



## Impact of chloride-rich environments on cement paste mineralogy



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### ABSTRACT

Chloride is widely present in the service environment in which Portland cement concretes are used. High local concentrations of chloride can develop by wicking and evaporation, as for example in splash zones. The parallel sequence of mineralogical changes with increasing chloride forms Friedel's salt and subsequently, compounds containing  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$  and  $\text{H}_2\text{O}$  in ratios 3:1:12 and 1:1:0. New X-ray and thermal analysis data are presented for these phases. Their phase equilibria are presented and it is shown that  $\text{Ca}(\text{OH})_2$  coexists with 3:1:12 at least up to 55 °C. It is suggested that the low physical density of 3:1:12, 1.62 g/cm<sup>3</sup>, and high water content contribute to the potential for expansion attending its formation in hardened matrices.

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### 1. Introduction

The durability of concrete may be limited in part by chemical interchanges between the paste and its environment. For example, exposure to chloride can deprive embedded steel of passivation against corrosion, alter the paste mineralogy and may solubilise cement components, processes which lead to degradation.

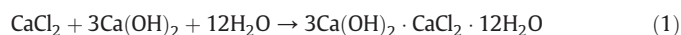
The nature and extent of reactions between chloride and cement phases have been much studied and depend on temperature, chloride concentration and pH. At low concentrations, typically millimolar, chloride forms Friedel's salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ , FS; see Table 1 for abbreviations and nomenclature). But at higher concentrations, formation of calcium hydroxychloride hydrates (also called chlorohydroxy or hydroxychloro hydrates),  $x\text{Ca}(\text{OH})_2\cdot y\text{CaCl}_2\cdot z\text{H}_2\text{O}$  (also written as  $x\text{CaO}\cdot y\text{CaCl}_2\cdot (z+x)\text{H}_2\text{O}$ ) is suspected of causing expansion and cracking in hardened concrete [1–9].

Previous studies of the formation of hydroxychlorides have been made mainly in the course of laboratory work but are broadly supported by field observations. However, the nature of compounds resulting from chloride attack is not unequivocally established and their stability and coexistence with other cement phases are not known with certainty.

Chatterji [1] observed the breakdown of Portland cement paste exposed to concentrated  $\text{CaCl}_2$  solution and reported formation of complex salts containing  $\text{CaCl}_2$ ,  $\text{Ca}(\text{OH})_2$  and/or  $\text{CaCO}_3$ . These complex compounds were reported to be stable at temperatures below 20 °C and  $\text{CaCl}_2$  concentrations above 15%. Bertsson et al. [2] noted that high chloride concentrations damaged concrete and attributed damage

to a combined effect of chemical, mechanical and physical processes including the formation of “(chloro)complexes”.

Monosi et al. [3] identified by X-ray diffraction (XRD) calcium hydroxychloride hydrate,  $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ , alternatively written as  $3\text{Ca}(\text{OH})_2\cdot\text{CaCl}_2\cdot 12\text{H}_2\text{O}$  (3:1:12) (see Table 1), in cement paste exposed to 30%  $\text{CaCl}_2$  solution at 5, 20 and 30 °C for 30 days. Subsequently Monosi et al. [4] reported the ‘disappearance’ of 3:1:12 when the samples were washed with alcohol, filtered and dried at RH below 1%. Others have observed 3:1:12 in hydrated cement exposed to  $\text{CaCl}_2$  and/or  $\text{MgCl}_2$  solutions [6,8,9]. The formation of 3:1:12 is reported to occur according to Eq. (1):



The formation of the hydroxychloride  $\text{Ca}(\text{OH})_2\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$  (1:1:1) (Table 1), alternatively written as  $\text{CaO}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ , has also been reported resulting from the drying of 3:1:12 or in synthetic preparations [4,8,9] but Smolczyk [10] has reported the formation of 1:1:1, identified by XRD, in concrete exposed to 3 M  $\text{CaCl}_2$  solutions for 2 years.

The data in [3,4,6,8,9] are based on laboratory exposures. However calcium chlorohydroxy hydrates have been observed in concretes removed from service: Justnes et al. [11] reported 3:1:12 occurring in the pores of concrete exposed to sea water in the tidal zone for 10 years; it was characterised by Scanning Electron Microscopy (SEM) and Wavelength Dispersive Spectroscopy (WDS). Justnes et al. also reported formation of calcium hydroxychlorides in a concrete bridge exposed to both salinity and guano [12].

Peterson et al. [9] proposed a scheme whereby 3:1:12, formed at low temperatures, ~5 °C, would, after heating and drying (and exposure to air), convert to a mixture of 1:1:1, portlandite (CH) and calcite. The

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**Table 1**  
Table of abbreviations.

Formula	Abbreviation (name)
$3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$	3:1:12
$\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$	1:1:1
$\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2$ or $\text{CaClOH}$	1:1:0
$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$	FS (Friedel's salt)
$\text{Ca}(\text{OH})_2$	CH (portlandite)

1:1:1 phase, rewetted with carbonated water at room temperature, converted to calcite.

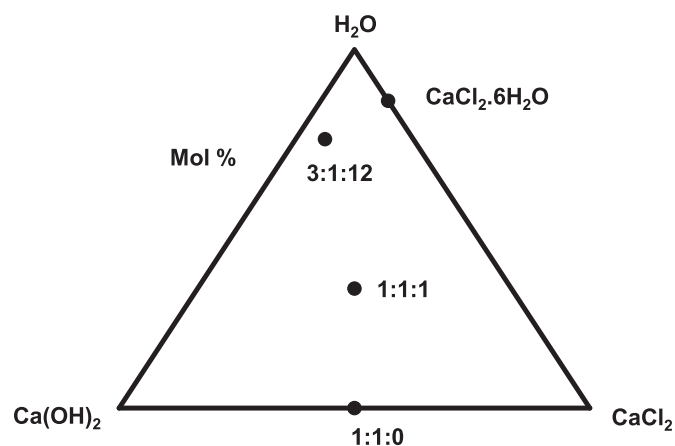
An intermediate carbonated state has been claimed by Sutter et al. [6], who reported phases with the formulae  $2.9\text{CaO} \cdot 0.2\text{CaCl}_2 \cdot 0.8\text{CaCO}_3 \cdot 15.8\text{H}_2\text{O}$  and  $2.9\text{CaO} \cdot 0.8\text{CaCl}_2 \cdot 0.2\text{CaCO}_3 \cdot 12.2\text{H}_2\text{O}$ , as determined by quantitative X-ray energy dispersive spectrometry (EDX).

Historically, different compositions were reported for the ternary phases  $x\text{Ca}(\text{OH})_2 \cdot y\text{CaCl}_2 \cdot z\text{H}_2\text{O}$ , or  $x\text{CaO} \cdot y\text{CaCl}_2 \cdot (z + x)\text{H}_2\text{O}$ , by assigning different numbers of water molecules [13–15]. Some of the reported differences could be related to preparation, temperature and evaporation effects: Demediuk et al. [14] found only one oxychloride at 38 and 94 °C, of composition  $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot x\text{H}_2\text{O}$ , with  $x$  varying between 8 and 13. It is now accepted that the ideal composition is 3:1:12. However, there is still a controversy about the number of water molecules in the other hydroxychloride, nominally 1:1:1. Markova [15] noted that above 20 °C and >35%  $\text{CaCl}_2$ , the anhydrous salt  $\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2$  (1:1:0), or  $\text{CaClOH}$ , replaced  $\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$  (1:1:1).

Currently accepted compositions of the ternary phases  $x\text{Ca}(\text{OH})_2 \cdot y\text{CaCl}_2 \cdot z\text{H}_2\text{O}$  at 22 °C are shown in Fig. 1. The notation, including  $\text{Ca}(\text{OH})_2$  in preference to  $\text{CaO}$ , is relevant to depict the composition of solids stable at the water saturation surface.

The JCPDS XRD data base does not help with the identification of the ternary compounds. First, the pattern used to identify 3:1:12, indexed as JCPDS card 02-0280, does not match the corresponding patterns presented elsewhere [3,4,9,16–18]. Since the paper by Monosi et al. [3] uses XRD to identify 3:1:12 in concrete samples, other authors have – rightly in our view – tended to use characterisation data given in [3] in preference to those recorded on JCPDS 02-0280.

Secondly, the patterns provided by the JCPDS for “ $\text{CaClOH}$ ” (JCPDS card 36-0983, taken from Westman et al. [19]) and for 1:1:1 (JCPDS card 2-1099) are very similar, which would suggest either that both cards refer to the same compound but one of the file names is in error, or, alternatively that both compounds have the same XRD pattern.



**Fig. 1.** The 22 °C isothermal section of the  $x\text{Ca}(\text{OH})_2 \cdot y\text{CaCl}_2 \cdot z\text{H}_2\text{O}$  system showing compounds stable in contact with an aqueous phase. Note that the choice of components affects the projection: if the lower left corner is taken as  $\text{CaO}$  instead of  $\text{Ca}(\text{OH})_2$ , the projected compound compositions will shift: for example, “3:1:12” will project at “3:1:15”. Some of the lower water hydrates of  $\text{CaCl}_2$ , e.g., the dihydrate, are also omitted.

According to Markova [15] the pattern assigned by some authors to  $\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$  (1:1:1) is actually due to  $\text{CaClOH}$  (1:1:0).

Crystal data and densities of the relevant phases are collected in Table 2.

The structure of the 1:1:1 phase is unknown. Birnin-Yauri [16] used data from Westman et al. [19] for 1:1:0 to index the compound claimed to be 1:1:1, obtaining very similar values for the cell parameters ( $a = 3.8610 \text{ \AA}$ ,  $c = 9.9050 \text{ \AA}$ ). This would again indicate that either the pattern assigned to the 1:1:1 belongs to  $\text{CaClOH}$  or accept that the two compounds, although differing in composition, nevertheless have the same pattern.

Stability regions, in terms of temperature and calcium chloride concentrations, have been reported for compounds in the  $\text{CaO}-\text{CaCl}_2-\text{H}_2\text{O}$  system [13,20–22]. Data for the quaternary system including  $\text{Al}_2\text{O}_3$ , and hence embracing the composition of Friedel's salt, are of particular interest for chloride binding in cement [23–25]. However the coexistence of hydroxychlorides with other phases, especially with Friedel's salt (see Table 1) is still not clear.

Damidot et al. [23] studied the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaCl}_2-\text{H}_2\text{O}$  system at 25 °C and defined six isothermal invariant points showing the coexistence of Friedel's salt with 3:1:12 and CH, and an aqueous solution with 3.3 mol/kg chloride. Another invariant point was located at 6.4 mol Cl/kg; the coexisting solids were FS + 3:1:12 + 1:1:1; note that portlandite is no longer stable. These observations find support from field studies: the coexistence of 3:1:12 with FS has been observed by petrographic examination and EDX in mortar samples exposed to  $\text{MgCl}_2$  at 4 °C for 84 days [6].

Brown et al. [25] reported two invariant points involving coexistence of 1:1:1 and Friedel's salt at  $23 \pm 2 \text{ °C}$  (1:1:1 + FS + CH and 1:1:1 + FS +  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) but claimed the absence of an invariant point including both 3:1:12 and FS. The two invariant points involving 3:1:12 and FS reported by Damidot et al. [23], but denied by Brown et al. [25], were hypothesized by Abate et al. [24] but were not detected experimentally.

The aim of this study is to determine the stability and coexistence of the calcium hydroxychloride compounds with Friedel's salt at 25 °C, resolve discrepancies in the literature, provide characterisation data for the solids and apply the results to the durability of cement paste in concentrated chloride environments. In this context it is noteworthy that the published literature shows that only exposure to  $\text{CaCl}_2$  or  $\text{MgCl}_2$  leads to formation of calcium hydroxychlorides in concrete; there is no evidence of a similar phase formation mechanism in  $\text{NaCl}$  [8,9,26].

## 2. Experimental

### 2.1. Synthesis, drying and storage

Calcium hydroxychloride salts were prepared by mixing  $\text{Ca}(\text{OH})_2$  (or, with care, fresh  $\text{CaO}$ ) with  $\text{CaCl}_2$  in different proportions (see Table 3).  $\text{CaCl}_2$  was first dissolved in  $\text{CO}_2$ -free distilled water and then mixed with either solid  $\text{Ca}(\text{OH})_2$  or free  $\text{CaO}$ . All mixes were prepared under nitrogen atmosphere to reduce uptake of  $\text{CO}_2$ . The preparations were sealed and agitated for 2 days. A water/solid ratio of ~1 was chosen. Ratios above ~1.5 do not form hydroxychloride compounds: the only solid phase detected was  $\text{Ca}(\text{OH})_2$ .

After 2 days at room temperature, ca. 20 °C, all samples except (2) were filtered. Sample (2) was sufficiently dry as not to need filtration. The samples were washed with acetone which does not affect the solids but removes excess soluble chloride. Washing with ethyl alcohol leads to dissolution of hydroxychlorides.

3:1:12 samples were filtered and dried by two different procedures: (i) over fresh silica gel at ~20 °C and (ii) in an oven at 55 °C. Wet and dry samples were also left exposed on the bench to air of variable humidity at 20–25 °C for 3 to 8 weeks to test their persistence.

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