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

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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_2ASH_8 may occur in blended cements. In service conditions AF_m phases may exhibit anion exchange, principally with carbonate, chloride, and additional sulfate. The chemistry, stability, and crystal chemistry of AF_m phases are reviewed briefly. New data are presented on the role of $3CaOAl_2O_30.5CaCl_20.5CaSO_410H_2O$, which, it is proposed, should be named Kuzel's salt after its discoverer.

Keywords: AF_m phases; Monosulfoaluminate; Chloride; Solubility; Friedel's salt

The AF_m 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, chloride, 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 AF_m 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 AF_m 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 AF_m 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 AF_m 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_4AH_{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_3AH_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 AF_m), which is stable at >40°C, or it may provide absolute thermodynamic stabilisation, as occurs in chloride-containing AF_m phases. Friedel's salt is an example. Energetics will be discussed subsequently.

The present study concentrates on four AF_m 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 AF_m phases.

The literature seems to be in agreement that approximately half the sulfate content of AF_m can be substituted by OH, giving as anion contents $OH \cdot 0.5SO_4$. 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 AF_m reported at ~20°C are labile, although persistent.

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

We also propose that the AFm-structured compound containing ordered chloride and sulfate anions, $3CaO \cdot Al_2O_3 \cdot 0.5CaCl_2 \cdot 0.5CaSO_4 \cdot 10H_2O$, be termed Kuzel's salt after its discoverer.

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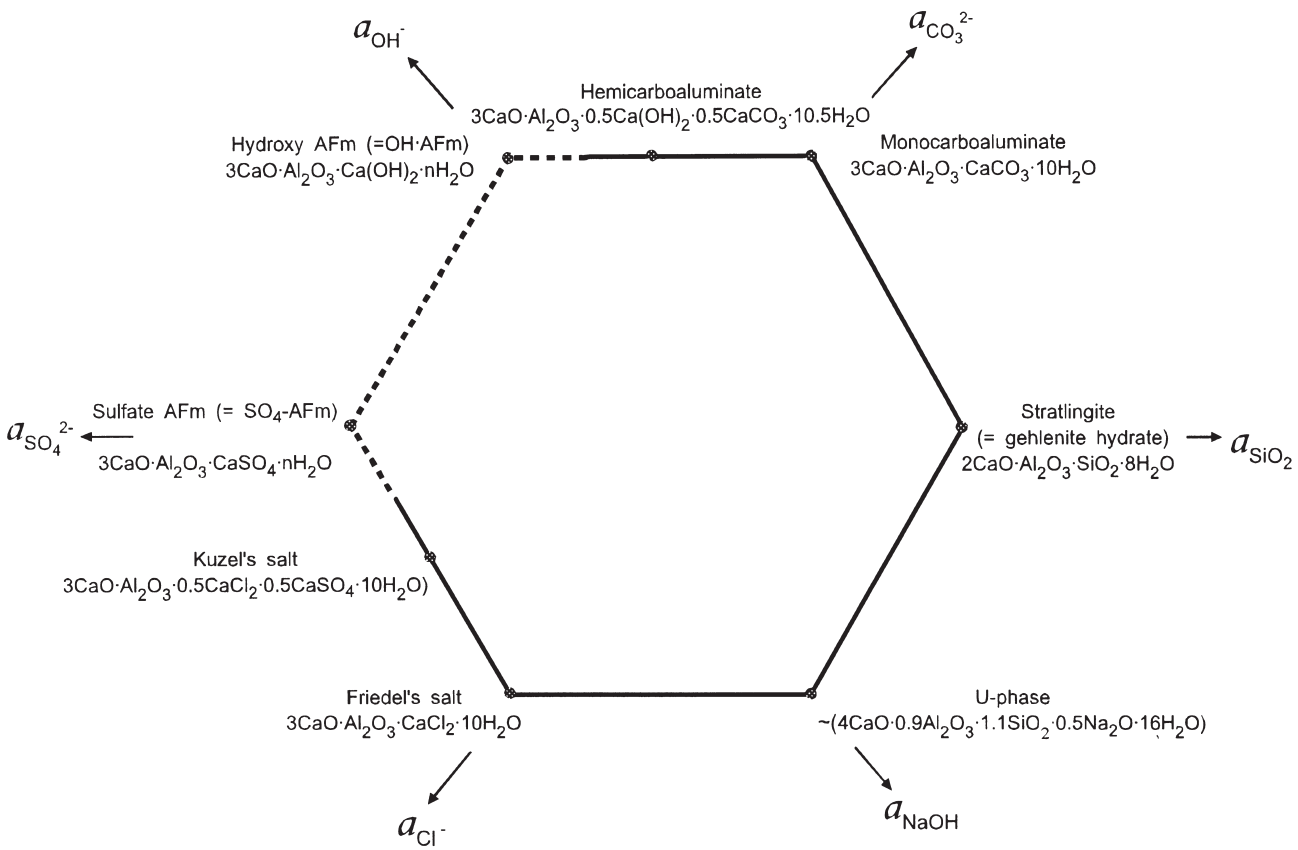

Fig. 1. Composition-activity diagram of the AF_m family at ~25°C. Phase regions believed to be thermodynamically unstable at 25°C are indicated by dashed lines. Solid dots indicate single-phase formation. Solid solutions between phases are not shown.

1. Synthesis

Mixtures were prepared from "AnalaR" reagent grade materials. As a first step, $CaCO_3$ and Al_2O_3 were heated in a Pt crucible to form phase-pure $Ca_3Al_2O_6$; lime (CaO) was prepared from $CaCO_3$. For other syntheses $CaCl_2$ (both dihydrate and hexahydrate were used), $CaSO_4 \cdot 2H_2O$, 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_3A and $CaCl_2 \cdot 2H_2O$ to a water:solid (w:s) ratio of ~10 and sealed into a plastic bottle for 30 days at ~20°C with daily agitation of the contents. Calcium monosulfoaluminate (formed from C_3A 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 different 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_3A and $CaCl_2 \cdot 2H_2O$ 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

$3CaO \cdot Al_2O_3 \cdot 0.5CaCl_2 \cdot 0.5CaCl_2 \cdot 0.5CaSO_4 \cdot 10H_2O$ 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 $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $CaSO_4 \cdot 2H_2O$ as reactants. In a typical preparation, C_3A was first made by heating repeatedly a 3:1 molar mixture of "AnalaR" grade $CaCO_3$ and Al_2O_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_3A product was mixed with 3.286 g of $CaCl_2 \cdot 6H_2O$ and 2.581

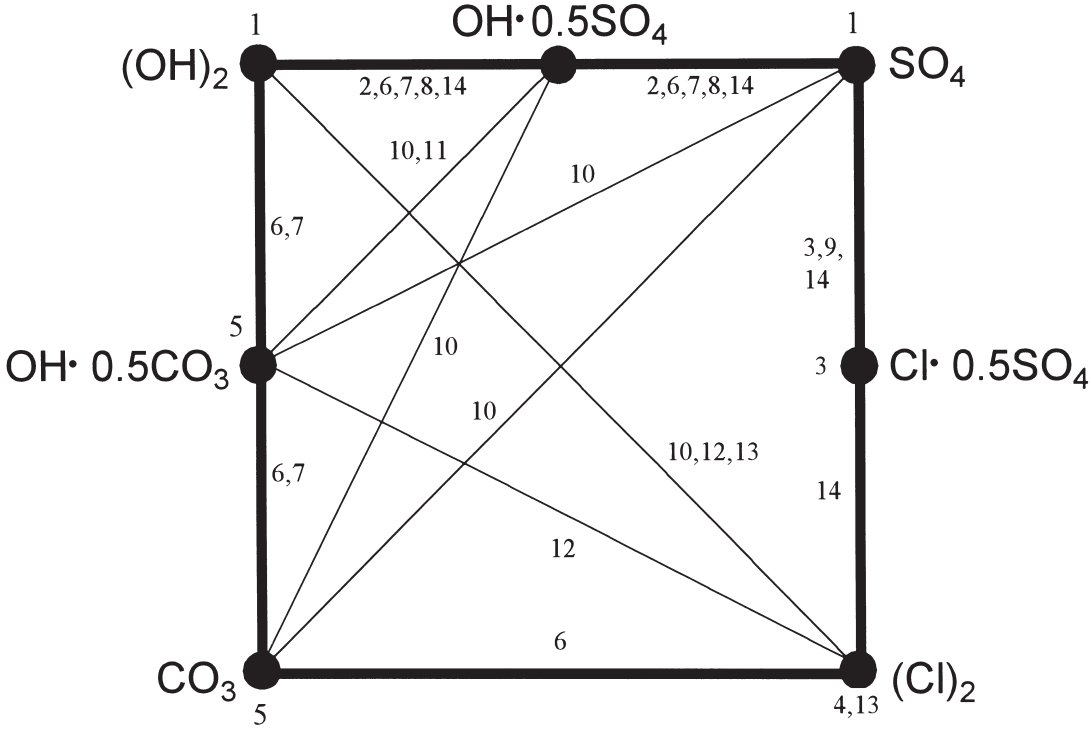

Fig. 2. AF_m compositions showing the principle anion types encountered in cement. Joins of interest are shown by straight lines. Smaller numbers indicate references to previous studies (see reference list and text for discussion).

g of $CaSO_4 \cdot 2H_2O$. 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 ~20–25°C. The product was essentially phase pure after ~3 months and has remained unchanged in contact with aqueous phase for ~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 μm maximum diameter.

2.2. Solubility

A portion of the solid was collected by filtration and reequilibrated 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.

Table 1
Solubility of Kuzel's salt

	Dispersion number		
Concentration, mM	First	Second	Third
Ca	**7.730**	6.710	2.360
Al	**4.610**	3.310	1.880
Cl	**3.960**	3.130	2.300
SO_4	**0.007**	0.002	0.010
pH	**12.20**	12.10	11.90

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 ~5 mol% of either Friedel's salt or sul-

fate AF_m in Kuzel's salt, but perhaps between 5 and 10 mol% sulfate AF_m 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_m phase relations on selected joins

The various investigations into the extent of solid solution in AF_m 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_m are complicated by the occurrence of aluminate solid solutions in several discrete hydration states (e.g., C_4AH_{13}, C_4AH_{19}) as well as by partial breakdown of C_4AH_x phases to the more stable solids, C_3AH_6 and AH_3. Even if the breakdown products are not included in the assessment, hydroxy AF_m 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^- for OH^- substitution. Birnin-Yauri [12] examined this join and concluded that solid solution between C_4AH_{13} 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_m and sulfate AF_m

Sulfate AF_m is reported to form extensive solid solutions with hydroxy AF_m, extending to ~50% of the latter; perhaps more. In this study compositions were prepared on the hydroxy AF_m-sulfate AF_m join at the following mole percentages of C_4AH_{13}: 12.5, 25, 37.5, 50, 62.5, and 87.5%. These compositions were duplicated by (1) mechanical mixing of C_4AH_{13} and sulfate AF_m and (2) mixing appropriate quantities of C_3A, $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$.

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_m end members: the hydroxy AF_m phase has a mean composition ~6 mol% sulfate while the sulfate AF_m 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_4-AF_m 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_2O_3-$CaCO_3$-H_2O system and found both the hemi- and monocarboaluminate phases had definite ranges of stability. Moreover, the observed occurrence of these phases in cement containing $CaCO_3$ accords well with calculations: the hemicarboaluminate is stable only over a limited range of CO_2 activities. This range lies below the self-generated activity of $CaCO_3$ at typical cement pore fluid pHs (approximately 12–13). Thus, of the two carbonate AF_ms, only monocarboaluminate is stable in contact with calcite, $CaCO_3$. Given the difficulty of excluding CO_2 so that $CaCO_3$ 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_2 creates experimental difficulties in studying its coexistence with other AF_m phases.

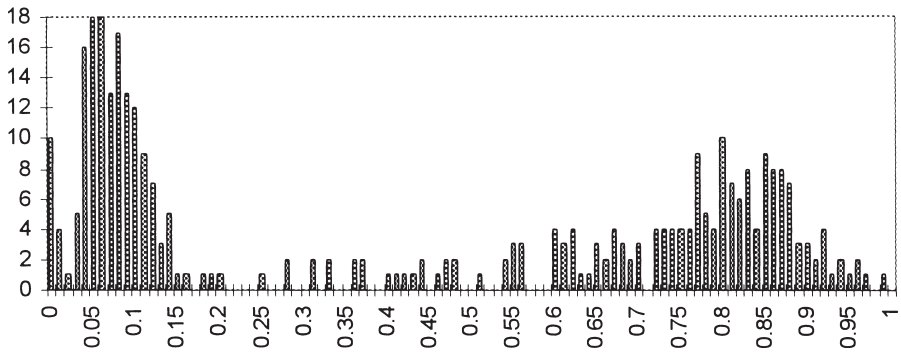

Fig. 3. Cumulative histogram showing analyses of crystals by electron microprobe for sulfur content. The data were compiled from laboratory preparations at 12.5–87.5 mol% sulfate AF_m after isothermal equilibration at 5°C for 9 months.

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 hemicarboaluminate and Friedel's salt must also be regarded as not proven and the occurrence of ordering on the join between hemicarboaluminate and "hemisulfoaluminate" to form an ordered "hemicarbosulfoaluminate" is uncertain.

As a general tendency, extensive or compete 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 ($OH^- \ldots CO_3^{2-}$) and ($Cl^- \ldots SO_4^{2-}$), although the pair ($OH^- \ldots SO_4^{2-}$) 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 be 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 of changing ionic strength could be related to changes in the water content of the AF_m phase. In particular, decreasing the ionic strength of 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 are thermodynamically metastable with respect to phase mixtures of C_3AH_6 + AH_3. Mixtures of solids are frequently encountered. Kinetically, the synthesis conditions most favourable for the metastable formation and preservation of hydroxy-AF_m phases are to keep temperatures low, for example ~5°C.
- Hydroxide AF_m phases may differ markedly in molecular water contents (e.g., C_4AH_x) 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 ~0–40°C, although it does became stable at or above 40°C. However, at approximately 20°C the thermodynamic driving force that stabilises AF_t 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 that 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 rates 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 thermodynamically 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 and Cl, or hemicarboaluminate, with CO_3 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_2ASH_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, Cl, and SO_4-containing phases before we can claim fully to understand the mineralogy of the AF_m phase and its implications to cement science.

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