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The system $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ at 23 ± 2 °C and the mechanisms of chloride binding in concrete

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Abstract

The stable quaternary diagram for the system $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ at 23 ± 4 °C has been constructed. Among the phases in this system are the calcium oxychlorides $Ca(OH)_2.CaCl_2.H_2O$ and $3Ca(OH)_2\cdot CaCl_2\cdot 12H_2O$. The formation of Friedel's salt (FS) and calcium oxychlorides provides a mechanism for chloride binding in Portland cement concrete. The compatibility relationships involving these compounds, FS and $Ca(OH)_2$, were established empirically, and $3Ca(OH)_2\cdot CaCl_2\cdot 12H_2O$ was found not to coexist in equilibrium with FS. The solubility behaviors of these compounds may play a role in affecting temperature-dependent corrosion rates. Additionally, the formation of oxychlorides from solutions containing elevated concentrations of NaCl may provide a mechanism by which ASR is facilitated.

Keywords: Friedel's salt; Calcium oxychloride; Corrosion; ASR

1. Introduction

There are a number of possible mechanisms by which chloride in concrete may be bound. These include the generally recognized mechanism involving the formation of Friedel's salt (FS). FS is $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$, and it is accepted that this compound forms in concrete exposed to chloride. FS formation provides a sink for chloride, and in doing so may decrease the concentration driving force for the migration of chloride towards embedded steel. Although it has been reported that chloride may also be bound in calcium silicate hydrate, there is no consensus regarding the extent or mechanism of binding. Chlorides may also be bound by the formation of Kuzel's salt, $3CaO\cdot Al_2O_3\cdot 1/2CaSO_4\cdot 1/2CaCl_2\cdot 10H_2O$, and by the formation of an iron-containing analog of FS, $3CaO\cdot(Al,Fe)_2O_3\cdot CaCl_2\cdot 10H_2O$ [1].

A further mechanism by which chloride can be bound is through the formation of calcium oxychlorides [2]. A number of calcium oxychlorides are known. The existence of $Ca(OH)_2\cdot CaCl_2\cdot H_2O$, the so-called 1:1:1 compound, is well established. A second compound having a $Ca(OH)_2/CaCl_2$ ratio greater than unity is also known. The literature variously describes the composition of this compound as $4Ca(OH)_2\cdot CaCl_2\cdot 10H_2O$ (4:1:10; [3]), $3Ca(OH)_2\cdot CaCl_2\cdot 12H_2O$ (3:1:12; [4]), and $3Ca(OH)_2\cdot CaCl_2\cdot nH_2O$ (3:1:n, where $n = 13$, 10 or 11, depending on temperature; [5]). Interestingly, the 3:1:12 compound was evaluated as an accelerating admixture for concrete [6].

As a consequence of FS and calcium oxychloride formation, establishing the stabilities of compounds in the system $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ is relevant to establishing the mechanisms influencing the corrosion of steel embedded in concrete. A variety of prior studies have been carried out to establish the stability relationships involving phases in this quaternary system and in the ternary subsystems. Two ternary subsystems involving water are relevant to concrete, $CaO\text{-}Al_2O_3\text{-}H_2O$ and $CaO\text{-}CaCl_2\text{-}H_2O$, and have been explored. Fig. 1 [7] shows the ternary subsystem $CaO\text{-}Al_2O_3\text{-}H_2O$. Stable invariant points are $Al(OH)_3\text{-}3CaO\cdot Al_2O_3\cdot 6H_2O$ and $Ca(OH)_2\text{-}3CaO\cdot Al_2O_3\cdot 6H_2O$ solutions. Fig. 2 shows an aspect of the ternary subsystem $CaO\text{-}CaCl_2\text{-}H_2O$ [4]. This diagram illustrates the sequence of phase formation with increasing proportions of $CaCl_2$. It also indicates the equilibrium relationships between $Ca(OH)_2$, the 3:1:12 and 1:1:1 compounds, and $CaCl_2\cdot nH_2O$, $n = 2, 4, 6$. Fig. 3 [2] shows the compatibility relationships at 20 °C and indicates these to involve the invariant points $Ca(OH)_2 + 3{:}1{:}12 + Aq$ and $1{:}1{:}1 + 3{:}1{:}12 + Aq$.

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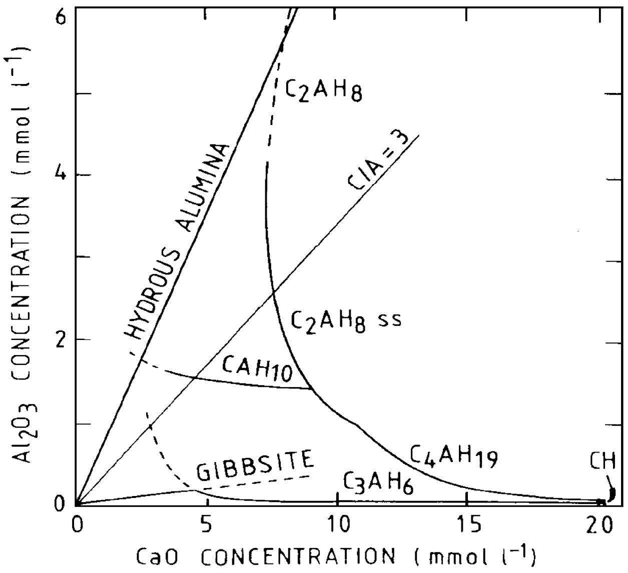

Fig. 1. The ternary system $CaO\text{-}Al_2O_3\text{-}H_2O$ at room temperature [7].

Damidot et al. [8] employed the *n*th root scaling technique, developed by one of us [9–11], to facilitate the representation of crystallization surfaces for phases having widely differing solubilities, and calculated the aspects of the quaternary diagram $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$. Abate and Sheetz [12] empirically determined a number of invariant points in this quaternary system, and the diagram that they produced is shown in Fig. 4. These latter authors suggested six invariant points involving FS. The following four invariant points were determined empirically by them:

$Al(OH)_3-3CaO\cdot Al_2O_3\cdot 6H_2O-3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[AH_3-C_3AH_6-FS]$

$Al(OH)_3 - CaCl_2\cdot 6H_2O - 3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[AH_3-CcH_6-FS]$

$Ca(OH)_2-3CaO\cdot Al_2O_3\cdot 6H_2O-3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[CH-C_3AH_6-FS]$

$CaCl_2\cdot 6H_2O-Ca(OH)_2\cdot CaCl_2\cdot H_2O-3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[CcH_6-(1:1:1)-FS]$

The following two could not be established, but were hypothesized

$Ca(OH)_2\cdot CaCl_2\cdot H_2O - 4Ca(OH)_2\cdot CaCl_2\cdot 12H_2O - 3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[(1:1:1)-(4:1:12)-FS]$

$Ca(OH)_2-4Ca(OH)_2CaCl_2\cdot 12H_2O-3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ $[CH-(4:1:12)-FS]$

2. Results and discussion

2.1. Ternary compatibility relationships in the $Ca(OH)_2\text{-}CaCl_2\text{-}H_2O$ subsystem

Following Fig. 2, we take the composition of the high-$Ca(OH)_2$ calcium oxychloride to be 3:1:12. With regard to chloride binding, the compatibility relationships involving $Ca(OH)_2$ and the 1:1:1 and 3:1:12 compounds are of particular interest. Fig. 2 indicates a number of compatibility relationships to be possible. Fig. 3 indicates the preferred ones to be $Ca(OH)_2$ + 3:1:12 + solution and 3:1:12 + 1:1:1 + solution.

2.2. Construction of the quaternary diagram

In experimentally establishing compatibility relationships, eight slurries containing various proportions of Cl, Ca and Al were produced and equilibrated for various periods of time. Some of these data have been previously discussed with regard to establishing the solubility behavior of FS [8]. In common with the results of Abate and Scheetz [12], the compatibility relations involving the oxychlorides were established with difficulty. In addition, it was common to observe assemblages in which CH, FS, 1:1:1 and 3:1:12 persisted. However, the assemblages CH + 3:1:12 or CH + FS + 3:1:12 were never observed, and these results are consistent with those of Abate and Scheetz [12], who

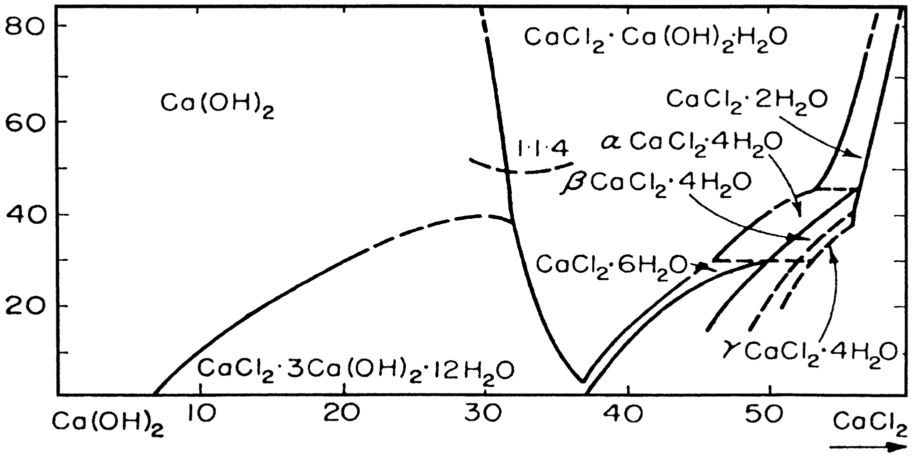

Fig. 2. Aspects of phase stabilities in the ternary system $CaO\text{-}CaCl_2\text{-}H_2O$ [4].

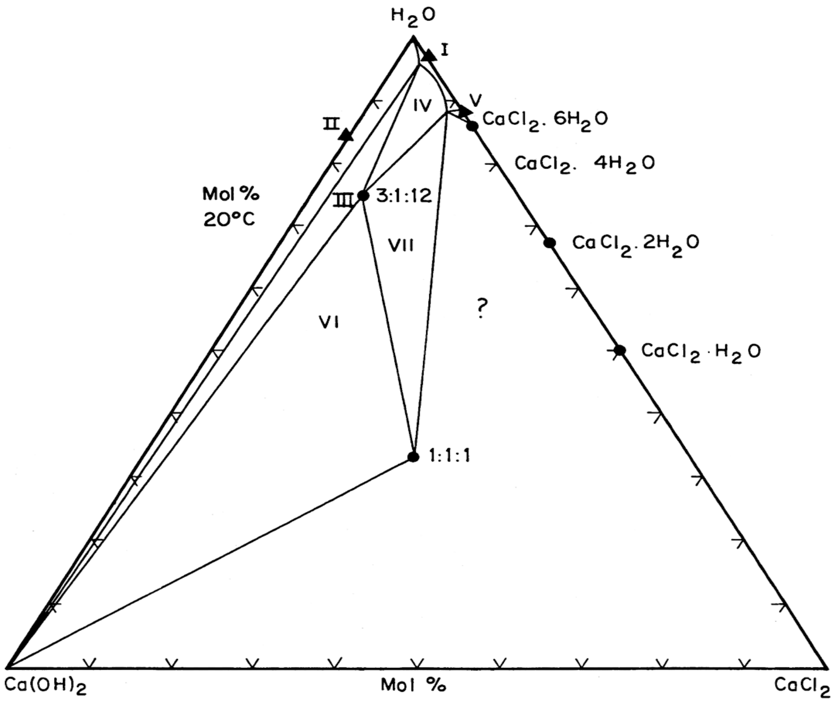

Fig. 3. The ternary diagram $CaO-CaCl_2-H_2O$ [2].

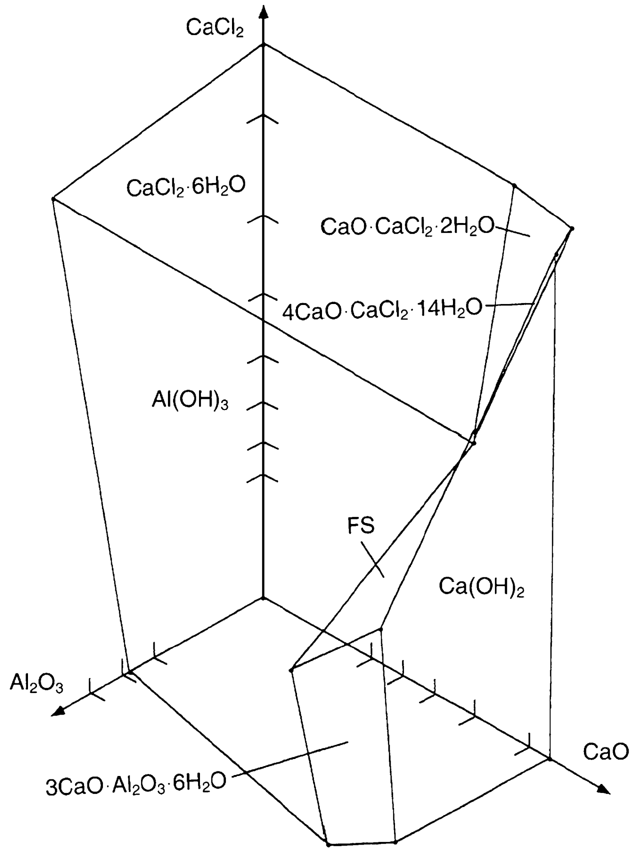

Fig. 4. The system $CaO-Al_2O_3-CaCl_2-H_2O$ according to Abate and Scheetz [12]. FS = Friedel's salt.

were unable to establish invariant equilibria involving the 3:1:12 compound. The experiments carried out demonstrated that 1:1:1 coexisted in univariant equilibria as follows: CH + 1:1:1 and FS + 1:1:1. Invariant equilibrium involving CH + FS + 1:1:1 was also established. The analytically determined concentrations of Al, Cl and Ca, at these points, are listed in Table 1.

Table 2 lists the concentrations presently obtained and those obtained by Abate and Scheetz [12] at the invariant points involving FS and C_3AH_6. Generally, the results are in good agreement, although the present results show higher chloride concentrations.

To construct a quaternary diagram in accord with the various empirical observations requires the existence of the ternary invariant point, $Ca(OH)_2$ + 3:1:12 + solution, and the quaternary invariant point, $Ca(OH)_2$ + 1:1:1 + FS + solution. The absence of the invariant point CH + FS + 3:1:12 suggests that 1:1:1 and 3:1:12 can only coexist in solutions that are undersaturated with respect to FS. In this instance, a quaternary invariant point $Ca(OH)_2$ + 1:1:1 + 3:1:12 + solution would exist. We point out, however, that this compatibility relationship is in contrast with the observations of

Table 1
Concentrations of Cl, Ca and Al in mol/l for various phase assemblages observed by X-ray diffraction

Coexisting solid phases	Cl	Ca	Al
CH + 1:1:1	1.72	0.80	4.19×10^{-4}
FS + 1:1:1	4.23	1.82	1.04×10^{-3}
CH + FS + 1:1:1	1.61	0.69	2.67×10^{-4}

Table 2
Concentrations of Cl, Ca and Al in mmol/l at the following invariant points

Coexisting solid phases	Cl	Ca	Al	pH
$CH + C_3AH_6 + FS$				
This work	5.08	21.96	0.11	12.13
Abate and Scheetz [12]	0.86	20.0	0.15	12.28
$AH_3 + C_3AH_6 + FS$				
This work	2.40	8.23	3.34	12.03
Abate and Scheetz [12]	0.37	8.3	4.2	11.60

Birnin-Yauri and Glasser [2] with respect to univariant equilibria involving 1:1:1 and the aqueous phase.

On the above-cited bases, the stable quaternary diagram $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ has been constructed and is shown in Fig. 5.

In constructing phase diagrams relevant to cement chemistry, it is typical to represent the components as water and anhydrous solids or their hydrates. In following that convention, the components are defined as H_2O, CaO, Al_2O_3 and $CaCl_2$. Using this convention, however, precludes consideration of some phase relationships, such as those involving $AlCl_3{\cdot}6H_2O$, which are not typically relevant to cement chemistry.

The diagram presented in Fig. 5 is that for the stable system. Birnin-Yauri and Glasser [13] reported the formation of solid solutions where the end members were FS and C_4AH_{13}. Such a relationship would be represented in the metastable quaternary system and was not observed in the present study. Although these invariant points were not observed by Abate and Scheetz [12], for completeness, we also point out that based on calculation, Damidot et al. [8] suggested the existence of invariant points: FS-$CaCl_2{\cdot}6H_2O$-Cl ettringite, FS-$Al(OH)_3$-Cl ettringite and $CaCl_2{\cdot}6H_2O$-$Al(OH)_3$-Cl ettringite. The phase boundary (position approximate) needed to realize a crystallization surface for chloro-ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaCl_2{\cdot}30H_2O$, has been shown in Fig. 5.

3. Relevance to durability

3.1. Corrosion

Based on the data in Fig. 2 and the solubility model of Harvie et al. [14], we suggest the formation of the 3:1:12 compound as a means for binding chloride during cold weather, limiting local chloride concentrations to values below those of the solubilities of $CaCl_2.6H_2O$ or NaCl.

The stability of the 3:1:12 compound appears to decrease substantially with increasing temperature. According to Ref. [3], it exists at $Ca(OH)_2/CaCl_2$ ratios of 8% at 0 °C, whereas this ratio increases to about 18% at room temperature. Decomposition of the 3:1:12 compound produces a calcium chloride solution and calcium hydroxide. As a consequence, rising temperature may liberate chloride that would otherwise be present in a solid. This suggests that the onset of accelerated corrosion of embedded steel with increasing temperature may, under some circumstances, be the consequence of both thermal activation and the liberation of chloride.

3.2. Alkali–silica reaction (ASR)

Chatterji observed that ASR could be induced using saturated NaCl solutions [15] and subsequently noted that the presence of $Ca(OH)_2$ was a requisite for ASR to occur [16]. The calcium oxychlorides are relevant to these observations in that their formation could result in the elevated pH values needed to facilitate ASR:

$$2NaCl_{(aq)} + 2Ca(OH)_{2(solid)} \rightarrow Ca(OH)_2{\cdot}CaCl_2{\cdot}H_2O_{(solid)} + 2NaOH_{(aq)}.$$

$$2NaCl_{(aq)} + 4Ca(OH)_{2(solid)} \rightarrow 3Ca(OH)_2{\cdot}CaCl_2{\cdot}12H_2O_{(solid)} + 2NaOH_{(aq)}.$$

The opportunity is thereby presented to generate sodium hydroxide solutions capable of presenting pH values in excess of that of a saturated calcium hydroxide solution. The data of Millikan [17] and the model developed by Harvie et al. [14] indicate that the formation of the 3:1:12 compound requires a chloride concentration of about 4 M, while that of the 1:1:1 compound requires a chloride concentration approaching 9 M [10]. The former molarity is below that of a saturated NaCl solution, which is nominally 5.6 M at room temperature. As pointed above, however, the solubility of the 3:1:12 compound decreases substantially with temperature, suggesting that cold weather could actually promote conditions favoring ASR.

4. Summary and conclusions

Modern experimental studies of the stabilities of the phases in the $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ system indicate the

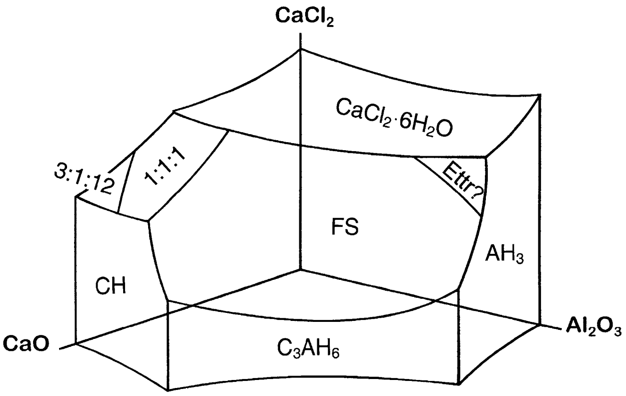

Fig. 5. The stable system $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$ at 23 ± 4 °C. The location of the phase boundary between 1:1:1 and 3:1:12 is uncertain. The approximate location of a phase boundary needed to realize a crystallization surface for chloro–ettringite has been shown.

absence of an invariant point: $Ca(OH)_2$-FS-3:1:12. Rather, $Ca(OH)_2 + 3:1:12 + 1:1:1$ appear to exist invariantly. In addition, $Ca(OH)_2$ was found to coexist univariantly with the 1:1:1 compound and invariantly with 1:1:1 and FS. While these observations are not in accord with prior thermodynamic calculations [8], they are consistent with compatibility relationships previously established among the solids in the CaO-$CaCl_2$-H_2O subsystem [2]. Namely, $Ca(OH)_2 \rightarrow Ca(OH)_2 + 3:1:12 \rightarrow 3:1:12 + 1:1:1$, with increasing concentrations of $CaCl_2$.

Consideration of the compatibility relationships and stabilities of phases in the quaternary system CaO-Al_2O_3-$CaCl_2$-H_2O provides insight to the mechanisms of chloride binding in concrete and suggests mechanisms affecting corrosion and ASR. In particular, the temperature dependence of the binding of chloride through the formation of calcium oxychlorides may influence the rate of corrosion of embedded steel. A temperature-dependent mechanism has also been suggested for the elevation of local pH by the reaction of NaCl with $Ca(OH)_2$ to produce the 3:1:12 compound, thereby facilitating the ASR.

We believe that Hal would have much enjoyed discussing these mechanisms.

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