Stability and solubility relationships in AFm phases
Part I. Chloride, sulfate and hydroxide

F.P. Glasser *, A. Kindness, S.A. Stronach
University of Aberdeen, Department of Chemistry, Meston Walk, Old Aberdeen AB24 3UE, Scotland
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Abstract

Portland cements contain an AFm phase whose anion content is initially dominated by OH\(^-\) (hydroxy) and SO\(_4^{2-}\) (sulfate); variants such as those based on C\(_2\)ASH\(_4\) may occur in blended cements. In service conditions AFm phases may exhibit anion exchange, principally with carbonate, chloride, and additional sulfate. The chemistry, stability, and crystal chemistry of AFm phases are reviewed briefly. New data are presented on the role of 3CaOAl\(_2\)O\(_3\)·0.5CaCl\(_2\)·0.5CaSO\(_4\)·10H\(_2\)O, which, it is proposed, should be named Kuzel’s salt after its discoverer. © 1999 Elsevier Science Ltd. All rights reserved.

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The AFm phase occurring in Portland cements and blended Portland cements is chemically and mineralogically complex. Its layer structure incorporates variable amounts of water as well as geochemically abundant anions such as hydroxyl, carbonate, sulfate, and silicate. Fig. 1 depicts some of these familial relationships. Arrows indicate directions of increased component activity that, at the pH of ordinary portland and blended portland cements (typically 12–13), favour particular AFm types. Since Fe substitution for Al is comparatively limited in ordinary Portland cement, the studies reported here concern the iron-free phases only.

Previous studies, often of an empirical nature, disclose that the constitution of the AFm phase(s) are very sensitive to the cement composition as well as to chemical changes induced by reaction of the cement solid-pore water system with its service environment. These reactions may have important practical consequences to concrete durability: for example, the AFm phase is believed to be an important “sink” for chloride ions, migration of which into concrete is known to accelerate corrosion of embedded steel.

Experimental work on AFm phases is handicapped by three factors: (1) difficulties of preventing progressive carbonation and in controlling the activity, \(a\), of CO\(_2\); (2) phase characterisation; and (3) stabilising the water content during characterisation, particularly of higher hydrates. For example, C\(_4\)AH\(_19\) is likely to lose water during the course of powder X-ray diffraction and a lower hydrate, or mixture of hydrates, is often identified.

All CAH\(_x\) phases are thermodynamically metastable with respect to a mixture of C\(_2\)AH\(_6\) and AH\(_3\), so mixtures with the latter two solids are frequently encountered. Anion substitution may partially stabilise CAH\(_x\) phases (e.g., in sulfate-containing AFm), which is stable at >40°C, or it may provide absolute thermodynamic stabilisation, as occurs in chloride-containing AFm phases. Friedel’s salt is an example. Energetics will be discussed subsequently.

The present study concentrates on four AFm types, containing OH\(^-\), Cl\(^-\), CO\(_3^{2-}\), and SO\(_4^{2-}\). Fig. 2 serves to reference much of the previous literature on the characterisation and stability of the AFm phases.

The literature seems to be in agreement that approximately half the sulfate content of AFm can be substituted by OH\(^-\), giving as anion contents OH · 0.5SO\(_4\). However, opinion divides as to the existence of “hemisulfate” as a distinct compound rather than as a solid solution. The extent of mutual solid solution is reported to decrease sharply with rising temperature. This unusual state of affairs suggests the possibility that the extensive or perhaps complete solid solutions between hydroxy and sulfate AFm reported at ~20°C are labile, although persistent.

There is disagreement concerning the extent of solid solution between hydroxy AFm and Friedel’s salt. See the discussion section.

We also propose that the AFm-structured compound containing ordered chloride and sulfate anions, 3CaO · Al\(_2\)O\(_3\) · 0.5CaCl\(_2\) · 0.5CaSO\(_4\) · 10H\(_2\)O, be termed Kuzel’s salt after its discoverer.
1. Synthesis

Mixtures were prepared from “AnalaR” reagent grade materials. As a first step, CaCO$_3$ and Al$_2$O$_3$ were heated in a Pt crucible to form phase-pure Ca$_3$Al$_2$O$_6$; lime (CaO) was prepared from CaCO$_3$. For other syntheses CaCl$_2$ (both dihydrate and hexahydrate were used), CaSO$_4$ · 2H$_2$O, and CaCO$_3$ were dried and mixed as appropriate. All preparations were made in a CO$_2$-free aqueous phase using double distilled, decarbonated water, handled in N$_2$ atmosphere, and carefully sealed to minimise CO$_2$ uptake during curing.

Friedel’s salt was made by mixing C$_3$A and CaCl$_2$ · 2H$_2$O to a water:solid (w:s) ratio of ~10 and sealed into a plastic bottle for 30 days at 25°C with daily agitation of the contents. Calcium monosulfoaluminate (formed from C$_3$A and ettringite) was prepared by a similar procedure, preferably at 5°C. Other preparations were made according to standard methods detailed in the literature. Phase relations were determined in several ways. For example, a particular composition could be achieved by:

- Mixing two end-member single phases and awaiting reaction, if any.
- Mixing appropriate reactants of appropriate chemistry but not including an AF$_m$-structured phase among the reactants (e.g., by mixing C$_3$A and CaCl$_2$ · 2H$_2$O with ettringite), potentially to form sulfate-chloride AFm compositions.

The progress of reaction in several combinations was monitored at intervals between 9 and 36 months. Phase characterisation was done by a combination of bulk analysis, electron microscopy with analysis, powder X-ray diffraction, and differential Thermal analysis (DTA) with simultaneous thermogravimetric analysis (TG) and its differential (DTG).

2. Kuzel’s salt: Preparation and stability

2.1. Preparation

3CaO · Al$_2$O$_3$ · 0.5CaCl$_2$ · 0.5CaCl$_2$ · 0.5CaSO$_4$ · 10H$_2$O could be made in two ways: by mixing previously prepared sulfate AFm with Friedel’s salt and allowing an aqueous suspension (w/s ~ 10) to react for several months at 25°C or by using C$_3$A · CaCl$_2$ · 10H$_2$O and CaSO$_4$ · 2H$_2$O as reactants. In a typical preparation, C$_3$A was first made by heating repeatedly a 3:1 molar mixture of “AnalaR” grade CaCO$_3$ and Al$_2$O$_3$, contained in a Petri dish, to ~1400°C until X-ray diffraction and a Franke test disclosed that free CaO and Ca(OH)$_2$ were virtually absent. 8.106 g of the C$_3$A product was mixed with 3.286 g of CaCl$_2$ · 6H$_2$O and 2.581...
g of CaSO$_4$ $\cdot$ 2H$_2$O. The resulting solid mixture was dispersed in 450 mL of double distilled, decarbonated water under a N$_2$ atmosphere and allowed to stand with intermittent agitation for several months at $\sim$20–25°C. The product was essentially phase pure after $\sim$3 months and has remained unchanged in contact with aqueous phase for $\sim$3 years. Phase purity was determined by optical and electron microscopy and by powder X-ray diffraction. The preparation contained a high yield of crystallites with a flat, platy morphology, having well-developed hexagonal or pseudohexagonal outlines, of approximately 20 $\mu$m maximum diameter.

2.2. Solubility

A portion of the solid was collected by filtration and re-equilibrated for 2–7 days with a minimum volume of distilled, decarbonated water. This process was repeated three times. Table 1 records the results. The dissolution of Kuzel’s salt into initially pure water is markedly incongruent and by the third redispersion, the X-ray diffraction pattern of the solid disclosed the presence of ettringite. The first redispersion is therefore regarded as giving the best value for the solubility of Kuzel’s salt; these data are shown in bold in Table 1.

3. Stability and stoichiometry of sulfate-chloride AF$_m$ phases

The stability of Kuzel’s salt relative to mixtures of sulfate-AF$_m$ and Friedel’s salt is considered to be proven because the two AF$_m$ end members, mixed in the 1:1 ratio, react to yield Kuzel’s salt. The product crystals have a morphology that differs significantly from those of the reactants, so reaction probably occurs by dissolution with precipitation. Mixtures not at the 1:1 ratio of sulfate AF$_m$ and Friedel’s salt yield Kuzel’s salt with an excess of the appropriate reactant, either Friedel’s salt or sulfate AF$_m$. However, among those mixtures of two AF$_m$ phases that depart from 1:1 stoichiometry, it is noteworthy that the X-ray intensities of the excess of reactant diminish with reaction time while those due to Kuzel’s salt increase in intensity. This is consistent with formation of three restricted ranges of solid solution based on Friedel’s salt, Kuzel’s salt, and sulfate AF$_m$. Thus Kuzel’s salt is probably somewhat soluble in binary combination with either Friedel’s salt or sulfate-AF$_m$. The methods used do not permit the extent of solid solution to be measured accurately, but it is estimated to be on the order of $\sim$5 mol% of either Friedel’s salt or sul-

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fate AF<sub>m</sub> in Kuzel’s salt, but perhaps between 5 and 10 mol% sulfate AF<sub>m</sub> in Friedel’s salt and vice versa. The system is thus marked by ordering as well as the formation of three ranges of solid solution.

3.1. Friedel’s salt and hydroxy AF<sub>m</sub> phase relations on selected joins

The various investigations into the extent of solid solution in AF<sub>m</sub> phases on this join do not agree as to the extent of miscibility [1–14]: the key to Fig. 2 gives supporting references. The extent of solid solution is partly a matter of interpretation of the X-ray powder data. Friedel’s salt gives a good, unequivocal X-ray powder diffraction pattern, whereas patterns from preparations containing hydroxy-AF<sub>m</sub> are complicated by the occurrence of aluminate solid solutions in several discrete hydration states (e.g., C<sub>4</sub>AH<sub>13</sub>, C<sub>4</sub>AH<sub>19</sub>) as well as by partial breakdown of C<sub>4</sub>AH<sub>x</sub> phases to the more stable solids, C<sub>3</sub>AH<sub>6</sub> and AH<sub>3</sub>. Even if the breakdown products are not included in the assessment, hydroxy AF<sub>m</sub> phases are frequently somewhat disordered and, on that account, give poor quality powder patterns. This leaves investigators the difficult task of deconvoluting these effects, as well as assessing the impact of Cl<sup>−</sup> for OH<sup>−</sup> substitution. Birnin-Yauri [12] examined this join and concluded that solid solution between C<sub>4</sub>AH<sub>13</sub> and Friedel’s salt was essentially complete although changes in stacking modification and hydration state occurred as the Cl/OH ratio of the solid changed, with concomitant abrupt changes to the powder pattern.

3.2. Hydroxy AF<sub>m</sub> and sulfate AF<sub>m</sub>

Sulfate AF<sub>m</sub> is reported to form extensive solid solutions with hydroxy AF<sub>m</sub>, extending to ∼50% of the latter; perhaps more. In this study compositions were prepared on the hydroxy AF<sub>m</sub>-sulfate AF<sub>m</sub> join at the following mole percentages of C<sub>4</sub>AH<sub>13</sub>: 12.5, 25, 37.5, 50, 62.5, and 87.5%. These compositions were duplicated by (1) mechanical mixing of C<sub>4</sub>AH<sub>13</sub> and sulfate AF<sub>m</sub> and (2) mixing appropriate quantities of C<sub>3</sub>A, Ca(OH)<sub>2</sub> and CaSO<sub>4</sub> ⋅ 2H<sub>2</sub>O.

After equilibration for 9 months at ∼5°C, the preparations were subject to analytical electron microscopy. Typically, 50 crystals were analysed from each preparation and histograms were plotted of the sulfate content. Fig. 3 combines six sets of analytical data with one population cluster in the range 0–20 mol% sulfate and another in the range 45–90 mol% sulfate. Of the 350 point analyses only 18 fell in the range 20–45 mol% sulfate and 18 in the range ≥90 mol% sulfate. These results are interpreted as indicating considerable, but incomplete, solid solution between hydroxy- and sulfate-AF<sub>m</sub> end members: the hydroxy AF<sub>m</sub> phase has a mean composition ∼6 mol% sulfate while the sulfate AF<sub>m</sub> has a mean composition ∼75–90 mol% sulfate. However, the spread of values indicates that although a miscibility gap probably exists it is not sharp and well-defined. Either equilibrium has not been attained despite a 9-month reaction period, or mixed intergrowths occur between OH- and SO<sub>4</sub>-AF<sub>m</sub> types, or both. It is also possible, but not proven, that the extensive solid solution encountered in the title study at ∼5°C is metastable.

3.3. Monocarboaluminate-hemicarboaluminate stabilities

Considerable confusion exists in the literature concerning the conditions for the existence of these phases. Damidot et al. [5] calculated phase relations in the CaO-Al<sub>2</sub>O<sub>3</sub>-CaCO<sub>3</sub>-H<sub>2</sub>O system and found both the hemicarboaluminate phases had definite ranges of stability. Moreover, the observed occurrence of these phases in cement containing CaCO<sub>3</sub> accords well with calculations: the hemicarboaluminate is stable only over a limited range of CO<sub>2</sub> activities. This range lies below the self-generated activity of CaCO<sub>3</sub> at typical cement pore fluid pHs (approximately 12–13). Thus, of the two carbonate AF<sub>m</sub>s, only monocarboaluminate is stable in contact with calcite, CaCO<sub>3</sub>. Given the difficulty of excluding CO<sub>2</sub> so that CaCO<sub>3</sub> does not crystallise, it is not surprising that the hemicarboaluminate is infrequently observed in “real” systems. Its rather small range of stability at 5–25°C with respect to PCO<sub>2</sub> creates experimental difficulties in studying its coexistence with other AF<sub>m</sub> phases.

Fig. 3. Cumulative histogram showing analyses of crystals by electron microprobe for sulfur content. The data were compiled from laboratory preparations at 12.5–87.5 mol% sulfate AF<sub>m</sub> after isothermal equilibration at 5°C for 9 months.
3.4. $AF_m$ phases with $OH^-$, $Cl^-$, $CO_3^{2-}$, and $SO_4^{2-}$ anions

First, we note the presence of incomplete solid solution as well as anion ordering on two $AF_m$ joins, $OH - CO_3$ and $SO_4 - Cl$, marked by formation of hemi-carboaluminate and Kuzel’s salt, respectively. Ordering has not been found to occur along the $OH - SO_4$ join and the join between $CO_3$ and $Cl$ has been so little studied that its phase relations must be regarded as uncertain. The continuous solid solution reported between hemi-carboaluminate and Friedel’s salt must also be regarded as not proven and the occurrence of ordering on the join between hemi-carboaluminate and “hemisulfoaluminate” to form an ordered “hemicarboaluminate” is uncertain.

As a general tendency, extensive or complete solid solution between the anionic contents of $AF_m$ seems to occur between anions of the same charge and shape, whereas only limited solid solution occurs between anions of the same charge but differing in shape (e.g., sulfate and carbonate, which are tetrahedral and planar, respectively). Ordering occurs between ions differing in both shape and charge, as between the pairs ($OH - CO_3^{2-}$) and ($Cl - SO_4^{2-}$), although the pair ($OH - SO_4^{2-}$) seems to be an exception. These generalisations might be usefully applied to other $AF_m$ phases that have not yet received much systematic attention: for example, the phase relationships between nitrate $AF_m$ and other more common $AF_m$ anion substituents.

The anionic content of $AF_m$ is very sensitive to the concentration of anions in the pore fluid. For example, it has been shown that $OH-AF_m$ begins to convert to Friedel’s salt when the local concentration of chloride exceeds a few mM and the process is essentially complete by 15 mM [13]. Since the hydration state of $AF_m$ is also affected by the nature of the anion, and since the bulk density of the $AF_m$ phase is affected by its hydration state, changes in $AF_m$ chemistry in response to changing pore fluid chemistry offer further scope for investigation. Some of the expansion occurring when cements are exposed isothermally to salt solutions increases the activity of water and this, in turn, favours higher hydration states of $AF_m$. The incorporation of more water leads to an increase in molar volume of the solid. Thus the specific volume of the $AF_m$ phase is sensitive both to ionic strength of pore fluid and to its anion chemistry.

4. Discussion

From the literature and from experimental studies made on $AF_m$ phases, the following generalisations are made concerning phase stability and limits of solid solution.

• Hydroxy $AF_m$ phases may differ markedly in molecular water contents (e.g., $C_xAH_y$) with $x$ ranging between 13 and 19. Considerable care is required to preserve the higher hydration states during subsequent analysis, particularly if the analytical technique requires the solid to be dried or if drying should occur inadvertently.

• Sulfate $AF_m$ is thermodynamically unstable below $-40°C$, although it does become stable at or above 40°C. However, at approximately 20°C the thermodynamic driving force that stabilises $AF$ relative to $AF_m$ must be very small, with the result that sulfate $AF_m$ is very persistent: The kinetics of its transformation are controlled by this low driving force.

• Just as metastable $AF_m$ phases can occur and persist, metastable $AF_m$ solid solutions can also occur and persist. The solid solution between $OH$ and $SO_4$- $AF_m$ is perhaps the most relevant to cement chemistry. Solid solution between the two is variously reported as complete or extensive. The title study favours extensive, rather than complete, solid solution as the preferred state in preparations allowed to equilibrate for several months or longer at $5°C$. However, it is believed that the extensive solid solutions encountered may actually be metastable with respect to mixtures of hydroxy $AF_m$ and $SO_4$- $AF_m$ both of which are, in turn, metastable with respect to mixtures of ettringite, hydrogarnet, and gibbsite. Thus the apparent extent of solid solution between $OH$ and $SO_4$-$AF_m$ may well be an artefact of the preparation method and cure. It would be interesting to determine if cement clinkers differ in their ability to form ($OH$, $SO_4$) $AF_m$ solid solutions of different compositions during hydration. It is suggested that compositional changes may be related to the rate at which they release sulfate and aluminate.

• Anion exchange in $AF_m$ occurs relatively rapidly requiring days or at most weeks at $20°C$. Thus $AF_m$ phase compositions are sensitive to their local chemical environment.

• $AF_m$ phases with carbonate, chloride, and with ordered chloride and sulfate, including hemi- and monocarboaluminate, Friedel’s salt, and Kuzel’s salt, respectively, all appear to have definite ranges of thermodynamic stability at $20°C$. Solubility data are given for Kuzel’s salt.

• In appropriate environments, hydroxy and sulfate $AF_m$ phases are readily transformed to carbonate, chloride, and chloride-sulfate phases. These processes are driven even by low concentrations of the relevant anions. Deterioration and alteration reactions thus occur in response to a drive towards thermodynamic equilibrium. Since we know the physicochemical outlines of the “windows” of stability of these phases, $AF_m$ chemistry serves as a valuable marker of the changing internal chemistry of cement paste in the course of its interaction with the environment.
• Both anion ordering and disordering occur. Examples of anion ordering include Kuzel’s salt, containing essential SO$_4^{2-}$ and Cl$^-$, or hemicarboaluminate, with CO$_3^{2-}$ and OH. Examples of disordering are also known (e.g., between OH and Cl substituents). Ordering most commonly occurs among anions differing in charge and shape (e.g., OH$^-$ and CO$_3^{2-}$ in monocarboaluminate and Cl$^-$ and SO$_4^{2-}$ in Kuzel’s salt). No ordered OH$^-$-SO$_4^{2-}$ phases has yet been proven to occur.

• We have no direct experimental evidence, but from reported syntheses, occurrences, and analyses, it is probable that silicate and aluminate AF$_m$ types are incompletely miscible. Nevertheless, the ability of OH and sulfate AF$_m$ to incorporate alkalis (i.e., to form limited solid solution with U phase) needs to be determined. On the other hand substitution of sulfate and chloride for OH anions in “C$_2$ASH$_8$” probably occurs. The partition of these anions between aluminate and silicate AF$_m$ phases needs to be determined.

• The U phase, a sodium-containing AF$_m$ phase, has not been included in the scope of the present study. Its general formula and the structural role of sodium are not known with certainty. However, the minimum level of sodium concentration necessary to stabilise the U phase seems to be on the order of 0.2–0.3 M NaOH and thus probably does not exceed intrinsic sodium levels found in the pore fluid of portland cement. Thus it is important to investigate its phase relations with other, arguably better known, AF$_m$ types.

• This paper describes some of the relationships among AF$_m$ phases. The stability of two more phases, the sodium-containing U phase and the silicate AF$_m$ phase, needs to be elucidated with respect to the arguably better known OH, CO$_3^{2-}$, Cl, and SO$_4^{2-}$-containing phases before we can claim fully to understand the mineralogy of the AF$_m$ phase and its implications to cement science.

Acknowledgments

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