not result in the disruption of mortars or concretes depending on the storage solution. It all starts with the destruction of ettringite when cementitious systems are heat-cured at elevated temperatures above 70 °C. The immediate outcome is the adsorption of sulphates in the C–S–H.

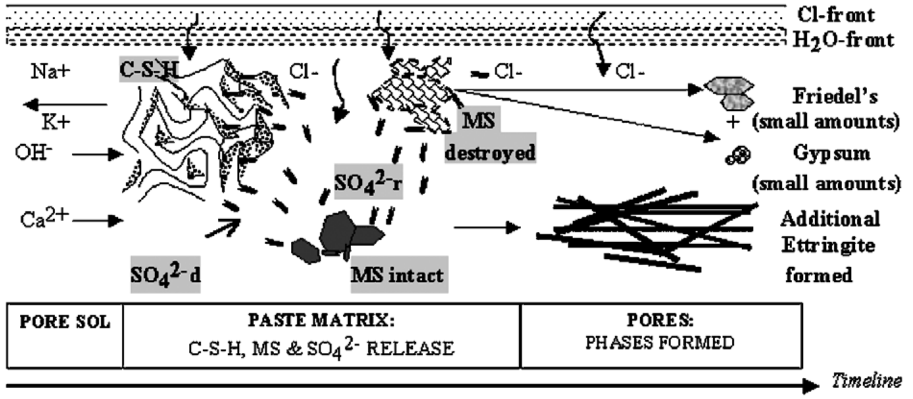
3.2.2.1. Delayed ettringite formation under moisture. Under moist conditions at later ages, the adsorbed sulphate ions are released from C–S–H into the pore solution. During the desorption process they encounter monosulphate present in confined spaces within the paste matrix and react with it forming ettringite (see Figs. 5, 9(a) and 10(a)). This formation of late ettringite, often referred to as *delayed ettringite formation*, in confined spaces in already hardened concrete is disruptive and results in expansion [20]. Under these storage conditions the only source of sulphate ions responsible for DEF is the C–S–H adsorbed sulphate ions.

3.2.2.2. Chlorides and ettringite formation or destruction. In the case where chlorides and water penetrate into the relatively ettringite-free, heat-cured cementitious system, the desorbed SO_4^{2-} from C–S–H and the penetrating Cl^-have to compete for monosulphate At this point the final reaction products are determined by the salt concentration. In this hypothesis, it has been assumed that the penetration of chloride solutions into cementitious systems occurs in two fronts with the water-front going ahead of the chloride- front. This allows some of the desorbtion of SO_4^{2-} to take place under the pioneering water-front. These sulphate ions then react with monosulphates forming ettringite in certain regions of the cement matrix prior to the arrival of chloride ions. However, the desorption of SO_4^{2-} still continues after the arrival of the chloride front. At the same time monosulphate found in the regions already occupied by chloride ions is attacked forming Friedels salt, some gypsum and releasing another source of sulphate ions into the pore solution [12]. This process is schematically shown in Fig. 10 describing a hypothesis of the suggested mechanism.

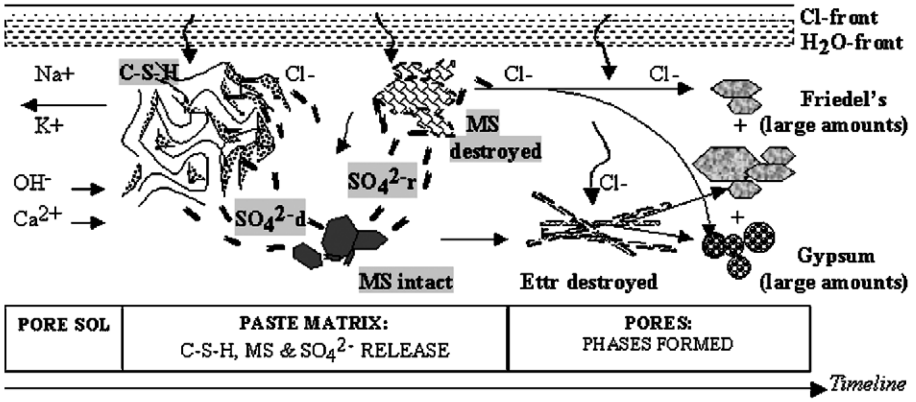
The released sulphates from monosulphate will meander through the pore network and react with unaffected monosulphate in another region of the paste matrix forming additional ettringite. Provided the ettringite formed remains stable under chlorides, the two separate sources of sulphates,



(a) Storage in Water: MODERATE EXPANSION



(b) Storage in Salt Solution of Intermediate Chloride Concentration: HIGH EXPANSION



(c) Storage in Salt Solution of High Chloride Concentration: NO EXPANSION

Fig. 10. Proposed mechanism describing the pessimum effect of externally applied chlorides on DEF expansion. (a) Under water storage, ettringite forms following sulphate ion desorbtion (SO d) from C–S–H as the only source of sulphate ions. (b) At low to intermediate concentrations, chlorides attack some monosulphate (MS) releasing sulphate ions (SO_4^{2-} r) into the pore solution. In this case, both the sulphate ions released from MS and the desorbed sulphate ions come in contact with unaffected MS in another location leading to a greater accumulation of ettringite and greater expansion. Ettringite formed under low chloride concentrations is not destroyed. (c) At high concentrations, chlorides attack both MS and any ettringite present destroying both phases and forming Friedel's salt and gypsum. Expansion here is completely mitigated.

the desorbed SO_4^{2-} from C–S–H and released SO_4^{2-} from monosulphate under chloride attack, cause more accumulation of late ettringite resulting in greater subsequent expansion. This scenario has been found to occur at intermediate levels of chloride concentrations including 0.5 M NaCl where monosulphate is destroyed while most ettringite remains stable (see Figs. 5, 9(b) and 10(b)). At high chloride concentrations such as 2.8 M NaCl, however, both monosulphate and ettringite are destroyed transforming both phases into Friedel's salt and gypsum as the main final products (see Figs. 5, 9(c) and 10(c)). This formation of Friedel's salt is non-expansive as seen in expansion studies.

4. Conclusions

The following conclusions have been drawn from the foregoing investigation in which sodium chloride was used to study the influence of externally applied chlorides on delayed ettringite formation.

1. Externally applied chlorides have a pessimum effect on expansion due to delayed ettringite formation in direct relation to the types and quantity of final products formed under different salt concentrations.
2. A mechanism describing the processes associated with various phase transformations and final products under the influence of different chloride concentrations has been proposed: Under water storage, ettringite forms following sulphate desorbtion from C–S–H as the only sulphate source. At low to intermediate salt concentrations, chlorides attack some monosulphate releasing sulphate ions into the pore solution. In this case, both the sulphate ions released from monosulphate and those desorbed from C–S–H come in contact with unaffected monosulphate in another location leading to a greater accumulation of ettringite and greater expansion. The ettringite formed is stable in solutions of low to intermediate levels of salt concentrations. At high salt concentrations, expansion is totally mitigated as chlorides attack both existing monosulphate and any ettringite present or formed, destroying both phases and forming Friedel's salt and gypsum as the final phase products.

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