Pergamon

Cement and Concrete Research, Vol. 28, No. 12, pp. 1713–1723, 1998

0008-8846/98 $–see front matter

PII S0008-8846(98)00162-8

FRIEDEL'S SALT, $Ca_2Al(OH)_6(Cl,OH)\cdot 2H_2O$: ITS SOLID SOLUTIONS AND THEIR ROLE IN CHLORIDE BINDING

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(Received January 23, 1998; in final form September 14, 1998)

ABSTRACT

Solubility relationships between Friedel's salt and hydroxy AF_m suggest an essentially complete solid solution with only minor discontinuities. Solid–aqueous partitions were determined by equilibration of 11 compositions at 10 mol % intervals at ~20 °C in experiments of 6–17 months' duration. Aqueous chloride concentrations >2mM, approximately, are required to incorporate significant Cl in hydroxy AF_m; the process is complete, giving essentially pure Friedel's salt, at a chloride content of ~14 mM. The self-generated pH of the solid solutions are high: pH >12 for all compositions. The implications for diffusion of chloride ions through cement paste are discussed. © *1998 Elsevier Science Ltd*

Introduction

The AF_m phase in Portland cement has a complex chemical and structural constitution. A general formula for the aluminate phase is $[Ca_2(Al,Fe)(OH)_6]^{+}x^{-}\cdot mH_2O$ (1), where brackets indicate the constitution of a positively charged layer unit. The excess positive charges are balanced by anions, x, in interlayer spaces, e.g., OH^-, Cl^-, SO_4^{2-}, and CO_3^{2-} molecular water, m, also is essential. This paper is concerned particularly with one of the phases, Friedel's salt, $Ca_2Al(OH)_6Cl\cdot 2H_2O$, and its relationships with hydroxy AF_m.

Friedel's salt is important for a number of reasons. First, it is more stable than the hydroxy aluminate AF_m. A range of hydroxyaluminates differing in molecular water contents is known, but all are unstable with respect to mixtures of C_3AH_6 (hydrogarnet) and alumina hydrate, AH_3 (gibbsite) Second, AF_m phases exhibit anion exchange: their composition is sensitive to their local chemical environment. Thus, when chloride diffuses into cement, diffusion profiles may be affected by ion exchange and binding into AF_m phases; the AF_m serves as a "sink" for chloride ions and thereby retards diffusion of chloride.

The need to protect embedded steel from chloride ions is well known. In this respect, the role of the AF_m phases has been the subject of much discussion, although the data necessary to quantify its role have not been obtained.

The stability of Friedel's salt in the system CaO-Al_2O_3-$CaCl_2$-H_2O has been determined

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(2), but less is known about the chemistry of its solid solutions with other AF_m type phases and the composition of the coexisting aqueous phase. These are described as a prelude to a more comprehensive investigation.

Experimental Methods and Results

Friedel's salt

Tricalcium aluminate, $3CaOiAl_2O_3$, was made by heating together a 3:1 molar ratio mixture, of reagent grades of $CaCO_3$ and low-alkali Al_2O_3 at ~ 300–1350°C. The heating was done in Pt crucibles and was continued, with intermediate grinding of the product, until x-ray powder diffraction and a modified Franke test disclosed that the free lime content was reduced to $<0.5\%$. Portions of this solid were mixed with weighed amounts of reagent grade $CaCl_2 \cdot 6H_2O$ and added to double distilled, CO_2-free water, generally at a w/s ratio ~10. The plastic containers, tightly sealed to prevent CO_2 uptake, were agitated for ~28 days at 20°C. The resulting bulk solid gave an x-ray powder pattern, obtained from (3), corresponding to Friedel's salt. A match for 18 reflections in the range of *d* spacings between 8 and 1.65A (CuKα radiation) were obtained. Bulk chemical analysis of the preparation gave a Ca:Al:Cl ratio of 2:1:1 ± 0.01.

The moist product was redispersed with two additional portions of distilled water and filtered. This was deemed acceptable because preliminary experiments indicated that the product had congruent solubility; hence, the additional redispersions purified the product. This moist product was used for solubility determination.

A microchemical analysis of the selected single crystals, cited as the mean of four determinations, gave the atomic ratios (relative to Al = 1.0) Cl:Ca = 0.97:1.98, both ±0.02. Figure 1 shows an electron micrograph of a well-cured product. The preparation consisted of two morphologies; the bulk of the crystals were flat hexagonal (or pseudohexagonal) platelets, about 1–5 mm maximum dimension. Occasional small spherulitic growths also occur. Energy dispersive X-ray analysis of the platelets gave a ratio (relative to Al = 1.0) of Cl:Ca = 0.98:1.96, both ±0.05. The spherulites were too small to analyse quantitatively, but contained Al, Ca, and Cl in approximately the same ratio as in Friedel's salt.

Figure 2 shows the Fourier transform infrared (FTIR) spectrum of this preparation. A partial assignment of its features is as follows: the feature at $\sim 786\ cm^{-1}$ is due to an Al-OH bending mode (4,5). The band at $\sim 1623\ cm^{-1}$ is an H-O-H vibration ($\nu_2 H_2O$) of interlayer water, whereas the broad band at $\sim 3495\ cm^{-1}$ is due to vibration of OH ions, (νOH) in structural water. Chloride does not absorb in the range $400-4000\ cm^{-1}$. Bensted (6) attributed this to the ionic nature of the chloride bonding.

Thermal analysis data are shown in Figure 3. the differential thermal analysis (DTA) and thermogravimetric analysis (TG) traces were recorded simultaneously in dry N_2. A double endotherm centred at 120° and 290° is matched by two well-resolved weight loss steps. Supplementary X-ray diffraction patterns, samples for which were obtained by interrupting the heating programme at appropriate points, confirmed that the ~120°C event is due to removal of interlayer water giving a product with reduced crystallinity. Upon analysis, it has the composition $3Ca(OH)_2 \cdot 2Al(OH)_3 \cdot CaCl_2$. With further heating, this phase persists up to ~290°C at which the remaining water is lost, giving a largely X-ray amorphous product. The

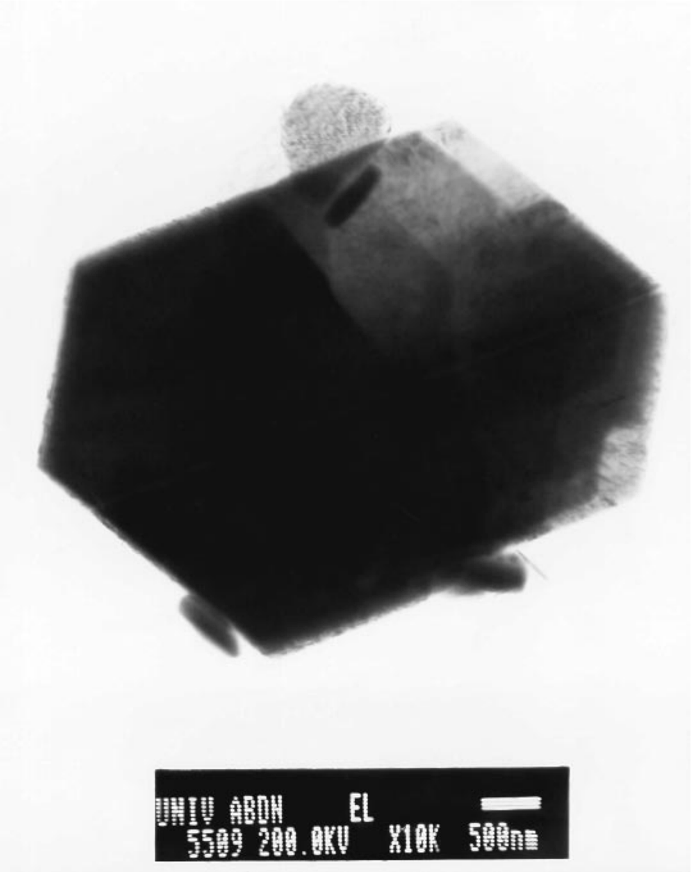

FIG. 1.
Electron micrograph showing two morphologies of Friedel's salt. Cured 17 months at 20°C.

product recrystallises exothermically at ~670°, yielding mainly calcium chloroaluminate, $11CaO\cdot7Al_2O_3\cdot CaCl_2$.

The total water loss, 100–700°, was 89.5% of theoretical value. The low water total is attributed to some loss occurring in dry N_2 during the initial period of purging and thermal stabilisation at temperatures $<100°$.

Solubility and thermochemistry

Four portions of Friedel's salt were mixed at approximately 1:10 weight ratio with (i) double distilled, decarbonated water (two samples) and (ii) with about 100 mL of a saturated $Ca(OH)_2$ solution, to which 0.5 g of extra $Ca(OH)_2$ had been added (7). The mixtures were agitated for 28 days at 20°C ± 2°C, after which the slurries were filtered by suction. Aliquots of the solutions were filtered through a 0.45-μm disc (Millipore^{TM}) and analysed for Ca,Al (atomic absorption), Cl (ion chromatography), and OH (pH meter), as well as by titration

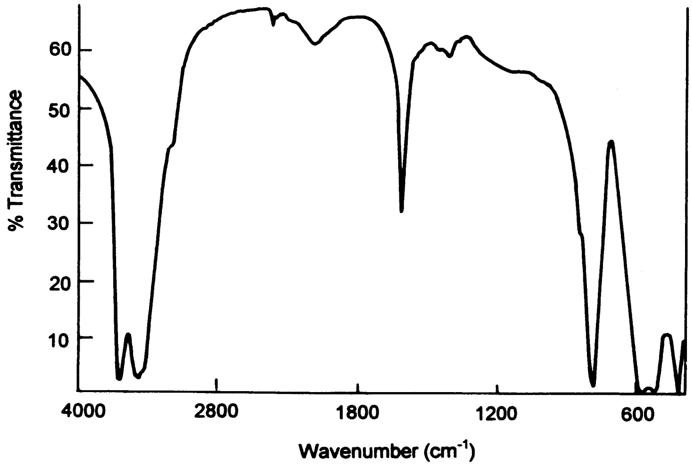

FIG. 2.
Fourier transform infrared spectrum of phase pure Friedel's salt.

with standard acid using phenolphthalein indicator. The solids were redispersed in batches of four, as before, for an additional ~150 days. After a total of ~180 days, the solids, analysed by X-ray powder diffraction and chemically for total Ca, Al, and Cl, were unchanged in composition. Friedel's salt persisted unchanged in set (i), whereas set (ii) was also unchanged and consisted of $Ca(OH)_2$ and Friedel's salt. Table 1 reports the means of the four replicate

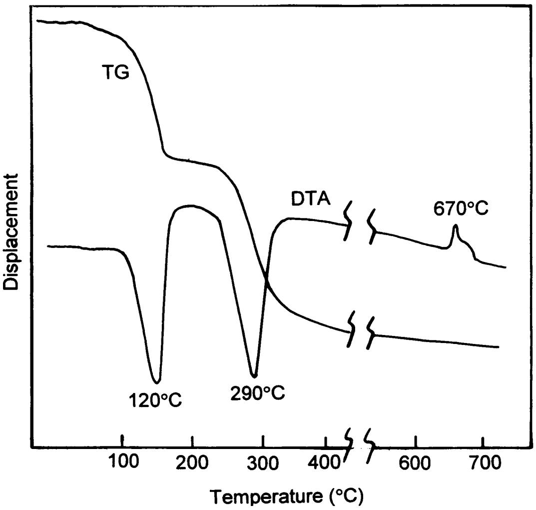

FIG. 3.
Combined DTA/TG of phase pure Friedel's Salt. Downward direction is endothermic on DTA and corresponds to weight loss on TG. Heating rate was 10°C in N_2.

TABLE 1
Solubility of Friedel's salt at 20°C.

Dispersion no.*	Mean solution composition (mM)			
	Al	Cl	Ca	OH
1	4.40	6.03	9.17	10.29
2	5.04	4.80	9.48	10.28
3	4.89	4.89	9.11	11.30
4	4.97	4.40	8.67	9.90
5	5.07	4.49	8.73	10.27
Mean	4.87	4.92	9.03	10.51

* Each concentration is the mean of four separate determinations. Two sets of $[OH]^-$, calculated and observed, were obtained. Both procedures for determining [OH] suffer from potential errors, but the observed titration values are considered to be the most reliable, even though the complete data set used to calculate Ksp may not be in accord with strict electroneutrality.

analysis after each of the five consecutive samplings. The OH^- values (calculated) are determined from charge balance: Σ positive charges = Σ negative charges. The solubility products, Ksp, calculated from the data are defined by the relationship:

$$\mathrm{Ksp} = [Ca]^4[Al(OH)_4]^2[Cl]^2[OH]^4.$$

The Ksp and solubility values for Friedel's salt may be compared with others reported in the literature (Table 2).

Both congruent and incongruent dissolution have been proposed. However, previous reports differ markedly in the extent to which an excess of the most soluble component, chloride, may have been present and in the time allowed for complete reaction. It is probably

TABLE 2
Solubility of Friedel's salt, $Ca_2Al(OH)_6\ Cl{\cdot}2H_2O$.

Proposed dissolution	Ksp (congruent)	Reference	Other comment
Congruent	−27.10	This study	20°C
Congruent	−27.09	Nacken and Mosebach (8)	30°C: C_3AH_6 impurity
Congruent	—	Zhang et al. (9)	
Incongruent	—	Roberts (10)	
Incongruent	—	Lafuma (11)	(Ca:Cl) aqueous: 3.54
Incongruent	—	Foret (12)	Ca:Al:Cl (aqueous) = 3.57:1.006:1.79

TABLE 3
Aqueous phase analyses in the Friedel's salt–C_4AH_{13} series: 20°C ± 2°C.

Nominal	Concentration (mM)				Observed
x	Ca	Al	Cl	OH	Cl/OH
0	38.05	1.30	64.17	223.17	2.77
0.1	26.20	0.69	14.46	24.55	0.59
0.2	24.82	0.70	13.94	37.32	0.37
0.3	23.45	0.72	13.40	38.90	0.34
0.4	22.20	0.75	8.82	39.82	0.22
0.5	20.96	0.75	4.23	40.74	0.10
0.6	20.21	0.70	2.33	43.65	0.05
0.7	19.96	0.66	2.07	45.71	0.05
0.8	19.21	0.67	1.90	45.71	0.04
0.9	16.22	0.64	<1.0	41.69	—

significant that the reports claiming incongruent dissolution exhibit wider data scatter than those showing congruent dissolution.

Friedel's salt–hydroxy AFm solid solutions

Roberts (10), Pöllmann and Kuzel (13), and Pöllmann (14) report the occurrence of a miscibility gap between chloride and hydroxy end members, whereas Turriziani (15) and Turrizianii and Schippa (16) report complete miscibility. Experimentally, the system is difficult to study. The hydroxy AF_m end member, nominally C_4AH_{13}, often occurs together with C_4AH_{19} and, moreover, all C_4AH_x phases are unstable and exhibit a pronounced tendency to recrystallise, at least in part, to mixtures of the more stable solids, C_3AH_6 and AH_3 (gibbsite). The present authors also observe these features. The literature also reports (13,14) an α and β polymorph of Friedel's salt but only one of the polymorphs, the low-temperature phase, was encountered in the course of the title study, which had as its main objective isothermal characterisation of the compositions of coexisting solid and aqueous phases. Characterisation of the solid(s) was therefore essential and a determination of the continuity of the solid solution was made.

A range of compositions were prepared in the AFm series with $(1 - x)\ CaCl_2.xCa(OH)_2$ at intervals of $x = 0.1$. Experiments with Friedel's salt and C_4AH_{13} showed that OH/Cl exchange occurred rapidly and, because the experiments were made in an excess of an aqueous phase, it was sufficient to mix and equilibrate the appropriate starting materials. With intermittent agitation, no significant changes to either solid or aqueous phase compositions occurred after 1–3 months at 20°, although the time allowed for reaction was eventually extended to 17 months. Table 3 lists thhe aqueous phase compositions. Each reported datum is the average of three replicate determinations.

The hydroxide value is from titration . Despite the range of chloride concentrations, the pH of the aqueous phase remains high, >12.0 even for pure Friedel's salt (FS): mixtures of $Ca(OH)_2$ and Friedel's salt give a pH only slightly higher, about 12.2 at 20°C.

TABLE 4
Combined X-ray diffraction and energy dispersive *X*-ray analysis of solid phases: 17 months at 20°C ± 2°C.

Nominal x*	AF_m phase:atom ratio (Cl:Ca)†	Composition of AF_mphase‡
0	1.05 ± 0.05:1.91 ± 0.07	Friedel's salt
0.1	0.98 ± 0.06:1.93 ± 0.03	0.98 $CaCl_2$ 0.20 $Ca(OH)_2$
0.2	0.71 ± 0.08:1.83 ±0.06	0.71 $CaCl_2$ 0.29 $Ca(OH)_2$
0.3	0.61 ± 0.05:1.83 ± 0.08	0.61 $CaCl_2$ 0.39 $Ca(OH)_2$
0.4	0.52 ± 0.09:1.82 ± 0.08	0.52 $CaCl_2$ 0.48 $Ca(OH)_2$
0.5	0.44 ± 0.06:1.83 ±0.07	0.44 $CaCl_2$ 0.56 $Ca(OH)_2$
0.6	0.39 ± 0.05:1.85 ± 0.07	0.39 $CaCl_2$ 0.61 $Ca(OH)_2$
0.4	0.25 ± 0.04:1.90 ± 0.05§	0.25 $CaCl_2$ 0.75 $Ca(OH)_2$§
0.8	Insufficiently resolved:	
0.9	phase mixtures	

* Value of x in the formula $C_3A{\cdot}(1 - x\ CaCl_2){\cdot}x\ Ca(OH)_2{\cdot}10 + mH_2O$.
† Relative to Al = 1.00.
‡ Only variable part is shown.
§ Inferred from selective analysis of AF_m in mixture.

The solid phase coexisting with these aqueous phases also has been analysed by energy dispersive X-rays. Table 4 summarises the results. The limit of stable AF_m-type phase formation can be judged in two ways: from the appearance of its characteristic breakdown products and/or higher-hydrated AF_m phase, or by actual analyses of the crystals. Judged from the appearance of a second solid phase, the limit probably lies in the range between FS contents 30–40 mol %; at lower values the solid solutions show increasing tendency to break down. Nevertheless, analysis disclosed that Friedel's salt-like AF_m solid solutions at FS = 25% persisted in mixtures with C_3AH_6, etc., so that the lowest value stable at 20°C is tentatively taken as 25 ± 5 mol % FS.

Composition of the solid solution at these points is shown in Table 4. Tie lines connecting the compositions of coexisting solid and aqueous phases are shown in Figure 4. The tie lines form a self-consistent data set inasmuch as tie lines lie subparallel to each other and do not cross. With increasing aqueous chloride content, Friedel's salt becomes essentially chloride saturated at the point marked S in Figure 4. Once saturated, Friedel's salt is no longer able to bind additional Cl^- from the aqueous phase.

However, it remains the equilibrium solid phase up to [Cl] ~ 8M, so that the final tie line, at a nominal value of x = 1.0 ± 0.05, probably results from a solution that is somewhat oversaturated with respect to the minimum chloride content necessary to stabilise essentially pure Friedel's salt.

The disposition of the tie lines and supplementary X-ray data do not themselves reveal positive evidence for the existence of a three-phase region of (hydroxy AF_m, Cl^- AF_m, and aqueous) as would be required if a miscibility gap occurred. Of course, all other supplementary evidence, DTA/TG and FTIR, were assessed, but the FTIR patterns were not distinctive and the DTA/TG patterns were complicated by the effects of changing chemistry. During

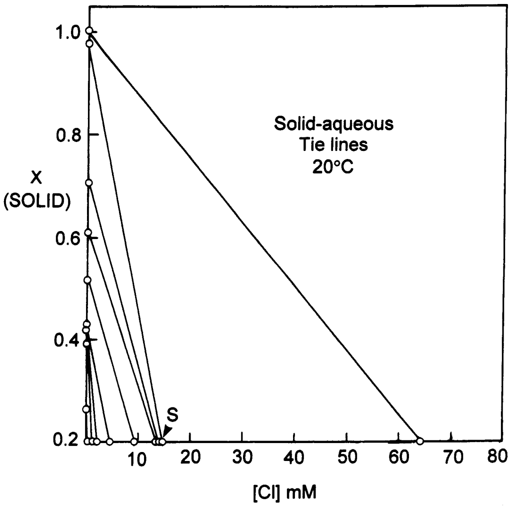

FIG. 4.

Solid–aqueous tie lines at 20 °C. Point S represents the coexistence of saturated Friedel's salt with an aqueous phase.

thermal analysis, water is lost from hydroxy AF_m, whereas Cl, which may replace OH in the precursor, is not lost. Thus, thermal analysis reflects changing chemistry, rather than changes in structure. The powder diffraction patterns do reveal minor discontinuities, but it must be recalled that the changing ionic strength of the aqueous phase, as well as handling and specimen preparation, affect the exact hydration state of the solid AF_m phases as the sample is finally presented to the X-ray beam. As a global conclusion, therefore, gaps in the solid solution may occur but, if so, they are more likely to result from second-order phase changes, e.g., polytypism or stacking disorder, or both, rather than from a first-order phase change. Because we do not identify a significant two-phase gap, we have chosen to present data as a regular solid solution. Ksp values tabulated on this basis are given in Table 5. These values should be used with care. Although dissolution of Friedel's salt is congruent, dissolution of the solid solutions departs increasingly from congruency as their chloride content diminishes. Nevertheless, the tabulation discloses that the solubility and free energy of formation do not change greatly over the range of x values between 0.0 to ~0.6. The value for x (nominal) = 0.0 is regarded as inaccurate, because of the presence of a substantial excess of Cl over the minimum required to stabilise Friedel's salt. The value for x = 0.02 probably represents the "best" value for the saturated solid.

Additional Discussion

Essentially phase pure Friedel's salt appears experimentally to be a stable phase at 20°C over a wide range of aqueous chloride concentrations greater than ~14.5 mM and extending to about 8M. It is not possible to reproduce by calculation numerical values for its upper stability limit or for solid solutions containing both [Cl,OH]. Thermodynamic data bases are

TABLE 5
Solubilities and free energy of formation: Friedel's salt.

Nominal x	Ksp formulation	Log Ksp (observed)	Log Ksp* (calculated)	ΔG (293K) (kJ/mol)
0	$[Ca^{2+}]^4[Al(OH)_{4-}]^2[Cl^-]^2[OH^-]^4$	−23.476	−24.768	−147.1
0.1	$[Ca^{2+}]^4[Al(OH)_{4-}]^{1.96}[Cl^-]^2[OH^-]^{4.04}$	−25.308	−24.662	−147.7
0.2	$[Ca^{2+}]^4[Al(OH)_{4-}]^{1.42}[Cl^-]^2[OH^-]^{4.58}$	−24.487	−24.785	−146
0.3	$[Ca^{2+}]^4[Al(OH)_{4-}]^{1.34}[Cl^-]^2[OH^-]^{4.66}$	−24.467	−24.581	−147.2
0.4	$[Ca^{2+}]^4[Al(OH)_{4-}]^{1.04}[Cl^-]^2[OH^-]^{4.96}$	−24.449	−24.701	−147.7
0.5	$[Ca^{2+}]^4[Al(OH)_{4-}]^{0.88}[Cl^-]^2[OH^-]^{5.12}$	−24.611	−24.799	−147.3
0.6	$[Ca^{2+}]^4[Al(OH)_{4-}]^{0.86}[Cl^-]^2[OH^-]^{5.14}$	−24.768	−24.065	−148.8

* Two data sets are reported. The observed values use measured aqueous pH and are not therefore electrostatically balanced. Calculated values determine $[OH^-]$ from electrostatic balances, but the value thus obtained may cumulate other analytical errors. ΔG is calculated from the electrostatically balanced Ksp values.

not yet able to treat systems in which several phases have variable compositions, although it is possible to calculate the impact of chloride on several related transformations. Data in (17) predict the following equilibrium assemblages (FS = Friedel's salt):

$$AH_3 + C_3AH_6 + CH\text{: stable at } < 9 \text{ mmol kg}^{-1}\text{ Cl}$$

$$AH_3 + C_3AH_6 + CH + FS\text{: stable at 9–11 mmol kg}^{-1}\text{ Cl}$$

$$AH_3 + FS + CH\text{: stable at 11–3285 mmol kg}^{-1}\text{ Cl.}$$

In the present study, C_3AH_6 together with a hydrocalumite-like phase persists up to an aqueous Cl of ~2 mM/1. For all intents and purposes, the two sets of units used in comparisons, molal and molar, are interchangeable at low concentrations. Given the limitations in comparing the two slightly different calculations as well as limitations of presently available computer protocols and data bases, the agreement between calculation and experiment is comfortable.

The results obtained in the present study have similarities and differences to those obtained by Abate and Scheetz (18). They had difficulties excluding carbonate and moreover appear to have encountered alumina as alumina hydrate, AlOOH, rather than as the more stable $Al(OH)_3$ phase, gibbsite.

The presence of other cement hydrates, such as $Ca(OH)_2$ and C-S-H, have little impact on these calculations because they do not significantly alter the aqueous pH and do not themselves interact, except weakly, with aqueous chloride. With this assurance, the impact of environmentally conditioned reactions can be assessed. This is important because chloride does not migrate alone, as occurs for example in NaCl solutions.

It is essential, of course, that a change in chloride regime must not be accompanied by other changes that would destabilise the AF_m, as, for example, if the local pH were to decrease markedly. The main source of ions that could potentially destabilise AF_m is likely to result from CO_2 permeation. However, in lightly carbonated cement, the remaining cement phases [$Ca(OH)_2$, C-S-H, etc.] continue to buffer pH so that the AF_m phase remains locally

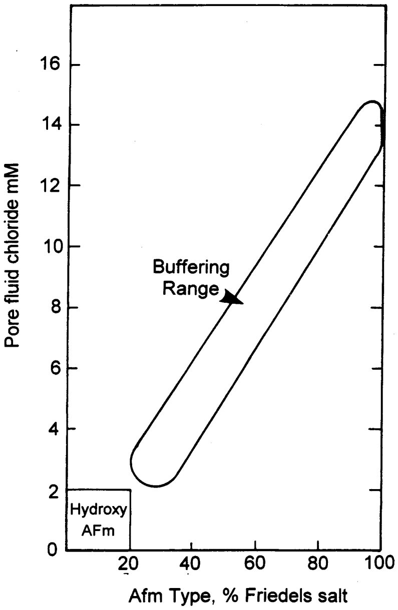

FIG. 5.
Schematic diagram showing how Friedel's salt buffers aqueous chloride ion concentrations. The width of the loop represents approximate analytic uncertainties.

stable and can continue to adjust its composition so as to uptake and bind chloride ions. Chloride, diffusing as NaCl, reacts so as to elevate pH, exchange of Cl for OH leaving Na effectively as NaOH. Thus, pH need not decline as a consequence of diffusive reactions. However, in the range of concentrations between 2 and 14.5 mM, the gain in pH attending removal of Cl, leaving Na effectively as NaOH, would be minor. These rather qualitative calculations find broad support from field evidence that Friedel's salt persists in a range of chloride-containing environments.

Thus, chloride diffusing into fresh cover concrete can react with the intrinsically chloride-free (or nearly so) $AF_{m.}$ This process may be envisaged with the aid of a semischematic diagram (Fig. 5). As chloride enters the matrix, reaction with aluminates commences at ~2 mM [Cl]. Buffering is provided by the AF_m, which changes in composition in response to rising chloride levels. The buffering is essentially exhausted above ~14.5 mM, at which point the AF_m phase is virtually pure Friedel's salt. The logic applied to the role of AF_m may also be applied to other aluminates, which potentially can be converted to Friedel's salt. Real cements may contain sulfate AF_m, or mixtures of sulfate and hydroxy AF_m, together with ettringite. Preliminary calculations by Damidot and Glasser (17) suggest that the numerical value of their thresholds for conversion to Friedel's salt, as given previously for hydroxy AF_m, will not be much affected by the presence of sulfate as an additional component. Thus, sulfate ettringite, AF_t, will also be destabilised and converted to Friedel's salt in about the same compositional range of aqueous chloride contents as hydroxy AF_m, and the "sink" available for chloride uptake must also include ettringite. This probably explains why previous attempts to relate chloride uptake with cement AF_m contents have given poor correlations: hydroxy AF_m, sulfate AF_m, ettringite, and, if present, hydrogarnet, C_3AH_6, all react with chloride in about the same concentration range. Wakeley and Roy (19) noted the ubiquitous formation of Friedel's salt in cement—fly-ash blends cured in NaCl brines; the Friedel's salt coexisted with "woodfordite," an ettringite containing SO_4, SiO_4 and CO_3 anions.

Calculation of the total buffering capacity, in terms of moles of chloride per volume of concrete, is an important durability-related engineering parameter. It is suggested that Friedel's salt formation will be limited by the total available Al content of the cement, rather than by the AF_m content alone, because all aluminate hydrates will convert in a similar concentration range to Friedel's salt. However, the extent to which Al, bound into clinker ferrite, can participate in Friedel's salt formation is uncertain. These factors will be explored in subsequent papers.

Acknowledgment

This paper is taken from the Ph.D. thesis of Dr. Birnin-Yauri (20), who acknowledges the Usmanu Danfodiyo University, Sokoto, Nigeria, for leave of absence and the Scholarship Board of Kebbi State Nigeria for financial support.

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