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The AFm phase in Portland cement

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Abstract

The AFm phase of Portland cements refers to a family of hydrated calcium aluminates based on the hydrocalumite-like structure of $4CaO{\cdot}Al_2O_3{\cdot}13\text{–}19\ H_2O$. However OH^- may be replaced by SO_4^{2-} and CO_3^{2-}. Except for limited replacement (50 mol%, maximum) of sulfate by hydroxide, these compositions do not form solid solutions and, from the mineralogical standpoint, behave as separate phases. Therefore many hydrated cements will contain mixtures of AFm phases. AFm phases have been made from precursors and experimentally-determined phase relationships are depicted at 25 °C. Solubility data are reported and thermodynamic data are derived. The 25 °C stability of AFm phases is much affected by the nature of the anion: carbonate stabilises AFm and displaces OH and SO_4 at species activities commonly encountered in cement systems. However in the presence of portlandite, and as carbonate displaces sulfate in AFm, the reaction results in changes in the amount of both portlandite and ettringite: specimen calculations are presented to quantify these changes. The scheme of phase balances enables calculation of the mineralogical balances of a hydrated cement paste with greater accuracy than hitherto practicable.

Keywords: AFm; AFt; Sulfate; Phase composition; Thermodynamics

1. Introduction

AFm is shorthand for a family of hydrated calcium aluminate phases structurally related to hydrocalumite and occurring mainly in hydrated cement paste. A representative formula is $[Ca_2(Al,Fe)(OH)_6]{\cdot}X{\cdot}xH_2O$ where X equals an exchangeable singly charged (e.g. chloride) or half of a doubly charged anion (e.g. sulfate, carbonate and aluminosilicate). Some Fe(III) may also substitute for aluminium.

The basic structure of "AFm" has been determined and recently refined for several subtypes [1–5]. It consists of sheets of $M(OH)_6$ octahedral ions, like those in brucite or portlandite but with one third of the M^{2+} ions replaced by a trivalent ion, mainly Al with minor Fe. The resulting charge imbalance gives the layers a net positive charge with the result that the interlayer spacing is much greater than in brucite or portlandite owing to the need to intercalate charge-balancing anions. The low reticular density of charge-balancing anions also allows space for additional water molecules. It would appear that the anion contents are sensitive to both cement compositions and cement service environment. Thus in Portland cement, the anions in AFm are hydroxide, sulfate and carbonate while in blended cement, e.g., slag cement, the characteristic anion is an aluminosilicate species. In service, chloride often displaces other anions. The content of AFm phase in hydrated pastes is variable but in many slag-blended cements it may exceed 20%.

With increased interest in the quantification of the phases in a hydrated paste, the AFm phase has proven a difficult subject for analysis both because of its low crystallinity, polytypism and because of variations in composition with corresponding changes to the position and intensity of reflections in its diffraction patterns. Therefore we have begun a systematic reexamination of the synthesis, stability and compositions of AFm phase. This paper presents data on the iron-free phases. Chloride is not normally present in fresh pastes and is omitted, except as noted, from the present study.

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1.1. Stability of the AFm phases

The absolute stability of selected AFm compositions is described in Table 1. The table needs to be used in conjunction with supplementary information. For example, cements normally contribute a high hydroxyl content to the mix water so OH^- is invariably present at high concentrations. Most modern cements contain sulfate, added as calcium sulfate, to control set times. But in the cement environment sulfate is sparingly soluble and carbonate even less soluble at high pH. Hence these species, carbonate and sulfate, have low aqueous concentrations.

Carbonate sources include (i) alkali "sulfates" condensed onto clinker in the course of cooling or from added clinker kiln dust; these "sulfates" are in fact solid solutions with carbonate partly replacing sulfate [6] (ii) carbonates gained by reaction with the atmosphere (iii) carbonate added as a permitted extender, normally in the form of interground calcite and (iv) carbonate present as impurity in gypsum. Damidot [7] showed that with rising carbonate activity, hydroxy-AFm was replaced, first by hemicarboaluminate and then by monocarboaluminate. As the carbonate content of the AFm solid increased stepwise, its stability at 25 °C also increased.

This pattern of stability means that, in addition to taking into account the bulk chemistry of cements, we must also note that some AFm compositions are metastable under all conditions and are prone to decomposition or reaction while others have a definite range of stability under conditions relevant to the internal environment achieved in commercial cements. The impact of small amounts of carbonate on the nature and stability of the AFm phase is noteworthy; Table 2 shows selected composition data for AFm phases, from which it can been seen that ideal hemicarboaluminate and monocarboaluminate contain only 3.9 and 7.7 wt.-% CO_2 respectively.

1.2. Solid solution between AFm phases

The literature reveals considerable divergence of interpretation concerning the existence and extent of solid solution between OH and SO_4-AFm phases, arguably the most important pair with respect to the constitution of fresh, carbonate-free Portland cements. Jones [13], D'Ans and Eick [14], Turriziani [15] and Kalousek [16] reported complete solid solution; Roberts [17], Seligmann [18], Poellmann [19] and Glasser [20] found only partial miscibility while Zhang [21] found no solid solution in aged samples.

Amongst those claiming complete solid solution, the evidence is sometimes equivocal. For example, Turriziani [15] based the conclusion that solid solution was complete on optical data, ignoring his own X-ray data which clearly show a miscibility gap. On the other hand, Zhang [21] examined samples after prolonged ageing and suggested that initially formed solid solutions were probably unstable: "In the sulfate-solid solution series, the enrichment of SO_4 in hydrocalumite is likely achieved by disproportionating the initially formed complete solid solution into the OH- and SO_4-rich phases." Since the aqueous solubility was measured at intervals, and was still declining at the end of the experiments, it was considered possible that solid solutions might have formed during the early stages of reaction but were not present at the conclusion, the only point in time at which samples were subject to X-ray examination. For present purposes we accept that solid solutions (OH^-, SO_4^{2-}) form, although incomplete, and are of sufficient persistence in our experiments, up to one year, as to warrant inclusion in a hydration model.

We also note the presence in AFm systems of at least two ordered phases. One, hemicarboaluminate, has already been noted. The other, Kuzel's salt, is an ordered phase, 1:1 with respect to the composition and structural positions of sulfate and chloride [20]. However chloride phases are not discussed here and its role will not be elucidated. But it is worth noting that systems which permit formation of anion-ordered AFm compounds must be independent compounds and hence have structures that differ sufficiently to preclude formation of complete solid solutions.

2. Experimental

To succeed in the synthesis of AFm phases, several precursors are needed. A desirable precursor is tricalcium aluminate, C_3A ($Ca_3Al_2O_6$). C_3A was prepared from a 3:1 molar ratio of $CaCO_3$ and Al_2O_3. All chemicals were analytical grade reagents. Lime, CaO, was obtained from decarbonation of analytical grade $CaCO_3$ at 900 °C for ~12 h. Anhydrite, $CaSO_4$, was used as sulfate source in the experiments. It was prepared by dehydration of gypsum in a muffle furnace at 750 °C for 5 h.

Table 1
Thermodynamic stabilities of selected AFm phases at 25 °C

Distinctive anion	Formulae	Designation	Stability at 25 °C and 1 bar	Reference
OH^-, hydroxyl	$C_3A{\cdot}Ca(OH)_2{\cdot}xH_2O$	Hydroxy-AFm	Unstable — decomposes to hydrogarnet C_3AH_6, and portlandite	[8]
OH^-; CO_3^{2-}	$C_3A{\cdot}Ca[(OH)(CO_3)_{0.5}]{\cdot}xH_2O$	Hemicarboaluminate	Stable — but not many thermodynamic data available	[7]
CO_3	$C_3A{\cdot}CaCO_3{\cdot}xH_2O$	Monocarboaluminate	Stable	[7]
SO_4^{2-}	$C_3A{\cdot}CaSO_4{\cdot}xH_2O$	Monosulfoaluminate	Calculated to be stable but only above 40 °C — at lower temperatures decomposition to AFt, C_3AH_6 and gibbsite possible	[10]
$[AlSi(OH)_8]^-$	C_2ASH_8	Gehlenite hydrate, strätlingite	Stable	[11]
Cl^-	$C_3A{\cdot}CaCl_2{\cdot}xH_2O$	Friedel' salt	Stable, but not described in this paper. Mainly occurs as an alteration product of cement paste in saline environments	[12]

Table 2
Sulfate- and carbonate-contents of minerals relevant to Portland cement

Mineral	Formula	Carbonate content CO_2 [wt.-%]	Sulfate content SO_3 [wt.-%]
Gypsum	$CaSO_4 \cdot 2H_2O$	–	46.5
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	–	19.1
Monosulfoaluminate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$	–	12.9
Calcite	$CaCO_3$	44.0	–
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12} \cdot 5H_2O$	7.7	–
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13} \cdot 5.5H_2O$	3.9	–

The AFm phases (monosulfoaluminate, monocarboaluminate and C_4AH_x) were prepared by suspending a 1:1 molar mixture of C_3A and either $CaSO_4$, $CaCO_3$ or CaO, respectively, in ultrapure previously degassed water. Monosulfoaluminate was most conveniently prepared in phase-pure form at 85 °C with ultrapure boiling water while the C_4AH_x synthesis was made at 5 °C. Monocarboaluminate was prepared at 25 °C.

The mixtures were stirred for 3–7 days and vacuum filtered under N_2 atmosphere with a Whatman 541 filter paper. The solids were placed in a desiccator and dried over saturated $CaCl_2$ solution at 37% r. h. According to XRD and SEM results the hydration products show the desired AFm phase with satisfactory purity. Some $CaCO_3$ was observed in the monocarboaluminate synthesis. A detailed description of the AFm synthesis will be available shortly on the website www.nanocem.net.

A focus of the current work was to determine if significant solid solution occurred between AFm end members. Phase relations in the following systems were considered as to be the most important for commercial cement systems:

- Monosulfoaluminate–hydroxy-AFm
- Monosulfoaluminate–monocarboaluminate
- Monocarboaluminate–hydroxy-AFm.

Two approaches have been applied to synthesise solid solutions:

i) by mechanical mixing of previously synthesised AFm end members (monosulfoaluminate, C_4AsH_x; monocarboaluminate, C_4AcH_x and hydroxy-AFm, C_4AH_x) [1]
ii) by precipitation from supersaturated solutions, formed by mixing appropriate amounts of previously synthesised C_3A, CaO, $CaSO_4$ or $CaCO_3$, respectively, depending on the desired phase or phase assemblage.

Approach i) was used to clarify whether reaction occurs, i.e. solid solution formation occurred spontaneously between the AFm phases; also, where reaction was complete, to derive solubility data. Approach ii) was applied to solubility determinations and derivation of thermodynamic data and to conduct experiments on the extent of solid solution formation between AFm phases. Additional solubility data commencing from undersaturation were obtained by redissolving the reaction products obtained from the mixed end member method as other preparation methods resulted in slight carbonate contamination.

The AFm solid-solution experiments were made at 25 °C. Water:solid ratios were restricted to <30 to reduce errors induced by incongruent dissolution. Solid and aqueous phases were analysed and prepared according to the procedure for pure AFm end members as described above. Care was taken to prevent access of CO_2. Aqueous calcium and aluminium concentrations were determined by AAS using a VARIAN SPECTRAA 10 flame AAS. A nitrous oxide/acetylene flame was used for atomising the elements. Sulfate was analysed by ion chromatography with a Dionex DX-120 IC. An ion exchange analytical column, IONPAC AS 4A, 4 mm, equipped with a guard column was fitted for sulfate analysis. The analyte was injected into a 25 µl sample loop. The applied pressure was set between 1000–1100 psi (67–74 bars). The eluent used was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$; eluent conductivity was suppressed by an ASRS Ultra self-regenerating suppressor with deionised water (>18 MΩ cm) regenerant. The pH was measured with a glass electrode suitable for high pH. The obtained solids were investigated after drying in a desiccator over saturated $CaCl_2$-solutions at 25 °C and ~37% relative humidity (r.h.). An environmental scanning electron microscope (ESEM) FEI XL 30 equipped with field emission gun was used to image reaction product morphologies. Mineralogical examination of the dried solid was made by X-ray diffractometry (XRD) using Cu–Kα/radiation; the angular scan was between 5–50° 2θ with a step size of 0.02 and a count time of 2 s per step.

2.1. Thermodynamic modelling

The process of thermodynamic modelling consists of calculating the energetics, defined in terms of the Gibbs free energy of a specified system. To undertake modelling requires a database of thermodynamic properties of substances, a formal statement of the problem and a routine or algorithm for the calculations. Numerous algorithms exist: we used either PHREEQCi or GEMS. Their general workings are described in Refs. [22] and [23] respectively. The database associated with the calculation permits special inputs: not all cement minerals are included in standard databases. For example the database associated with GEMS is described in Ref. [24] but supplementary data were required, some of which were generated in the course of the present study; these are given in Table 3. The

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[1] s and c appearing in chemical formulae are shorthand for sulfate and carbonate respectively.

Table 3
Thermodynamic data for calculations at 25 °C

Mineral	Reaction	Calculated log K_{sp} [a]	Solubility data from ref.
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O \rightarrow 6Ca^{2+}+2Al(OH)_4^-+3SO_4^{2-}+4OH^-+26H_2O$	−45.10 [b]	[32]
Monosulfoaluminate	$Ca_4Al_2(SO_4)(OH)_{12}·6H_2O \rightarrow 4Ca^{2+}+2Al(OH)_4^-+SO_4^{2-}+4OH^-+6H_2O$	−29.26	[7], this study;
C_4AH_{13}	$Ca_4Al_2(OH)_{14}·6H_2O \rightarrow 4Ca^{2+}+2Al(OH)_4+6OH^-+6H_2O$	−25.40	[8], this study
Monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12}·5H_2O \rightarrow 4Ca^{2+}+2Al(OH)_4^-+CO_3^{2-}+4OH^-+5H_2O$	−31.47 [b]	[7]
Hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13}·5.5H_2O \rightarrow 4Ca^{2+}+2Al(OH)_4+0.5CO_3^{2-}+5OH^-+5.5H_2O$	−29.75 [b]	[7]
C_2AH_8	$Ca_2Al_2(OH)_{10}·3H_2O \rightarrow 2Ca^{2+}+2Al(OH)_4+2OH^-+3H_2O$	−13.56 [b]	[8]
Portlandite	$Ca(OH)_2 \rightarrow Ca^{2+}+2\ H_2O-2H^+$	22.80	[24]
Calcite	$CaCO_3 \rightarrow Ca^{2+}+HCO_3^--H^+$	1.85	[24]

[a] The solubility products are averaged recalculated values based on solubility data from different sources (see references in the right column).
[b] Data are calculated by Lothenbach et al. [25] using GEMS with the Nagra/PSI database [24].

data are expressed as recalculated solubility products of the relevant phases. These additional data are in good agreement with solubility data for monosulfoaluminate given by Atkins et al. [9], with those for hydroxy AFm by Wells et al. [8] and by Damidot et al. [7] for mono- and hemicarboaluminate. A special restriction was imposed on calculation: although some AFm phases are metastable under the selected conditions, 25 °C and 1 bar pressure, they were generally admitted to the exclusion of other, more stable phases. This enables us to reproduce actual observations obtained in the course of hydration of commercial cements. The relationship between equilibrium and persistent but non-equilibrium states will be discussed subsequently. Where solid solution was encountered it was treated using the non-ideal Guggenheim approach of excess Gibbs free energy of mixing with the aid of the software MBSSAS, as described by Glynn [26]. A more detailed description how to treat these non-ideal solid solutions thermodynamically is in the course of preparation.

3. Results

3.1. Monosulfoaluminate–hydroxy-AFm-solid solution

Due to divergent literature results, particular attention was paid to the interactions between monosulfoaluminate and hydroxy-AFm. Fig. 1 shows the XRD patterns of powders of the monosulfoaluminate–hydroxy-AFm solid solutions, obtained from initially supersaturated solutions after 4 weeks of annealing. The AFm phase, as determined by XRD, generally corresponds to the 13 H_2O variant but even the gentlest drying could result in desiccation of the 19 H_2O variant. Our main aim was to avoid artefacts arising from carbonation; we have therefore not distinguished between 13 and 19 H_2O variants (or their anion-substituted forms) and simply report the phase as C_4AH_x. Up to a calculated substitution of 50 mol-% SO_4 by OH^-, the observed pattern is dominated by a single solid solution with reflections close to those of monosulfoaluminate. However the position of the main basal reflection, *0001*, shifts as a regular function of SO_4/OH ratio. At initial molar $SO_4/(SO_4+2OH)$-ratios <0.5 a second phase was detected by XRD. Its XRD-pattern is similar to that of C_4AH_{13} and is therefore associated with a hydroxy-AFm type phase. At a sulfate ratio $SO_4/(SO_4+2OH) \sim 0.05$ this hydroxy-AFm type phase became the only solid. Small amounts of C_2AH_8 were found in all mixtures within the range of sulfate ratios of $0.05 \leq SO_4/(SO_4+2OH) \leq 0.7$. Minor AFt was also found in one preparation, that of the monosulfoaluminate end member; C_2AH_8 was also somewhat labile and tended increasingly to convert to C_3AH_6 and alumina hydrate with time.

The systematic peak shift of the main basal reflections of the monosulfoaluminate type phase is shown in Fig. 2. This and other evidence disclose that significant change occurs up to a solid molar sulfate ratio $SO_4/(SO_4+2OH)$ of ~ 0.5; the interplanar distance for (0001) decreases from $\sim 8.94 \pm 0.02$ Å for pure monosulfoaluminate to $\sim 8.79 \pm 0.02$ Å for the limiting

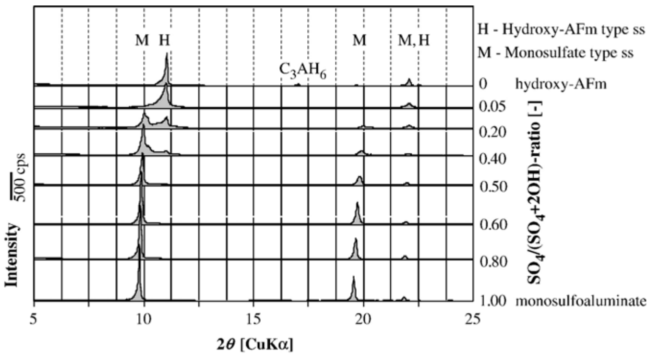

Fig. 1. XRD-pattern of selected AFm phase solid solutions.

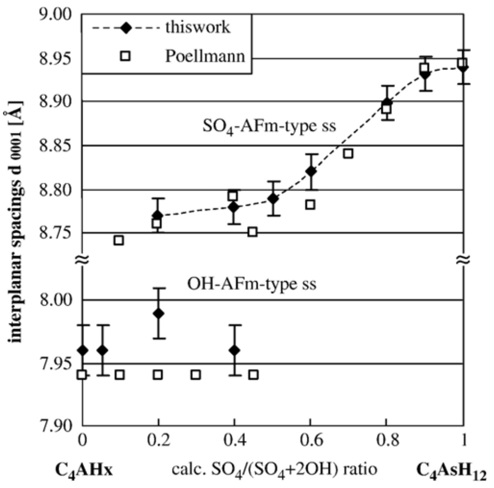

Fig. 2. Observed interplanar distances d_{0001} of monosulfoaluminate type solid solution (top) and hydroxy-AFm type solid solution (bottom).

monosulfoaluminate type solid solution at $SO_4/(SO_4+2OH) \sim 0.5$. At sulfate ratios <0.5–0.6, d_{0001} of the monosulfoaluminate type phase value did not change significantly. Instead a hydroxy-AF_m phase with $d_{0001} \sim 7.96 \pm 0.02$ Å was detected at a sulfate ratio of ~0.4, increasing in amount as the sulfate ratio decreased. These two observations, taken in conjunction, confirm the presence of a miscibility gap between both end members. At a $SO_4/(SO_4+2OH)$ ratio of 0.05 only one phase, with reflections similar to C_4AH_{13}, was observed. This might indicate limited sulfate incorporation into the hydroxy-AFm end member. Nevertheless, it is difficult to interpret the results with precision due to the prevailing detection limits; the limits shown are derived from solubility data, shown subsequently, but do not conflict with the XRD interpretation. As shown in Fig. 2, and in agreement with the data of Poellmann [19], no significant peak shift was observed within the hydroxy-AFm type phase. Therefore, and taking solubility data into account, its composition is assumed to be close to that of C_4AH_{13} although limited (maximum 5 mol%) sulfate AFm incorporation is not excluded.

SEM micrographs of the monosulfoaluminate end member and its solid solutions, Fig. 3(a) and (b) show well-crystallized hexagonal, platy crystals with diameters between 4–10 µm. In agreement with XRD data, needle-like AFt prisms with lengths up to 4 µm were found randomly distributed in the monosulfoaluminate preparation, Fig. 3(a). In contrast to the end member preparation, no ettringite was observed when ~10 mol% of the sulfate was substituted by hydroxide i.e., at a solid molar sulfate ratio $SO_4/SO_4+2OH \sim 0.9$, Fig. 3(b).

The XRD-investigation of the reaction products obtained from mixing previously synthesised monosulfoaluminate and hydroxy-AFm showed qualitative results similar to those obtained from supersaturation. Thus mixtures of hydroxy- and sulfate-AFm spontaneously react with formation of solid solutions extending between monosulfoaluminate and sulfate ratios of ~0.5. However the mixtures with high initial hydroxy-AFm contents ($SO_4/(SO_4+2OH) \leq 0.6$) showed generally higher d_{0001} values relative to the solids obtained from mixed raw materials. The reason is probably partial carbonation of the C_4AH_x phase; some hemicarboaluminate was also observed, leading to a lower content of reactive C_4AH_x. Therefore the real $SO_4/(SO_4+2OH)$ ratio is probably higher than calculated.

The solubility data, Fig. 4, confirmed the supposed solid solution formation between monosulfoaluminate and hydroxy-AFm; note however the large decrease in solubility attending the introduction of low sulfate concentrations to an apparently single hydroxy-AFm type phase. Minor initial carbonation of the C_4AH_x, initially present in the mixtures made by mixing end members, leads to small differences of the solubility data compared to results obtained from supersaturation, where carbonation could more effectively be prevented. Nevertheless the values obtained both from undersaturation and the mixed end member methods showed similar trends compared to the supersaturation values. Aqueous sulfate concentrations were below the limit of detection (<0.001 mmol SO_4^{2-}) at $SO_4/(SO_4+2OH) < 0.8$. However, sulfate concentrations increased from ~0.002 mmol at $SO_4/(SO_4+2OH) = 0.8$ to ~0.01 mmol for the monosulfoaluminate end member, where additional minor AFt was also present.

The composition of the aqueous phase (Fig. 4) changed significantly up to a calculated sulfate substitution of ~50 mol% in the solids; according to the XRD-analysis a single monosulfoaluminate type solid solution formed in this composition range. At $0.05 \leq SO_4/(SO_4+2OH) \leq 0.5$ the composition of the aqueous solution did not change significantly in the presence of two solid phases, one being the limiting monosulfoaluminate solution with ~50 mol% SO_4 substitution and the other, a hydroxy-AFm-type phase, possibly with slight sulfate substitution. The pH variation is subject to phase rule limits and must remain constant in the region of two solids.

3.2. Monosulfoaluminate–monocarboaluminate

Poellmann [27] reports that extensive solid solution does not occur between the sulfate- and carbonate-AFm end members and an experimental check was made to confirm this conclusion. The mixed end member method was used: previously synthesised monocarboaluminate and monosulfoaluminate were mixed in a 1:1 molar ratio with degassed ultrapure water with a final water/solid ratio of ~30.

After 4 weeks the solids were analysed by XRD. As shown in Fig. 5, no significant peak shift, which would indicate

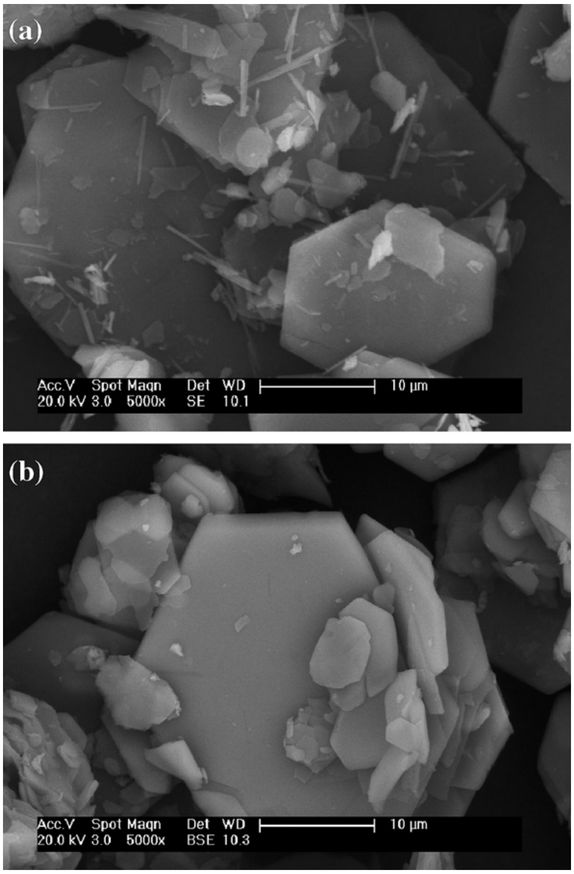

Fig. 3. ESEM micrographs of the monosulfoaluminate end member and ettringite (a) and the monosulfoaluminate type solid solution (~10 mol% of sulfate substituted by hydroxide) (b).

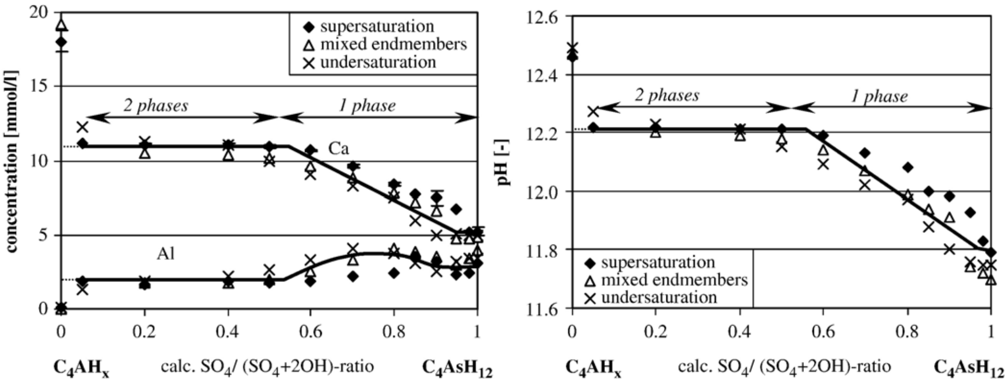

Fig. 4. Solubility data of monosulfoaluminate–hydroxy-AFm solid solution series (solid lines show our best fit).

changed anion population, was observed for either end member. The initial d_{0001} values remained unchanged at ~8.94 Å for monosulfoaluminate and ~7.6 Å for monocarboaluminate, respectively. In the absence of evidence for reaction, we provisionally accept that no extensive solid solution formation occurs between these two end members. AFt was found additionally to be present in small amounts.

The addition of portlandite to a mixture of monocarbo- and monosulfoaluminate resulted in the formation of hemicarboaluminate. As shown in Fig. 5, the intensities of the hemicarboaluminate basal reflection at ~8.2 Å increased with increasing reaction time in the presence of excess solid $Ca(OH)_2$ at 25 °C.

3.3. Monocarboaluminate–hydroxy-AFm

Solids were prepared from supersaturation having molar carbonate ratios $CO_3/(CO_3+2OH)$ of 1 (i.e., 100 mol% monocarboaluminate), 0.8, 0.5, 0.2 and 0 (i.e., 100 mol% hydroxy-AFm).

Table 4 gives the observed phase assemblages from XRD analysis of the solid phase at different carbonate:hydroxide ratios. The precipitation of a hemicarboaluminate-like phase was observed at ratios $0.2<CO_3/(CO_3+2OH)<0.8$. However hemicarboaluminate was the only solid phase at one ratio, $CO_3/(CO_3+2OH)\sim0.5$, suggesting a nearly ideal stoichiometric composition, $C_3A\cdot(CaCO_3)_{0.5}\cdot(Ca(OH)_2)_{0.5}\cdot xH_2O$.

Comparison of the d_{0001} values of the main basal reflection of the crystalline solids agrees well with those obtained by Fischer and Kuzel [28] using silicon as internal standard. Accordingly the values for monocarboaluminate and hydroxy-AFm were used as internal standards with which to compare d_{0001} values for hemicarboaluminate. As shown in Fig. 6, the main basal reflection of hemicarboaluminate increased slightly, d_{0001} increasing from ~8.15 Å to ~8.25 Å with decreasing carbonate contents in the solids. The contention that this is caused by ion exchange, $CO_3^{2-}\leftrightarrow 2OH^-$, requires more systematic investigations; for present purposes, stoichiometry is assumed, but it is possible, indeed likely, that hemicarboaluminate has a short range of (OH/CO_3) ratios. Table 4 summarises the relationships between molar carbonate and hydroxide ratios in the solid and solid phase development. The partial breakdown of hydroxy AFm is reflected by the appearance of the characteristic set of reflections in X-ray pattern for hydrogarnet.

3.4. Calculated relationships between sulfate-, carbonate and hydroxy-AFm

Fig. 7 shows the ternary AFm-system consisting of sulfate-, hydroxy-, and carbonate-AFm, calculated for 25 °C with the aid of data in Table 4. Fig. 7 is restricted to interactions between these three AFm phases; no other solid phases were admitted. The interactions and phase assemblages between these AFm

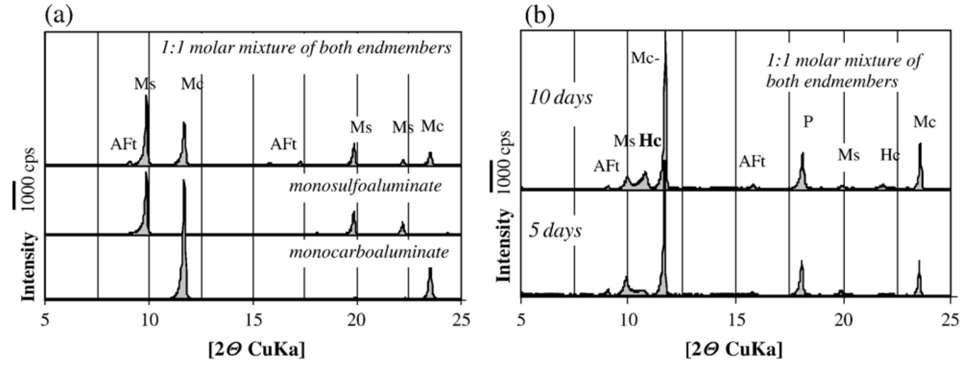

Fig. 5. Comparison of XRD-pattern of 1:1molar mixtures of synthesised sulfate-and carbonate AFm end members. a) no portlandite added; reacted 4 weeks at 25 °C. b) excess portlandite added; reacted 5 and 10 days at 25 °C. Ms — monosulfoaluminate, Mc — monocarboaluminate, P — portlandite, AFt — ettringite, Hc — hemicarboaluminate.

phases were calculated with a total solid content of 1 mol AFm dispersed in 1 kg water, but are not expected to be sensitive to the relative masses of solid and aqueous phases at water:solid ratios normally encountered in hydrating cement pastes. Fig. 7 is best used as a tool to understand the possible interactions between these three AFm phases in response to changes in anion activities: concentrations may be substituted for activities without affecting significantly any of the conclusions relevant to a hydrated cement paste. However the possible metastability of hydroxy AFm and monosulfoaluminate with respect to other solids, including C_3AH_6, portlandite and AFt, is suppressed in these calculations to present a complete picture of possible interactions between hydroxy-, sulfate- and carbonate-AFm.

A significant substitution of sulfate due to the incorporation of hydroxide in monosulfoaluminate characterises region A–C–D, Fig. 7. The experimental results show that the sulfate content of the solid solution is variable in the two-phase region A–B–D; the limiting solid solution has a composition of $\sim C_4As_{0.5}H_x$. The solid solution composition remains fixed at ~50 mol% in region B–C–D. As Fig. 7 shows, the C_4AH_x type phase will only occur as a phase of essentially fixed composition together with the limiting monosulfoaluminate solid solution and hemicarboaluminate in region B–C–D. C_4AH_x cannot persist together with both ideal monosulfoaluminate and monocarboaluminate. In a carbonate-free system, C_4AH_x will react with monosulfoaluminate to form a solid solution according to Eq. (1) (with $x+y=1$; $x \leq 0.5$):

$$x(C_3A\cdot Ca(OH)_2\cdot nH_2O)+y(C_3A\cdot CaSO_4\cdot nH_2O)\xrightarrow{+H_2O} \times (x+y)C_3A\cdot (Ca(OH)_2)_x\cdot (CaSO_4)_y\cdot nH_2O. \tag{1}$$

The addition of monocarboaluminate will initially cause hemicarboaluminate to form as a result of the reaction of monocarboaluminate with C_4AH_x according to reaction 2:

$$0.5(C_3A\cdot Ca(OH)_2\cdot nH_2O)+0.5(C_3A\cdot CaCO_3\cdot nH_2O)\xrightarrow{+H_2O} \times C_3A\cdot (Ca(OH)_2)_{0.5}\cdot (CaCO_3)_{0.5}\cdot nH_2O. \tag{2}$$

The reaction of monocarboaluminate with C_4AH_x is thermodynamically preferred relative to formation of the monosulfoaluminate–C_4AH_x solid solution series. Thus, while C_4AH_x is still present, it will react first with monocarboaluminate to form hemicarboaluminate (Eq. (2)); any remaining C_4AH_x will preferentially react with monosulfoaluminate to form a solid solution (Eq. (1)). Moreover, in the presence of excess monocarboaluminate, all available C_4AH_x will preferentially react to form hemicarboaluminate; extensive solid solution formation between monosulfoaluminate and hydroxy-AFm will not be observed in the presence of monocarboaluminate. Therefore no significant hydroxide for sulfate substitution will be observed to occur in the monosulfoaluminate phase in the region A–D–E of Fig. 7, i.e., "monosulfoaluminate" will have close to its ideal composition. Due to reactions Eq. (1) and Eq. (2), C_4AH_x will not persist at higher activities of sulfate and/or carbonate, i.e., in the presence of ideal monosulfoaluminate and monocarboaluminate.

Table 4
Observed phase assemblages and their dependence of the initial solid carbonate ratio

Molar carbonate ratio $CO_3/(CO_3+2OH)$	Observed solid(s)
1.0	Monocarboaluminate
0.8	Monocarboaluminate, hemicarboaluminate
0.5	Hemicarboaluminate
0.2	Hemicarboaluminate, hydroxy-AFm, hydrogarnet (C_3AH_6)
0	Hydroxy-AFm, hydrogarnet (C_3AH_6)

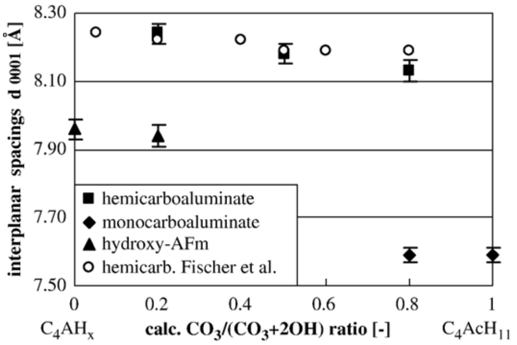

Fig. 6. Comparison of d_{0001} spacings for C_4AH_x–C_4AcH_{11} mixed solids.

The previous investigations and calculations show that, depending on the initial chemical composition of the mixture, several AFm phases might coexist: thermodynamic calculations demonstrated different possible phase assemblages among the AFm compositions included in the study. To apply these data to "real" cements, mass has to be conserved with the result that all solid reaction products have to be considered. The main hydration products of OPC are C–S–H and $Ca(OH)_2$. But other phases, such as AFt and $CaCO_3$, may also be present. To apply these data to commercial cements, we argue as follows: $Ca(OH)_2$ is of constant composition (but not necessarily in constant amount) and we assume for present purposes that sulfate and carbonate included in C–S–H require a small but constant correction of the chemical totals. Quantitative studies of sulfate incorporation in C–S–H are in progress and in due course, it will be possible to correct for sulfate sorbed by C–S–H but, in the absence of these data, we do not make a correction for sulfate sorption in specimen calculations. The activity of carbonate is controlled by calcite and is insufficient to carbonate either $Ca(OH)_2$ or C–S–H.

Fig. 8 shows the calculated phase assemblages that will typically occur in hydrated OPC and the dependence on initial sulfate and carbonate contents, expressed as ratios of SO_3/Al_2O_3 and CO_2/Al_2O_3 (subsequently abbreviated to sulfate and carbonate ratios respectively). The additional data needed for the calculation are shown in Table 3. Due to a lack of consistent thermodynamic data, other silica-bearing phases, e.g. C_2ASH_8

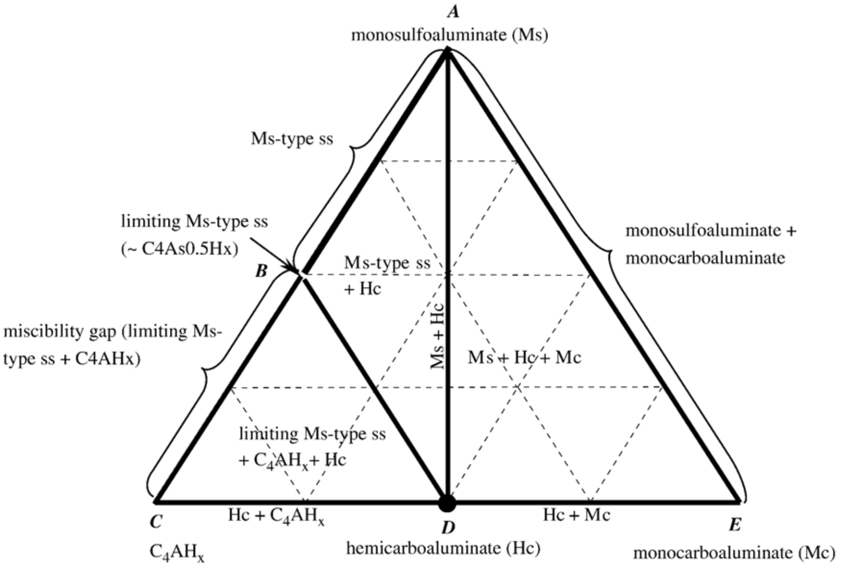

Fig. 7. Calculated phase assemblages between different AFm phases at 25 °C. A possible range of stoichiometry of hemicarboaluminate is not shown. (Note: the region of two solid phases Ms type ss + Hc in which the monosulfate-type phase has a variable composition; in this region, the lines are straight lines radiating from point D and terminating on the join AC between points A and B).

and silica-containing hydrogarnet, are not considered in this first approach. The main results of the calculations show:

- AFt, monocarboaluminate, calcite and portlandite (region V, Fig. 8) will be observed as an important stable phase assemblage in limestone-blended cements. However the chemistry necessary to achieve this assemblage is a function of SO_3/Al_2O_3 ratio as well as of CO_2/Al_2O_3 ratio.
- C_4AH_x has only limited persistence. It will not form if the initial solid SO_3/Al_2O_3 ratio is greater than 0.5 and it is not stable in the presence of monocarboaluminate. The long-term occurence of C_4AH_x in sulfated OPC hydrated at 25 °C is unlikely.
- Significant substitution of sulfate in monosulfoaluminate occurs only when the initial SO_3/Al_2O_3-ratio is lower than 1. At SO_3/Al_2O_3-ratio ≥ 1 the composition of this AFm phase has the ideal monosulfoaluminate stoichiometry. But, with increasing carbonate contents, the stability field of monosulfoaluminate solid solution decreases markedly. Monosulfoaluminate and the monosulfoaluminate-type solid solution will not be stable in the presence of monocarboaluminate and are unlikely to persist in cements with a carbonate ratio >0.5.
- OPC with very low carbonate contents will form hemicarboaluminate as an additional AFm phase in the course of hydration. But hemicarboaluminate is not stable at 25 °C in the presence of excess calcite.
- C_4AH_x is metastable. In the course of hydration and normal ageing it may spontaneously decompose to C_3AH_6 (hydrogarnet) and $Ca(OH)_2$ (portlandite). The stability of monosulfoaluminate solid solutions at 25 °C is marginal. Thus the phase assemblages comprising as solids monosulfoaluminate, C_3AH_6, hemicarboaluminate and portlandite may in time, replace compositions in areas II and III in Fig. 8.

3.5. Application of the data

Diagrams of complex systems presented on plain paper are often unsuited to calculations of amounts of phases. Therefore Fig. 9, derived from the same dataset, has been constructed to afford a more quantitative insight into the sequence of phase changes as calcium carbonate increases. The calculation requires to be made with some restraint; we apply a fixed SO_3/Al_2O_3 ratio, in this instance 1.0. Excess portlandite is present in all assemblages; for convenience we added 1.25 moles. The exact amount is not critical to the results except insofar as portlandite is actually consumed as the initial CO_2/Al_2O_3-ratio increases in the range of CO_2/Al_2O_3 ratios 0 to ~0.33 approximately and it is a

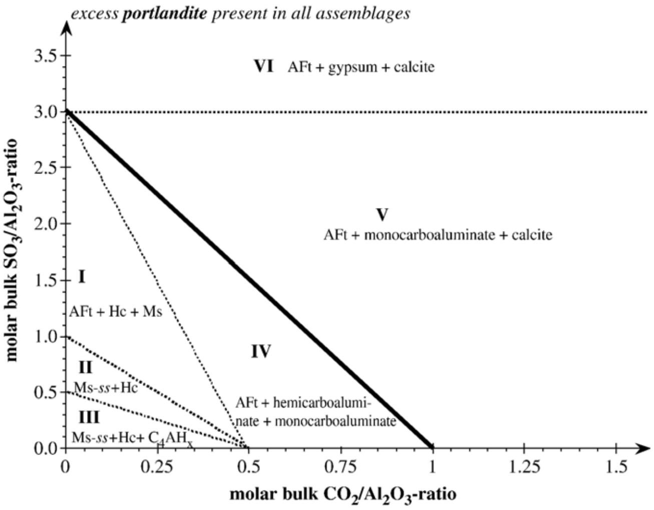

Fig. 8. Calculated phase assemblages of a hydrated mixture consisting of C_3A, portlandite and varying initial sulfate (SO_3/Al_2O_3) and carbonate ratios (CO_2/Al_2O_3) at 25 °C.

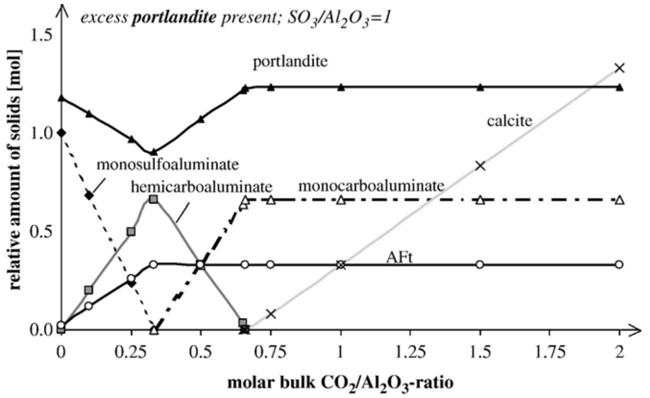

Fig. 9. Relative amount of hydrate phases of a hydrated model mixture consisting of 1 mol C_3A, 1.25 mol portlandite and with fixed initial sulfate ratio ($SO_3/Al_2O_3 = 1$) showing phase development and its dependence on changing carbonate ratios (CO_2/Al_2O_3) at 25 °C.

requirement of the calculation that positive quantities of portlandite always remain. If the calculation results in apparently negative portlandite, it is invalid. Hence we add sufficient to assure an excess, as will normally obtain in the case of Portland cement hydration. It can be seen that the amount of monosulfoaluminate type solid solution will decrease continuously with increasing carbonate content. Due to progressive displacement of sulfate from AFm, the calculation reveals that sulfate thus released will form additional ettringite. Therefore, other factors being equal, the amount of ettringite initially increases with increasing carbonate ratio. The amount of ettringite reaches a maximum when all sulfate in AFm has been replaced by carbonate, i.e. when monocarboaluminate is present and hemicarboaluminate is maximised. Further increases of carbonate content diminish hemicarboaluminate and it will not persist if a permanent excess of calcite remains. However, the conversion of hemicarboaluminate to monocarboaluminate does not result in further increases in AFt content although the amount of portlandite will increase in the course of the conversion of hemi- to monocarboaluminate.

Calcium carbonate in excess of that required to maximise monocarboaluminate will appear as free $CaCO_3$. Below this critical amount, which in this example occurs at a molar ratio of $CO_2/Al_2O_3 \sim 0.66$, $CaCO_3$ behaves as a reactive admixture. However excess of $CaCO_3$ above this ratio behaves as an inert filler. Thus the transition between reactive and inert $CaCO_3$ depends on cement C_3A content. But, if reactive ferrite and other alumina sources need to be included, using total chemical alumina content as the basis for calculation.

Carbonate substitution in AFt is neglected due to lack of thermodynamic data. In this context Poellmann [31] showed an extensive substitution of sulfate by carbonate in the ettringite structure. However, carbonate activity in hydrated Portland cement is controlled by the buffering capacity of hemicarboaluminate, monocarboaluminate, or calcite, or mixtures thereof, dependent on amount of carbonate and initial CO_2/Al_2O_3 ratio of the cement. According to calculations by Damidot et al. [7], carbonate-AFt will only become stable at high carbonate activities significantly above those that can be generated by the solubility of calcite at pH ~ 12. Thus the carbonate activities in hydrated cements subject to internal carbonation by calcite, i.e., not in contact with an air atmosphere, are predicted to be too low to stabilise carbonate-AFt. Work is in progress to provide additional thermodynamic and experimental data on CO_3-AFt, but in the present approach AFt is not considered to be a potential host for significant carbonate at 25 °C.

4. Discussion

4.1. Extent of solid solution

Perhaps surprisingly, AFm phases form only limited mutual solid solutions under conditions likely to obtain in cement environments. Thus, for example, hydroxide and carbonate AFm phases are not directly miscible but instead form an ordered solid solution, i.e., a definite compound, ideally with the 1:1 ratio. Part of the reason for lack of miscibility is associated with the difficulty of generating high component activities of some species, e.g., carbonate. In normal cement environments the solubility of carbonate (which we equate with activity) is invariably low, being limited by the solubility of carboaluminates and calcite. Where it is possible to achieve a relatively broad spectrum of component activities, as for example can be achieved for sulfate and, especially, hydroxide, significant ranges of solid solutions may form in response to the expanded range of species activities. It is shown that at self-generated aqueous concentrations of sulfate and hydroxide, solid solution extends from sulfate-AFm to approximately 50-mol% of a C_4AH_x end member. This limit is widely but not invariably agreed in experimental studies [17,19]. In some cases, data pointing to complete solid solution contain internal conflict and the interpretation is thus suspect. It is nevertheless possible to envisage conditions, for example where precipitation of AFm occurs from highly supersaturated solution, or in the presence of cations interacting only weakly with solids but promoting high concentrations of hydroxyl, e.g., sodium or potassium hydroxides, that solid solution involving replacement of other anions by OH^- might become more extensive or even complete. But the results we report are probably applicable to normal OPC compositions and water:cement ratios, <1.0.

Besides need for conditions favouring formation of solid solutions, we also have to consider kinetics; solid solutions of exotic compositions may form, but will they be stable or persistent? In this connection, it is worth recalling that C_4AH_x is not only metastable, it is also labile. Its labile behaviour is manifested by its slow decomposition at ambient temperature to the more stable solid phases, hydrogarnet (C_3AH_6) and portlandite ($Ca(OH)_2$). Sulfate AFm, on the other hand, while believed to be thermodynamically metastable at <40 °C, is nevertheless relatively persistent at 25 °C although Zhang [21] made preparations which might initially have contained AFm (sulfate/hydroxy) solid solutions but after prolonged aging, more than 1 year at 25 °C, were found to have decomposed to mixtures of sulfate AFm and other solids, e.g., C_3AH_6. But because the hydroxide-substituted sulfate AFm solid solutions are persistent in our experiments and, moreover, are widely observed to occur both in “real” cements, we deem it important to include them in our phase development model. In this connection, it is noteworthy that we were able rapidly to achieve hydroxide-substituted AFm by mechanically mixing the two solids, hydroxy- and sulfate-AFm, at 25 °C, suggesting that we may associate good persistence with a range of solid solutions: partial OH^- for SO_4^{2-} substitution does not necessarily detract from the ability of these solid solutions to form and persist. As will be shown, a variety of mechanisms contributes to the ultimate decomposition of these phases.

4.2. Transformation mechanisms

It has always been assumed that changes in the anion chemistry of an AFm phase occur by ion exchange. In this view, the $[Ca_2Al(OH)_6]^+$ layers are relatively fixed, while water and charge-balancing anions in interstitial spaces are more regarded as more mobile and hence exchangeable. Thus the chemistry of the interlayer ions adjusts itself to that of the pore fluid. So, for example, if a cement develops C_4AH_x but carbonate ions become slowly available, perhaps from dissolution of added calcite, a change in composition proceeds via ion exchange, first to hemicarboaluminate and eventually to monocarboaluminate. But the structures of the three phases differ in detail and, as shown, they do not form continuous solid solution. It is therefore difficult to envisage the transformation proceeding by other than by a reconstructive process; that is, one phase dissolves while another, differing in composition and structure, nucleates and crystallises. While transformation by ion exchange could permit the morphology and microstructure to persist throughout the conversion(s), nucleation and crystallisation are more likely to require a reconstitution of the microstructure. Putnis et al. [33] have recently described a novel mechanism for pseudomorphic replacement of one phase by another and this may have relevance for the mechanism of transformations amongst AFm phases driven by anion exchanges. The net result of the title study is to create uncertainty concerning the actual mechanism of the transformation and consequently, the potential for changes in microstructure associated with transformations amongst AFm phase(s).

Elucidation of the actual mechanism of transformation remains a goal. More accurate structure determinations of individual AFm phases would be helpful: the structures may have a common plan, but differ significantly in detail and these details are important in the present context. It is possible to envisage the transformation between AFm phases occurring by ion exchange but with some simultaneous reordering and rearrangement within the $[Ca_2Al(OH)_6]^+$ layers avoiding, or partly avoiding, need for a nucleation and crystallisation step, as described in Ref. [33]. However, the discontinuous nature of the AFm phase, requiring that it be treated as a series of discrete phase rather than a single solid solution must affect subsequent treatments of paste mineralogy.

4.3. Solubility data and its interpretation

Interest in the solubility of AFm phases centres on the solid solution series between sulfate and hydroxyl end members: these data are shown in Fig. 4. Special problems arise in determining the solubility of C_4AH_x at 25 °C because several hydration states may occur, notably the 19 H_2O state stable at >88% r.h. and the 13 H_2O state at <88% r.h. [34]. The impact of lower r.h. parallels the behaviour of solutions with altered species activities corresponding to the high ionic strengths observed in cement pore fluids [20]. Consequently, it is difficult reliably to perform solubility measurements on a single hydration state, although we believe solubility data reported here are obtained on C_4AH_x, with x close to 19, after allowing for other anionic substituents. However, the preparation for X-ray diffraction, done in a dry protective atmosphere to avoid carbonation, may result in dehydration of C_4AH_x with the result that the XRD-data actually relate to the 13 H_2O state, or 13-x if some sulfate solid solution occurs. The extent of solid solution, as well as its persistence, may be influenced by the hydration state of C_4AH_x. Thus it is not surprising that solid solution would be incomplete between C_4AsH_{12} and C_4AH_{19}, although the higher ionic potential of the aqueous phase of cements resulting from dissolution of alkalis, etc. tends to favour the 13 H_2O state [20] and calculations of volume changes have accordingly been based on the assumption that this hydration state is the most relevant to commercial cements. Secondly, the lability of the C_4AH_x phase results in a difficult experimental choice: either prolong the time allowed for equilibration with an aqueous phase and its risk decomposition to other solids, thereby influencing solubility, or else use only brief equilibration times, thereby minimising decomposition but perhaps failing to saturate the aqueous phase. Nevertheless, our calculated value for the solubility product of C_4AH_{13}, log $K_{sp}=25.40$, compares well with the solubility data given by Wells et al. [8].

C_4AH_x almost certainly takes into solid solution a small amount of sulfate. Best estimates of the extent of solid solution are on the order of 1–5%. This small sulfate content apparently causes a drastic lowering of calcium solubility. However the lowering is not necessarily a consequence of solid solution; if it were, it would imply strong crystallochemical stabilisation by sulfate. Addition of a small amount of sulfate significantly reduces the labile nature of C_4AH_x. The solubility measurements, supposedly on C_4AH_x, may actually relate to a self generated spurious invariant point of an aqueous solution coexisting with a mixture of phases; hydroxy-AFm as well as the stable phases arising from C_4AH_x decomposition, hydrogarnet and portlandite. However decomposition has much less impact on the rest of the system and the solubility trends are consistent with a broad two (solid) phase gap and continuous solid solution ranging between about 50% SO_4^{2-} and the monosulfoaluminate end member. Almost certainly, the kinetics of formation and decomposition of the labile AFm phases and their solid solutions deserve further and more detailed study.

4.4. Discussion of the implications for cement hydration

In the quantitative analysis of cement hydrates it has become customary to refer to “the AFm phase” as if it were a single phase, albeit with a variable anion content and limited Fe for Al substitution. We now know that this is incorrect: many types of cement can be expected to contain two or even three AFm-type phases. Nor is this coexistence necessarily a temporary feature. For example, a promising instrumental method for the determination of paste mineralogy rests on X-ray diffraction using Rietveld analysis to quantify measured reflection intensities. However a key requirement for application of the method is its requirement for a structure determination of each corresponding phase, including correct atomic positions and unit cell atom contents or, in the absence of accurate atomic positions, physical samples for calibration and semi-quantitative analysis. At present we identify need for additional and more accurate AFm structure determinations, especially for hemicarboaluminate. But as the study continues, the need for more calibrants may emerge to cope with the AFm phases encountered in blended cements.

We also determine that, although several AFm anion chemistries are metastable, notably those with high hydroxyl or sulfate, the two carbonate AFm phases are thermodynamically stable at ambient conditions in unaltered cement matrices [7]. Cements contain carbonate from many sources some of which are not obvious. For example, during clinker cooling in contact with kiln gases, sulfates may condense onto the clinker. This sulfur oxide is swept through the kiln together with alkalis, water, carbon dioxide, etc. As the hot gas stream cools, it may reach the dew point of alkali sulfates. Calculations on vapor-melt equilibria by Barry and Glasser [6] disclose that these alkali “sulfates” are actually alkali sulfate-alkali carbonate solid solutions. Thus vapour condensates onto cooling clinker introduce significant carbonate as well as sulfate. Carbonate contributions may also arise in the same manner if clinker kiln dust is recovered and added to clinker. Moreover “gypsum” interground with cement often contains significant calcite. These several sources of carbonate are often sufficient to stabilise hemicarboaluminate in the course of hydration, even of fresh and nominally uncarbonated cement.

The thresholds for carbonation are often defined in terms of the equilibrium carbonate activity or of CO_2 pressure (or fugacity) necessary to drive reaction. But what should be recalled is that significant reaction leading to formation of much carbonate-AFm requires mass transport as well as a certain activity and mass of carbonate. For C_4AH_x to transform, first to hemicarboaluminate and then to monocarboaluminate, uptake of carbonate is required. The gain in carbon, calculated as carbonate, is about 4 wt.-% at each step (see Table 2). Thus, in order to transform C_4AH_x, not only must a minimum carbonate activity be exceeded but also a reservoir of carbon dioxide (or carbonate: the species equilibrate rapidly) is required. In the example considered, a simple way of supplying the necessary carbonate is to add ground limestone (calcite) to the cement. Note that added calcite will *not* react directly with portlandite or C–S–H but *will* react with AFm phases, including C_4AH_x, or its solid solutions with monosulfoaluminate, with monosulfoaluminate or with hemicarboaluminate, or with mixtures thereof. Fig. 7 shows the relationships between the three most common AFm anion chemistries in cement. The diagram differs in some respect from that shown by Nielsen et al. [35] who do not admit hemicarboaluminate to the diagram, arguing that it is only stable over a range of low carbonate contents. Moreover they do not show a range of hydroxide-substituted sulfate-AFm solid solutions. This is justified on the grounds that the AFm phase found in cement hydration experiments was “pure monosulfoaluminate”. While pure or nearly pure monosulfoaluminate does occur in some assemblages, we disagree with the underlying logic. Firstly, hemicarboaluminate has a range of carbonate concentrations over which it is stable. But so too does monocarboaluminate; indeed a range of stability is characteristic of many important cement phases. Metastability is, in any event, not grounds for exclusion from a phase development model unless the range of conditions for persistence does not coincide with that commonly encountered in commercial cements. But this range of low carbonate concentrations is shown to be especially important to the mineralogical development of cements with added calcite. Moreover, the characterisation data reported in Ref. [35] for monosulfoaluminate was determined from elemental ratios by energy dispersive X-rays. Since the detector is not sensitive to OH, substitution of sulfate by hydroxide cannot be excluded: a sulfur signal could arise from other phases or phase mixtures and may not be interpreted as arising uniquely from SO_4-AFm.

A further important difference is that Fig. 7 is only relevant to the system of three AFm phases, i.e. it embraces a very restricted range of compositions. This restriction on compositions is rather artificial and for that reason only partially reflects the mineralogy of chemically more complex Portland cement pastes. To address these considerations Figs. 8 and 9 have been constructed. They are realistic in terms of (i) assuming an excess of $Ca(OH)_2$ to be present and allowing portlandite to react as required and (ii) allowing phase relations to be depicted as functions of SO_3/Al_2O_3 and CO_2/Al_2O_3 ratios of the reactive fractions. Note that the “reactive fraction” is subject to uncertainties: the fraction of clinker minerals reacted at a given time, and hence the supply of alumina, carbonate, etc., as well as corrections for absorbed species, e.g. sulfate in C–S–H. The supplementary calculation, shown in Fig. 9, has to have an additional restriction imposed: in the example we arbitrarily fix the sulfate ratio at 1.0 and, by fixing the ratio, are able to calculate the amount of relevant minerals. The trends observed are dominated by composition as well as by the greater thermodynamic stability of AFt and monocarboaluminate relative to other phases. Of course the calculation can be made for other SO_3/Al_2O_3 ratios but other ratios will mainly affect (i) the % of $CaCO_3$ addition required to saturate the solids, i.e. the point at which increments of calcite are no longer reactive but instead become an inert diluent and (ii) the relative proportions of phases, although the greater stability of AFt and monocarboaluminate relative to other phase assemblages continues to dominate the assemblages of aluminate hydrate phases.

The diagrams presented in Ref. [35] show monosulfoaluminate and monocarboaluminate as a compatible pair of minerals in the presence of excess portlandite. In fact the pair is not compatible in the presence of $Ca(OH)_2$. We have confirmed this experimentally as well as by calculation: as predicted in Fig. 9, AFt and hemicarboaluminate are the solid phases resulting from reaction of monosulfoaluminate with monocarboaluminate and portlandite. Thus the importance of this pair of phases diminishes in real cements where excess $Ca(OH)_2$ is present. This conclusion, calculated as well as experimental, agrees with that reported previously by Kuzel [29,30] whose perceptive contributions to cement mineralogy we have come to appreciate in the course of our work. Eq. (3) shows the balanced reaction mechanism of the additional hemicarboaluminate formation.

$$\begin{aligned} &x(C_3A\cdot CaCO_3\cdot nH_2O)+y(C_3A\cdot CaSO_4\cdot nH_2O)\\ &\quad + zCa(OH)_2 \xrightarrow{+H_2O} \frac{y}{3}C_3A\cdot 3CaSO_4\cdot 32H_2O\\ &\quad + \frac{x}{3}(C_3A\cdot CaCO_3\cdot nH_2O)\\ &\quad + \frac{2}{3}(x+z)\left(C_3A\cdot\left(CaCO_3\right)_{0.5}\cdot Ca(OH)_2\right)_{0.5}\cdot nH_2O\\ &\quad + \frac{z}{3}Ca(OH)_2. \end{aligned} \tag{3}$$

The limited data on phase densities suggest that transformation of one AFm phase to another is not attended by significant changes in the molar volumes of the solids. But attention is directed to the observation that, as sulfate AFm carbonates by conversion to monocarboaluminate, the sulfate thus expelled forms AFt, ettringite. On account of the physically low density of ettringite, its development in increasing amounts within a hardened matrix is sometimes – but not necessarily correctly – associated with expansive reactions. The model developed here can be used to calculate the specific volume of solids and results of these calculations will be presented in a subsequent paper [36].

4.5. Extensions of this work

Slag-blended cements are characterised by their content of strätlingite, or gehlenite hydrate, nominally C_2ASH_8. The structure of this phase is known at least approximately; it contains cationic layers characteristic of an AFm phase but the necessary charge balance is supplied by an aluminosilicate ion, $[AlSiO_8H_8]^-$, according to Kuzel [37]. Presumably these interlayer contents are stabilised by the higher Al and Si activities achieved in slag-blended cements. However, AFm phases with “normal” interlayer contents (OH^-, SO_4^{2-}, CO_3^{2-}) appear to coexist with strätlingite in many cements leading to the supposition that at least one and possibly more AFm phases have to be included in the phase development model in order to describe adequately the mineralogy of slag blends.

5. Conclusions

A basic thermodynamic description of the AFm phase(s) necessitating collection of new data, and its coupling to experimental investigations, has enabled new insights into the role of AFm, the relationships between calcite, added as a “filler”, and the paste mineralogy. The principal findings are:

- AFm phases containing as principal anions OH^-, SO_4^{2-} and CO_3^{2-} are incompletely miscible with each other. Thus several AFm phases may coexist in a matured paste at ~25 °C.
- Carbonate provides thermodynamic stabilisation for the AFm phase. Thus monocarboaluminate is stable at 25 °C. The stability of monosulfoaluminate is marginal at 25 °C. Hydroxy-AFm, as well as a part of the extensive range of solid solutions formed by partial replacement of sulfate by hydroxide, are metastable at ~25 °C.
- Thermodynamics and experiment agree in support of the above conclusions. However hydroxide-substituted sulfate AFm have only a small driving force for decomposition at ~25 °C, as a consequence of which they are persistent.
- Hemicarboaluminate is a persistent phase over a short range of carbonate activities at ~25 °C. This range, although short, coincides with commonly encountered conditions in cements, e.g. the presence of minor carbonate even in fresh clinker, and for this reason it should not be excluded from consideration in a mineralogical model for paste hydration.
- The anion balance in AFm cannot change without requiring formation/dissolution of other phases. A process identified as of particular importance to the constitution of modern cement pastes is the formation of ettringite as a consequence of carbonate additions to cement; sulfate displaced from AFm in the course of forming hemi- and monocarboaluminate contributes to ettringite formation.
- Moreover, while portlandite does not react directly with calcite, the amount of free portlandite must be affected by calcite additions as a consequence of the changing AFm/AFt phase balances.
- Quantitative calculations are presented on the use of $CaCO_3$ as a blending agent. These show clearly a quantitative distinction between reactive and inert $CaCO_3$.

As is almost always the case, unsolved problems remain. Data on the kinetics of decomposition of possibly labile AFm solid solutions will be provided in due course, as well data on Fe substitution in AFm phases. Arguably a more important area is the response of AFm to the more aluminosilicate-rich environment of blended cements. This work has been commenced and will also be reported in due course. The development of quantitative calculation of hydrated paste mineralogy has been successfully commenced. Results thus far obtained have far-reaching implications for our understanding of the microstructure and space-filling properties of Portland cement pastes.

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