

# The Distribution of Sulfate in Hydrated Portland Cement Paste

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## Abstract

Much of the sulfate in Portland cement paste is contained in AFm and AFt phases; measurements of sulfate sorption by C-S-H disclose that it is also a host for sulfate. The distribution of sulfate in AFt and AFm is also affected by carbonate. Quantitative calculations are presented for a model cement. Calculation shows how these balances are affected by temperature: three characteristic distributions are obtained applicable in the ranges 0-30°C, 30-50°C and 50-85°C. The extensive nature of changes suggests that changes to the AFt phase are one of several factors involved in dimensional instability arising from thermal cycling.

## Introduction

Early Portland cements appear to have been made without deliberate addition of sulfate [1]. A retarder became necessary as the contents of tricalcium silicate (alite) increased and as the fineness of grinding increased. Calcium sulfate (dihydrate) became the almost universal choice of retarder because it was cheap, readily available and did not interfere with strength gain in the longer term. However adding another component, sulfate, increases the complexity of the hydration process particularly as much of the sulfate is reactive in early stages of hydration. For example, ettringite (AFt) is an important product of cement hydration in the first few days or weeks but tends to become less abundant relative to other hydrates at longer ages and as readily soluble sulfate sources are depleted. In recent decades, sources of sulfate other than calcium sulfate have also become more important. To decrease fuel consumption modern suspension preheaters allow contact between kiln offgas and raw materials; as a result a cycle of sulfur transport is set up in the kiln resulting in condensation of alkali sulfates onto the clinker [2]. Clinker kiln dust from the dry process, also rich in sulfate, may be judiciously blended with finished cement. Thus, as a result of adding calcium sulfate as well as sulfates from various sources, the SO<sub>3</sub> content of Portland cements has tended to rise in recent decades.

We also know that modern cements are adversely affected by thermal cycles used in accelerated cures and that sulfate is involved. Thermally-accelerated cure can initiate a process known as “delayed

ettringite formation" (DEF). The problem arises after fresh cements and concretes are deliberately warm cured, typically at  $>70^{\circ}\text{C}$ , to accelerate strength gain. In the course of cure and shortly afterwards, ettringite is observed to disappear or greatly reduce in amount. The heat-cured products are satisfactory after cure but subsequently, after months or years of moist exposure, expand and crack. Much effort has been expended into investigating the causes of this expansion without complete agreement but it is generally agreed that a symptom, if not the cause, is the slow reformation of ettringite at or near ambient temperatures [3].

The DEF problem has been a learning experience for cement scientists inasmuch as it shows how little we know about the mineralogy of hydrated cement pastes, of the quantification of paste mineralogy and of its dependence on temperature, cement composition (including the presence in low quantities of permitted blending agents) and of the relationships between on the one hand, paste mineralogy and microstructure and on the other, engineering properties. If cements and concretes are to enjoy the status of advanced materials, it is imperative that progress must be made towards quantification of these relationships.

This contribution has as its objective reviewing, with new data, the role of sulfate in Portland cement particularly with respect to quantification of its role in hydrated pastes. It reflects a start on the overall goal of linking mineralogy, microstructure and engineering properties.

The approach we take combines experimental science and thermodynamics. The persistence of metastable phases in cement pastes, notably C-S-H, has been said to reduce the value of the thermodynamic approach to cement hydration and possibly render it inapplicable. But this is not so. Vast strides have been made in other fields, e.g., geochemistry, in the application of thermodynamic methods. Another serious deficiency, lack of thermodynamic data with which to undertake calculations, has gradually been rectified. For example, thermodynamic calculations reproduce well the mineralogical and chemical characteristics of a hydrated cement paste [4]. What is remarkable is not the persistence of certain metastable features of cement mineralogy but the extent to which pastes conform to equilibrium and, in response to chemical and thermal fluxes, readjust their mineralogy to minimise the free energy of the solids. Also, the sensitivity of the mineralogy to small changes in composition, for example of mass of sulfate and carbonate, as well as to temperature change. The presentation concentrates on sulfate: carbonate is described elsewhere in these proceedings [5] but because the two anions interact, the two contributions should be read in conjunction.

## Distribution of sulfate in Portland cement pastes.

### *General remarks*

Sulfate is widely distributed in Portland cement amongst AFm, AFt and C-S-H phases. However it is an *essential* constituent of only one, namely AFt (ettringite). We will show that the presence of sulfate creates a series of reactions in hydrated cement paste that buffer the sulfate concentration of the pore fluid much as the pH is buffered by certain mineral pairs, e.g., portlandite and C-S-H. Also, that sulfate and carbonate interact strongly with each other.

While much is now known about the role of sulfate in individual phases such as AFt and AFm [6,7], relatively little is known about the fractionation of sulfate between coexisting phases and the relationship of this fractionation to the constitution of the pore fluid. But before we describe the interactions, we explain the constitution of the individual phases, commencing with the AFt family.

### *The AFt family: ettringite and thaumasite*

Ettringite is well known from its natural occurrences. It is also an early-formed crystalline component of Portland cement hydration and is readily recognised from its characteristic XRD-pattern or by microscopy, typically growing into water-filled space in the form of hexagonal needles or columnar growths. The existence of carbonate ettringite is well established [8], but the carbonate activity conditioned by the presence of calcium carbonate at 25°C is insufficient to replace more than ~6% of the sulfate in ettringite by carbonate [9]. Thus the composition of ettringite in commercial Portland cements, even if the cement has been blended with calcite, always appears to be close to theoretical,  $C_6As_3H_{32}$ <sup>1</sup>, in shorthand notation.

The high water content and low physical density of ettringite, *ca.* 1.77 g/cm<sup>3</sup>, are noteworthy. The upper thermal stability limit of ettringite has been the subject of contention. In contact with its saturated solution, ettringite is stable to 114°C [10]. However at lower activity of water, or at less than 100% humidity, decomposition temperatures decrease rapidly [11]. The complex constitution of cement pore fluids and opportunity for sulfate to partition into other phases, notably AFm, may also cause the ettringite content in phase mixtures to deplete at temperatures less than 100°C. Its upper persistence temperature decreases with increasing alkali concentration of the pore fluid [12]. The increased solubility of ettringite at elevated temperatures, coupled with its reappearance upon cooling, is basically responsible for the potential for expansion that initiates DEF. The reversibility of this process is a manifestation of equilibrium: however while dissolution occurring with rising temperature is rapid, the reappearance of

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<sup>1</sup> C - CaO; A - Al<sub>2</sub>O<sub>3</sub>; s - SO<sub>3</sub>; H - H<sub>2</sub>O

ettringite with decreased temperature is typically slow. These kinetics are characteristic of many if not all reactions requiring nucleation and precipitation stage(s).

Thaumasite,  $\text{Ca}_3(\text{SO}_4)(\text{CO}_3)[\text{Si}(\text{OH})_6] \cdot 12\text{H}_2\text{O}$ , is isostructural with ettringite: silicate replaces the alumina found in ettringite. Ettringite and thaumasite share the same structure but form only limited mutual solid solution, as shown in Fig 1. Therefore thaumasite must be treated thermodynamically as a separate phase. Note that thaumasite, characteristically thought of as a “low temperature” phase, is stable at least to  $30^\circ\text{C}$ .

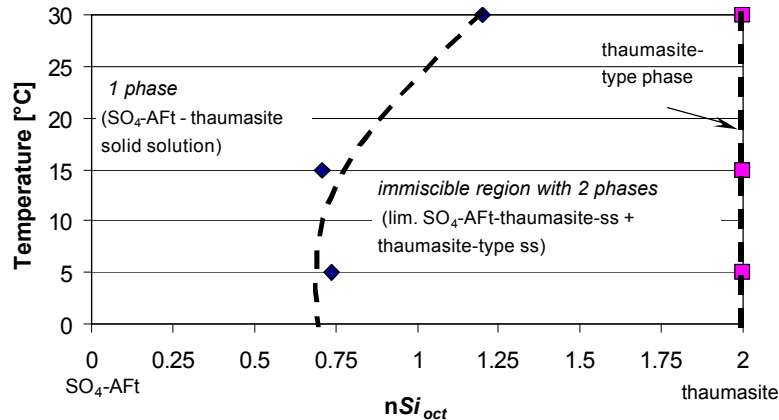


Fig. 1: Temperature dependence of the phase relations between thaumasite and ettringite,  $\text{SO}_4\text{-AFt}$  (according to Macphee et al. 2004 [13]).

The chemistry of plain cements is unsuitable for forming thaumasite: the low activity of silica and low carbonate content preclude thaumasite formation. But the carbonate necessary for thaumasite formation can readily be supplied, either externally from the service environment, or internally from calcium carbonate, perhaps added in the form of blending agents or from aggregates. Limestone aggregates are an obvious carbonate source but many other rock types contain calcite as an accessory mineral, often in sufficient abundance to condition thaumasite formation within its stability domain. This stability domain was delineated by Damidot, et al [14], who compiled the stable assemblages containing thaumasite at  $25^\circ\text{C}$  relevant to Portland cement.

#### The AFm family of phases

Much controversy in the literature surrounds the number and identity of AFm phases in normal Portland cements. Briefly the current state of knowledge is as follows. All AFm phases contain an elementary layer, for example  $\text{Ca}_2[\text{Al}(\text{OH})_6]^+$ . The layer has positive charge and appropriate charge balancing anions must be inserted between layers. However, the interlayer spaces have unsatisfied van der Waal's charges and sufficient space to contain charge-balancing anions as well as water molecules. We treat mainly the variant containing 11-13  $\text{H}_2\text{O}$ . The iron content of the AFm solids in cement pastes is typically

low, so substitution of iron for aluminium can be neglected as a first approximation. But anion substitution involves both mono- and divalent ions, typically hydroxide, sulfate and carbonate. These differ sufficiently in charge, size and polarity that miscibility between the various AFm chemistries is always incomplete with the result that commercial cements may contain as many as three coexisting AFm phases (although this is unlikely). Fig. 2 shows the current position regarding the extent of solid solution between OH- and SO<sub>4</sub>-end members. Under portlandite-saturated conditions (pH ~ 12.5), up to about 50 mol % of OH can substitute for sulfate.

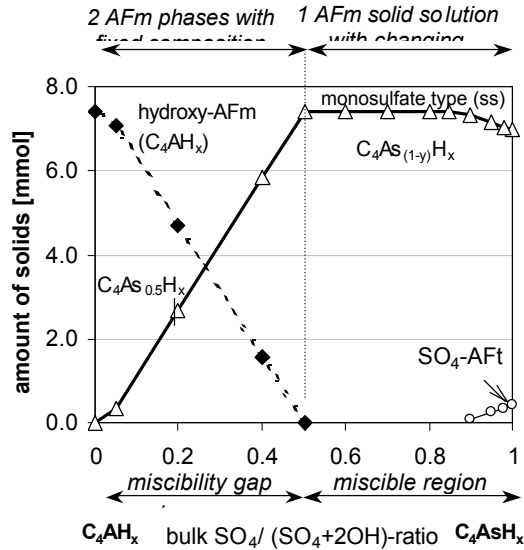


Fig. 2: Calculated phase relations between hydroxy -AFm and monosulfoaluminate at 25°C (excess portlandite present)

The stability of AFm phases is also sensitive to chemistry and this is relevant to their occurrence in cement. Hydroxy AFm is thermodynamically metastable at all temperatures with respect to mixtures of hydrogarnet and portlandite; this reaction, in which low-density AFm, formed in the course of initial hydration, converts in service conditions to denser products, mainly hydrogarnet has caused problems in the past. The sulfate AFm phase has also been reported to be metastable at temperatures below about 50°C [15] but our calculations disclose that (i) sulfate AFm is stable at 25°C (and probably less), albeit by only a few kJ/ mole, and (ii) positional disorder, resulting from random substitutions of OH and SO<sub>4</sub> in anion positions, results in an additional entropy contribution stabilising AFm solid solutions against decomposition. Nevertheless, the most stable AFm phases achieved in plain Portland cement systems result from maximising carbonate on the anion sites, with formation of either (or both) the anion-ordered (OH and CO<sub>3</sub>) phase, hemicarboaluminate, and the fully carbonate substituted monocarboaluminate. Fig 3 shows the coexistence of AFm phases at 25°C.

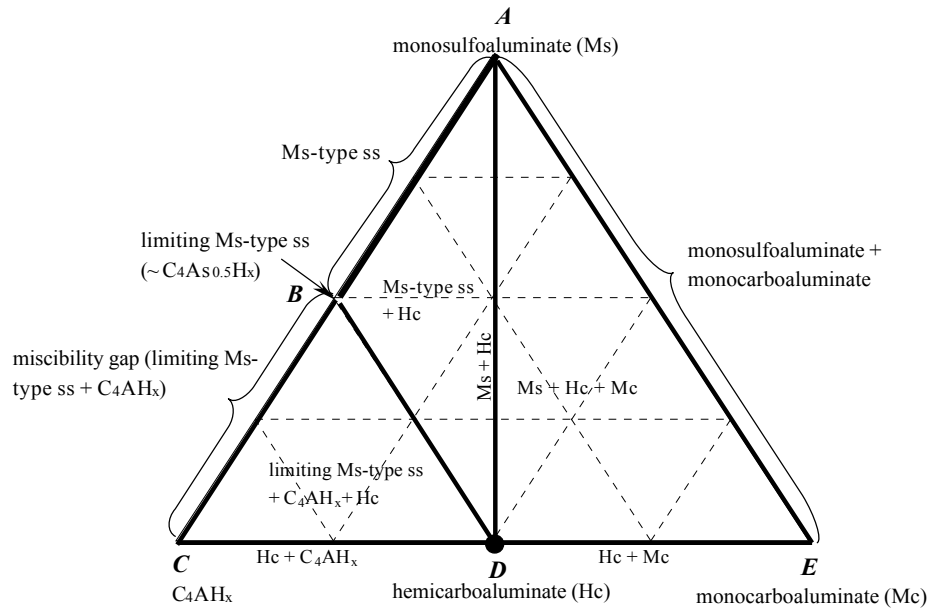


Fig. 3: Ternary phase diagram of AFm (hydroxide, carbonate and sulfate) coexistence

The disposition of the lines in the region of two coexisting AFm-phases, region ABD in Fig. 3, consists of lines radiating from point D towards AB; fixing the sulfate/carbonate/hydroxide-ratio will define the appropriate tie line. These calculations are, however, not directly applicable to commercial cements, where excess portlandite is present and the hydroxide content is independently variable owing to the presence of alkalis, effectively as hydroxides, dissolving in variable amounts of water.

#### Sulfate distribution in limestone-blended Portland cements

When calcium carbonate is blended with cement, perhaps by intergrinding limestone with cement, enough calcite will generally be present completely to displace hydroxide and sulfate from AFm resulting in formation of monocarboaluminate [6]. Calcite thus consumed must be considered as a reactive admixture: it is not a “filler”. Sulfate thus displaced from AFm instead appears as AFt; since the paste is generally undersaturated in gypsum, ettringite, not gypsum, is favoured. It seems paradoxical that calcite, itself free of sulfate, should, when added to cement, *increase* the amount of ettringite but this prediction is supported by experiment [16]. The resulting ettringite increases the molar volume of the cement solids and consumes liquid water. Thus controlled calcite additions show promise to improve the physical space filling of pastes and reduce free porosity: nomographs to facilitate calculation of the amount of calcite to optimise space-filling by the paste are presented in [7] and a typical calculation set is shown in Fig. 4 [17]. Note that the maximum specific volume of

cement paste solids is coincident with the maximum content of ettringite. This is a generic feature of the calculations: while the % added calcite to maximise ettringite varies with cement composition a maximum will occur for all cement compositions containing  $Al_2O_3$ . Although the ettringite-forming reaction yields an increase in volume, experiences show it tends not to be expansive. Simple calculations of  $\Delta V$ , the volume change indicate a potential for dimensional change but not an actual change. As shown by Herfort [18] the addition of low amounts of limestone to Portland cement resulted in a significant reduction of capillary porosity of the concrete and an increase of compressive strength.

a) mass balance changes

b) specific volume changes

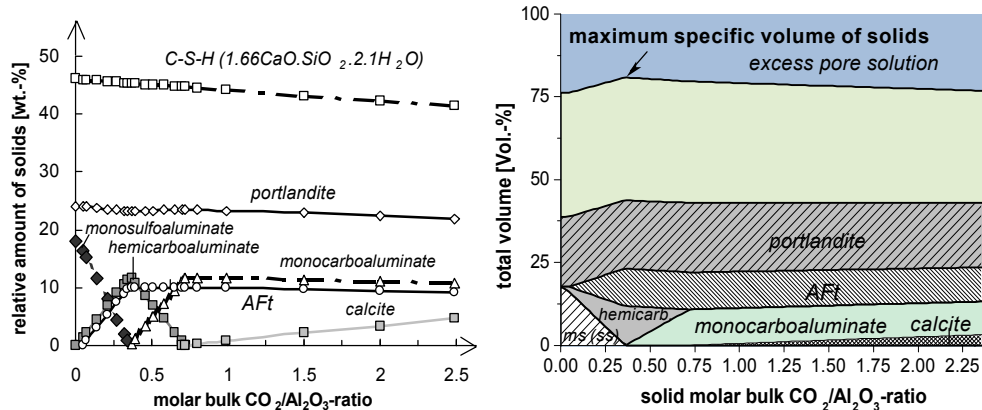


Fig. 4: Phase distribution (a) and specific volumes (b) of the phases of a model cement (initial composition: 68.5% CaO, 22%  $SiO_2$ , 4.5%  $Al_2O_3$  and 5%  $CaSO_4$ ) as functions of added calcite [17]

This calculation shows that the changing composition of the cement affects not only the amounts of AFm and AFt but also the chemistry of the AFm. But it is not just AFm and AFt that are affected: amounts of both free water and portlandite also change. Microstructural studies of cement hydration have tended to emphasise the nucleation and precipitation reactions occurring via solution but the impact of phase change reactions dissolution on microstructure, such as those driven by local consumption of portlandite, have not perhaps received the attention they deserve.

### Sulfate in C-S-H

Most analyses of industrial cement pastes disclose the existence of sulfate in C-S-H. However the state or condition of this sulfate is not clear: is it part of the C-S-H or does the C-S-H occlude crystallites of a second phase, presumably sulfate AFm, or both? And if the sulfate is part of the C-S-H, is it surface sorbed or in the bulk? Much of the evidence for sulfate in C-S-H is from electron beam analysis but with insufficient spatial resolution to answer these questions. However in recent decades experimental studies have measured sulfate uptake by

C-S-H. These utilise synthetic C-S-H and measure sulfate uptakes from solution and disclose the existence of much sulfate sorption contributing to the current belief that a significant part of the sulfate content of modern Portland cement is in C-S-H [19]. These laboratory experiments sometimes utilise unrealistically high concentrations of sodium sulfate (up to 300-600mM): in cements cured at 25°C, pore fluid sulfate contents may be high for the first day or two but thereafter, during the period when most C-S-H forms, pore fluid sulfate concentrations are more typically on the order of ~ 2 - 20 millimolar. Our studies have therefore concentrated on low sulfate concentrations, as more representative of commercial cements. For example Fig. 5 shows a sorption diagram of sulfate on C-S-H obtained from equilibrating C-S-H with calcium sulfate solutions of different initial sulfate concentrations in comparison with literature results in the range 0- 18 mmol SO<sub>4</sub><sup>2-</sup>/l.

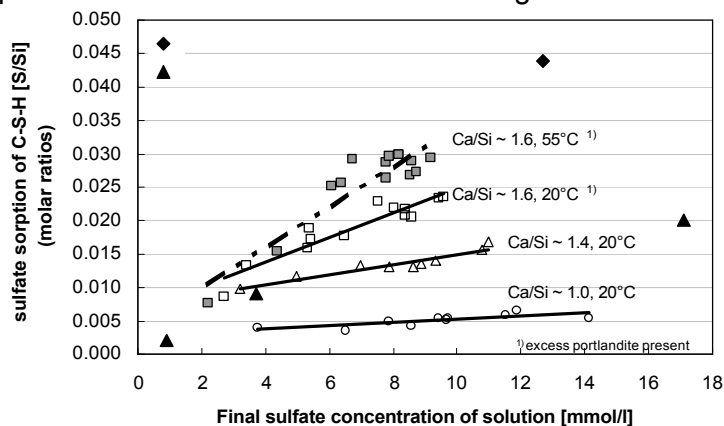


Fig. 5. Sulfate sorption of C-S-H

The binding capacity of C-S-H for sulfate is generally low ( $\leq 0.15$  mmol SO<sub>4</sub><sup>2-</sup> per gram D-dried C-S-H). The sulfate sorption depends on both Ca/Si-ratio of the C-S-H and temperature. With increasing Ca/Si ratio the sorption of SO<sub>4</sub><sup>2-</sup> increases. Thus in portlandite-saturated cements (Ca/Si of C-S-H ~ 1.7) a higher sulfate sorption will be observed than, for example, in slag-blended cements from which portlandite is absent and the Ca/Si-ratio of C-S-H is < 1.7. In general agreement with the literature [20], temperature increase enhances, but only slightly, sulfate sorption on C-S-H.

Preliminary experiments disclose that Al in C-S-H increases slightly the sulfate sorption. As noted, these studies are as yet incomplete and full quantification of the sulfate partition is still in progress. For example, Wieker and Herr [21] reported a significant increase of sulfate concentrations in the pore solution with increasing alkali content and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-ratios of the cement during heat curing at 60 - 100°C, which will influence the amount of adsorptive bound sulfate in C-S-H. However the available studies lead us to conclude that C-S-H in Portland cement does not sorb sulfate sufficient to preclude AFm formation, although it may help explain why AFt may be an ephemeral constituent.



### Temperature dependence of AFm/AFt phase development

Thus far, results have been shown for 25°C. However data are sufficient to sustain calculations at other temperatures. Calculations applicable to the range 0-30°C are shown in Fig. 6 as functions of two ratios: the sulfate and carbonate ratios. These are respectively the molar ratios of  $\text{SO}_3/\text{Al}_2\text{O}_3$  and  $\text{CO}_2/\text{Al}_2\text{O}_3$ . The numerical values of the defining ratios are obtained from the cement analysis, assuming complete reactivity. If reaction is incomplete, and the fractional reactivity can be measured by some experimental means, corrected values of the ratios can be used. C-S-H, if present, is inert as the compositions depicted cannot form thaumasite at the carbonate activities conditioned by the presence of carboaluminates or calcite [14]. The heavy line marks the boundary between calcite acting purely as a reactive admixture (regions I, II, III and IV) from those in which it is excess and behaves partly as a reactive admixture and partly as an inert filler (V, VI). Commercial compositions are unlikely to fall into region VI as cements are normally undersaturated with respect to gypsum. Note the occurrence at low carbonate ratios of hemicarboaluminate and the coexistence of both hemi- and monocarboaluminate with ettringite (AFt).

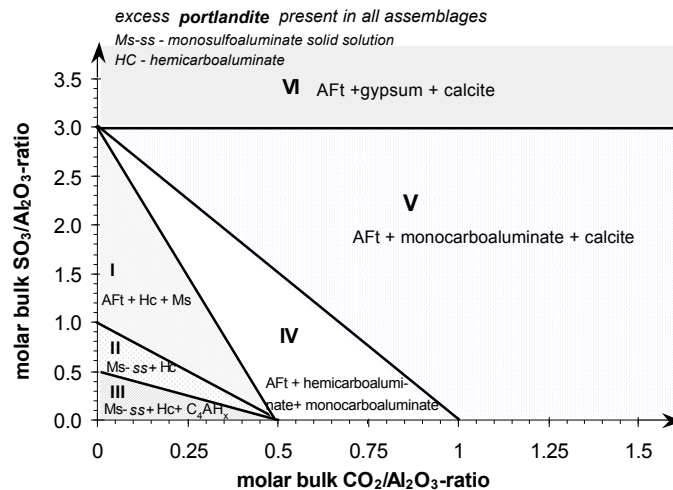


Fig. 6: Calculated phase assemblages relevant for hydrated Portland cements with varying initial sulfate ( $\text{SO}_3/\text{Al}_2\text{O}_3$ ) and carbonate contents ( $\text{CO}_2/\text{Al}_2\text{O}_3$ ) at 1-30°C (note  $\text{C}_4\text{AH}_x$  is metastable with respect to  $\text{C}_3\text{AH}_6$  and  $\text{Ca}(\text{OH})_2$  at temperatures  $> \sim 5^\circ\text{C}$ )

At or above 30°C, hemicarboaluminate becomes unstable in contact with monosulfoaluminate; phase relations are shown in Fig 7. Moreover, the increasing thermodynamic instability of  $\text{C}_4\text{AH}_x$  with rising temperature permits a stable region containing hydrogarnet to develop at low carbonate and sulfate ratios; hydrogarnet is only destabilised at higher sulfate and /or carbonate ratios. Whereas monosulfoaluminate, region II Fig. 6, may have about 50% of its theoretical sulfate replaced by hydroxide at  $< \sim 30^\circ\text{C}$  (compare with Fig. 2), these solid solutions

become increasingly unstable at higher temperatures [22]. The boundary between saturated and undersaturated compositions with respect to calcite as the saturating phase remains unchanged between 1-50°C. However at and above 50°C, hemicarboaluminate becomes unstable. Its disappearance with rising temperatures results in drastic changes to the patterns of coexistence, as shown in Fig. 8. At low carbonate and sulfate ratios, monosulfate and hydrogarnet coexist and are compatible with monocarboaluminate, but not hemicarboaluminate. The limit of calcite saturation now becomes independent of carbonate ratio and occurs at a fixed value of the sulfate ratio, 1.0.

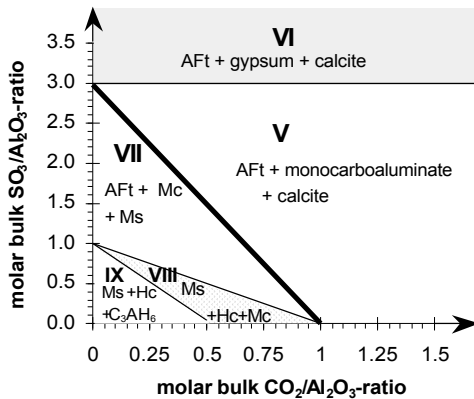


Fig. 7: Calculated phase assemblages relevant for hydrated Portland cements at 30°C-50°C

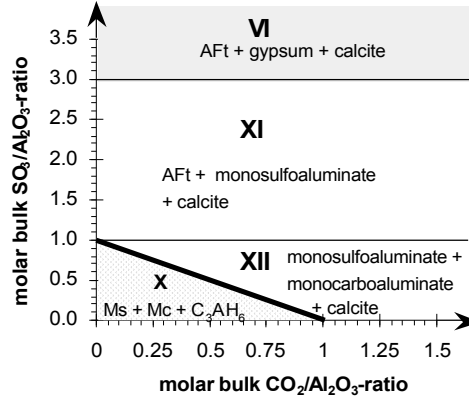


Fig. 8: Calculated phase assemblages relevant for hydrated Portland cements at 50°C-85°C

## Discussion

The role of sulfate on cement pastes mineralogy has been subject of hundreds if not thousands of papers, but relatively few generic conclusions emerge. We apply thermodynamic calculations. These are rapid and flexible and enable the strong interactions between added sulfate and carbonate to be quantified.

Much indirect evidence, as well as some direct evidence, shows that the internal mineralogy of a cement paste is much influenced by its sulfate content. Moreover, a sulfate balance is reached rapidly, in hours to months depending on the kinetics of the specific reaction, so that the internal state is reproducible but is of course, dependent on the composition of the reactive fraction of the paste. Temperature is also an important variable. It is shown that at least three characteristic thermal regimes exist, 10-30°C, 30-50°C and 50-85°C. Thus cements cured in warm and hot conditions are predicted to differ in mineralogy from those set at lower temperatures. The presented diagrams, Figs. 6-8, can be applied in two ways: to cements cured isothermally, or to cements undergoing thermal excursions. In isothermal cure, significant differences in mineralogy are predicted for warm curing, i.e., above 30°C. Since this temperature is frequently exceeded in some climate

conditions, it means that cements cured in a warm environment have potential for phase change if subsequently exposed to temperatures less than 30°C. On the other hand, warm cure >50°C, as may be encountered in accelerated cures or adiabatic cures of large masses, can introduce greater scope for sequences of phase changes including precipitation of calcite at elevated temperatures and its resorption in the course of cooling, or at some time thereafter. The concomitant potential for volume changes have yet to be explored but it is apparent that phase changes involving ettringite may not be the only factor set that needs to be considered to explain “DEF”.

It is also noteworthy that at ~ 25°C small amounts of sulfate destabilise hydrogarnet, ideally C<sub>3</sub>AH<sub>6</sub>, thereby combining much of the available alumina as ettringite rather than as hydrogarnet. The critical sulfate content necessary to destabilise hydrogarnet was calculated by Damidot, et al [23]: gypsum supplies sufficient soluble sulfate to destabilise hydrogarnet at normal hydration temperatures.

The C-S-H-phase is largely unaffected by temperatures in this range but does contain aluminate and sulfate. However the constitution of the aluminate phases is sensitive to temperature and, since the densities of aluminate hydrates vary, from ettringite (~1.77 g/cm<sup>3</sup>) to hydrogarnet (~2.52 g/cm<sup>3</sup>, but higher if silica substituted) have a major impact on the space-filling abilities of the paste. Calculations in support of this assertion show how heat curing unexpectedly favours formation of denser phases, thereby creating a potential for expansion upon a return to lower temperature service conditions.

Strong interactions occur between sulfate and carbonate. Thus modern cement pastes with carbonate “filler” (which may actually comprise a reactive admixture) differ in mineralogy, including sulfate mineralogy, from plain cements. Carbonate stabilises carboaluminates, which in turn, drive the incorporation of sulfate into ettringite. This effect, it is suggested, can be optimised to enhance space filling by the paste.

The ultimate goal of this research must be to link paste mineralogy to microstructure and in turn to engineering properties of concretes. This paper reports the first step, quantification of paste mineralogy.

### **Acknowledgement**

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