

**Mechanisms
of
Alkali-Aggregate Reaction**

A MODELLING APPROACH TO THE PREDICTION OF PORE FLUID ALKALINITY IN CONCRETES

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ABSTRACT

The prediction and control of alkali-aggregate reactions (AAR) is dependent on a clear understanding of the underlying chemistry driving these reactions. Unfortunately, this chemistry is complex, sometimes misunderstood and used inappropriately in the design of simulate experiments. This paper reviews and clarifies some aspects of the basic chemistry associated with AAR. Starting from the premise that the reaction is initiated by hydroxide ions, not sodium or potassium¹, the paper goes on to develop the inter-relationship between aqueous species and precipitated solids. For example, it will be shown why sodium chloride additions may increase the pore fluid hydroxide concentration.

Recent advances in the application of speciation codes have enabled pore fluid chemistry to be modelled. Based on validated thermodynamic constants for aqueous and solid species, both empirical and theoretical models are available which permit relatively rapid prediction of the evolution of pore fluid composition. The empirical models enabled alkali partitioning between solid and aqueous phases to be estimated. The theoretical models enable the same balances to be calculated but additionally, to assess the impact of sulphate and chloride on pore fluid alkalinity.

Examples are given of the application of these models. The ability to predict hydroxide ion activity and hence alkalinity of multi-component solutions is illustrated so that the formulation of simulants can be critically examined and the alkalinity function can be calculated for a range of cements and blended cements.

Keywords: *chloride, Friedel's salt, modelling, pH, pore fluid alkalinity.*

INTRODUCTION

Having established a chemical basis for the alkali-aggregate reaction, the attention of cement scientists has moved on. One problem, which is addressed in this paper, is the role of sodium chloride as a promoter of AAR. Sodium chloride is a common component of the environment, occurring in sea-water, brackish groundwater and water infiltrating from de-icing salts, etc. At first sight, it is not easy to see why sodium chloride should promote alkali-induced reactivity. Aqueous solutions of NaCl are neutral, i.e., their pH is close to 7, yet in cement systems, they appear to enhance the alkalinity. This paper focuses on the underlying chemistry of this effect. The basic mechanisms are simple but their quantification is made difficult by the complex nature of cementitious systems.

ANALYSIS OF THE PROBLEM

A mortar or concrete can be viewed as containing three components: aggregate, cement paste and pore fluid. Of these three components, only the pore fluid is truly homogeneous, but for the moment, the three-component model suffices. The paste has a high specific surface area and, moreover, in a well-matured paste, the pore fluid is contained in small pores and capillaries, most having an effective diameter of $< 5\mu\text{m}$. The paste and pore fluid tend, by virtue of their intimate contact, to be in equilibrium or nearly so but reactions between aggregate and the other two components are relatively slow. This slow reaction, leading to the occurrence of volume changes long after set, is characteristic of the alkali-aggregate reaction.

The paste-pore fluid portions of the system, as noted, reflect an equilibrium. Numerous analyses of pore fluid, obtained by expressing pore fluid from a paste under pressure, disclose that anions other than hydroxyl (OH^-) are removed from the aqueous phase by incorporation in solids. Thus the OH^- concentration in pore fluid is typically very much greater than the sum of all the other anions (i.e. sulphate, silicate, etc.). This conditions the observed pH since $\text{pH} = -\log\{10^{-14}/[\text{OH}^-]\}$ at 20°C : [] denotes concentrations in mol.l^{-1} . Strictly speaking, we should use activities rather than concentrations and this refinement as well as concentrations in molal units, can if needed, be introduced subsequently. Several sources of hydroxyl ions can be identified in cement pastes. C-S-H and $\text{Ca}(\text{OH})_2$ are quantitatively the most significant phases in Portland cement pastes and together, their dissociation is sufficient to generate a pH of about 12.4 at 18°C . Moreover, their presence as solids provides a buffer for the pore fluid such that a pH decline below 12.4 is inhibited. However, other alkalis in cements (Na_2O and K_2O) are more soluble than C-S-H and $\text{Ca}(\text{OH})_2$ and if present, condition aqueous pH's in excess of the buffer threshold. Pore fluid pH's greater than 13 are frequently observed. Taylor² has given empirical formulae to calculate the steady state pH of pore fluid from a bulk analysis of the cement clinker and a specified water:cement ratio (w/c). But the free OH^- concentration and hence the alkalinity of the pore fluid can be influenced by the presence of other ions so that it is now appropriate to consider how one of these other ions can affect the chemical balances in the system.

Impact of Chloride

Chloride is a unique but important case. It is not normally a constituent of fresh paste but, when present, it is less completely removed from pore fluid than other anionic constituents (excepting OH^-). Several mechanisms for its partial removal have been postulated. These include:

- (i) sorption on solid components of paste, e.g. C-S-H
- (ii) substitution of Cl^- for OH^- in more crystalline hydrates
- (iii) formation of cement phases containing essential Cl^- for their stability, e.g. Friedel's salt

Friedel's salt has been the subject of much speculation concerning its stability and role as a sink for chloride ions. Any assessment of the effectiveness of Friedel's salt, if it is to proceed from a physicochemical basis, requires consideration of the relationships between paste mineralogy and pore fluid composition. Basic stability data have been reported by Birnin Yauri *et al.*³ and these are especially relevant under mechanism (iii) above, which is believed to be the most important source of binding at all except the lowest levels of chloride content, e.g. sub-ppm levels.

Friedel's salt is a member of the AF_m family of structurally-related phases. All AF_m phases have layered structures, the basic building unit of which has the constitution [Ca₄Al₂(OH)₁₂]²⁺. Its net positive charge is balanced by anions: either monovalent, e.g. OH⁻, Cl⁻ or divalent, e.g. CO₃²⁻, SO₄²⁻, etc. To maintain charge balance, the number of interlayer anions may be variable; for example, 2Cl⁻ ~ SO₄²⁻. The different numbers of anions required for charge balance, as well as their different sizes and polarisabilities control the variable interlayer water contents and control the exact layer stacking sequence. Hence Friedel's salt (in which the balancing ion is mainly Cl⁻) is readily distinguished from monosulphoaluminate, the main AF_m type phase occurring in Cl⁻ free cement pastes. The distinction between Friedel's salt and hydroxy-substituted AF_m, e.g. C₄AH₁₃, is not easy and supplementary microprobe analyses may be required.

As a first approach, the conversion of hydroxy AF_m to Friedel's salt can be analysed by following the conversion process as a function of added NaCl. However, while this seems the obvious way to proceed, it can be shown that NaCl behaves not as a single component but as two components, Na⁺ and Cl⁻. In this instance, [Na⁺] becomes greater than [Cl⁻] in the aqueous phase of cements because the Cl⁻ becomes structurally incorporated into the precipitating Friedel's salt. It is perhaps easier to consider an alkali-free model of Ca(OH)₂ and aluminates where the chloride is introduced as CaCl₂ rather than NaCl. In this case, the Ca concentration in solution is defined by the monosulphoaluminate (and Ca(OH)₂) at about 0.02M and the added calcium and chloride will both contribute to Friedel's salt formation. Having considered this case, it will then be easier to undertake the more complex calculations assuming NaCl to be the source of Cl⁻.

Impact Of Different Chloride Salts On Cement Properties

CaCl₂: A hydrated Portland cement paste, initially, Cl⁻ free is assumed. Its AF_m phase consists of OH⁻ (or sulphate) AF_m, C-S-H, Ca(OH)₂ and perhaps some AF_t. We neglect AF_t to avoid complications arising from significant amounts of sulphate. Preliminary experiments disclose that the absorptive properties of C-S-H for Cl⁻ have little significance in comparison with those of the AF_m phase. CaCl₂ is now added to the cement paste. At the start of the process, the pore fluid aqueous phase will be conditioned to a pH of ~ 12.4 by the solid phases, principally Ca(OH)₂ and C-S-H. As the chloride content rises, a threshold value is reached which, when exceeded, causes hydroxy (or sulphate) AF_m to transform to Friedel's salt. Birnin-Yauri³ has obtained experimental data relevant to this point: Table 1 gives data obtained by equilibrating mixtures of laboratory grade Ca(OH)₂, Ca₃Al₂O₆, CaCl₂.2H₂O and distilled water for 28 days at 20 ± 2°C with constant stirring. The solid reactants were totally

Table 1: Analysis of co-existing phases in the system $\text{Ca}(\text{OH})_2$ -Friedel's salt (FS) - Aqueous at $20 \pm 2^\circ\text{C}$

Mole Ratio of Solids FS:Ca(OH)	[Ca] (mM)	[Al] (mM)	[Cl] (mM)	[OH] (mM)	pH	x values of solid in FS*
5:1	24.0	0.024	21.2	31.6	12.5	0.24
3:1	23.1	0.030	19.1	30.9	12.5	0.26
1:1	21.3	0.026	18.7	30.9	12.5	0.41
1:3	21.6	0.070	18.3	30.2	12.5	0.41
1:5	22.3	0.097	19.6	28.2	12.5	0.41

* Value of x in the formula $\text{Ca}_4\text{Al}_2\text{O}_7\text{Cl}_{2-x}\text{OH}_{2x}\cdot n\text{H}_2\text{O}$

consumed and it is believed that the resulting solution and solid phase analyses reflect an equilibrium. All preparations were made and handled in N_2 -flushed, CO_2 -free atmospheres and the aqueous phase was doubly filtered, finally through $0.45 \mu\text{m}$ filter prior to analysis. The solid phase was analysed by isolating selected crystals under a scanning electron microscope and determining chloride, shown in Table 1 as x values, by energy dispersive X-ray analysis.

Consideration of the results shown that, within limits of error, the aqueous phase composition is very insensitive to the ratio of solids, $\text{Ca}(\text{OH})_2$ to Friedel's salt. However, as is typical of a system with a degree of freedom, x values in the Friedel's salt vary with the ratio of solid phases; Friedel's salt increases somewhat in OH^- content as the $\text{Ca}(\text{OH})_2$ content increases. Nevertheless, the aqueous pH remains essentially constant at 12.5, a value not significantly different than that which would be obtained from a saturated $\text{Ca}(\text{OH})_2$ solution or from a saturated solution equilibrated with $\text{Ca}(\text{OH})_2$ and C-S-H. Thus, adding CaCl_2 does not significantly alter the pH of a cement system provided sufficient Al is present to stabilise Friedel's salt. Note also that the pH is not dependent on the amounts of phases present at invariant points.

NaCl: If chloride is added instead as NaCl, a different situation obtains. Friedel's salt still remains a stable phase at 20°C , at least up to 0.5M NaCl, but the aqueous phase balance is altered. Some sodium is taken up into cement solids but uptake is not very efficient and, in general, the removal of chloride into Friedel's salt is more efficient than sodium removal mechanisms i.e., chloride has a more favourable partition coefficient than does sodium into their respective solid forms.

Because of the complexity and high ionic strength of the aqueous phase, results have been calculated using Pitzer activity corrections⁴. Several checks were performed on the accuracy of the calculations. The calculations disclose that Friedel's salt is stable over a wide range of chloride concentrations. For example, it is calculated to exist with $\text{Ca}(\text{OH})_2$ in the Cl^- concentration range from $0.009 \text{ mol}\cdot\text{kg}^{-1}$ to $3.285 \text{ mol}\cdot\text{kg}^{-1}$. In these calculations, the stable chloride-free aluminate was taken as $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (or C_3AH_6 in cement terminology). This, as well as the use of molal rather than molar units of concentration, and performing calculations corresponding to 25°C rather than

20°C, introduces some differences in numerical values but should not inhibit order-of-magnitude comparisons. Table 2 shows a comparison of data, taking the equilibria most closely related to those of Table 1. Table 1 gives the self-generated compositions and pH achieved by dissolving mixtures of Friedel's salt and Ca(OH)₂ in water whereas Table 2 gives data for dissolving Friedel's salt, Ca(OH)₂ and calcium aluminate hydrate (Ca₃Al₂(OH)₁₂ in this instance). This shifts the aqueous phase composition somewhat, but a salient point is that calculations of numerous phase combinations containing Ca(OH)₂ all tend to give aqueous pH values close to 12.5. This may be contrasted with the situation obtaining when NaCl is added. When the addition is such that [Na⁺] = 0.25 mol.kg⁻¹, the corresponding aqueous pH is raised by nearly one unit, from 12.4 to 13.4. Preliminary calculations show that the pH enhancement is directly related to the concentration of NaCl, provided sufficient aluminium exists to support the continuing formation of Friedel's salt.

Table 2: Equilibrium calculations of coexisting phases in the system Ca(OH)₂-calcium aluminate-Friedel's salt (FS)-aqueous

Na ₂ O (mol.kg ⁻¹)	Solids present	[Ca] (mol.kg ⁻¹)	[Al] (mol.kg ⁻¹)	[Cl] (mol.kg ⁻¹)	pH
0	C ₃ AH ₆ -CH-FS	0.0259	7.0E-6	0.0096	12.50
0.25	C ₃ AH ₆ -CH-FS	1.396E-3	7.398E-5	1.049E-1	13.43

Equilibria in the CaO-Al₂O₃-CaCl₂-H₂O system are conveniently summarised in Figure 1 which shows calculated⁴ solubility surfaces for the identified phases; AH₃ is gibbsite, 3-1-15 is 3CaO.CaCl₂.15H₂O and 1-1-2 is CaO.CaCl₂.2H₂O. These last two phases are unlikely to appear in cement pastes, except at very high chloride levels. Note that the concentration scales are not linear. This diagram provides a useful illustration of the range of aqueous phase compositions over which Friedel's salt will be stable, e.g. with appropriate Ca and Al concentrations, Friedel's salt is stable in the chloride

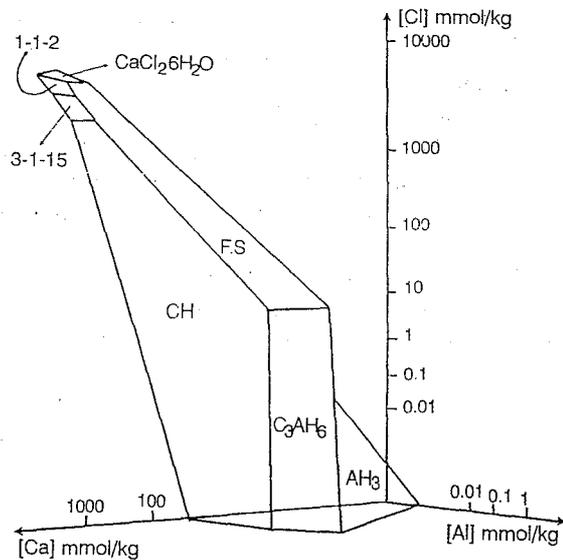


Fig. 1: Solubility surfaces for precipitates in the system CaO-Al₂O₃-CaCl₂-H₂O. FS represents Friedel's salt, AH₃ is gibbsite, 3-1-15 is 3CaO.CaCl₂.15H₂O and 1-1-2 is CaO.CaCl₂.15H₂O.

concentration range $9.6E-3 \text{ mol.kg}^{-1}$ to 8 mol.kg^{-1} , i.e. a $[\text{Cl}^-]$ range covering 3 orders of magnitude.

Discussion

It can be shown from thermodynamic analysis that Friedel's salt is stable in cement systems. These calculations are general and do not depend on the type of cement being used. When chloride is present in the cement pore solution as aqueous sodium chloride, the more rapid absorption of chloride ions into solid phases (particularly Friedel's salt) means that the less efficiently absorbed sodium requires to be balanced by another anion. Thus, hydroxide is released into solution and the pH is increased. Pore fluid of increased pH enhances the risk of AAR.

The calculations presented in this paper assume steady state conditions, i.e. it is assumed that no leaching is taking place. The nature of the thermodynamic treatment however means that the chemistry predicted (and confirmed by experiment) does not depend on there being substantial amounts of each phase present. Indeed, as long as any quantity of each phase is in equilibrium with the aqueous phase (pore fluid), the above predictions will be valid. This is also true if the composition of an interacting fluid is such that more of the phases already existing in the cement paste can form but if, for example, seawater interacts with the cement, ultimate exhaustion of the available aluminium required for Friedel's salt formation will cause a reduction in the residual capacity for chloride binding. This means that a period of buffering of the pore fluid by solid phases can be expected in certain cases which will further protect underlying steel from intruding chloride solutions.

Sodium chloride permeation into cement concretes has two potentially adverse consequences; enhancement of steel corrosion and alkali-aggregate reaction. Of course, an impermeable concrete is desirable but once permeation has occurred, the alumina content of the cement has an important role to play. With calcium, it binds chloride as Friedel's salt, thereby reducing the rate at which chloride can penetrate to the embedded steel. On the other hand, by removing chloride, the local alkalinity is increased by the mechanisms described, thereby increasing the susceptibility of aggregate to attack. There is a trade off; enhanced chloride binding in the paste and protection for embedded steel but at the expense of increased alkalinity and risk of alkali reactivity. This conclusion is important in the design of concrete systems.

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