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The C-S-H gel of Portland cement mortars: Part I. The interpretation of energy-dispersive X-ray microanalyses from scanning electron microscopy, with some observations on C-S-H, AFm and AFt phase compositions

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Abstract

Scanning electron microscopy (SEM) microanalyses of the calcium-silicate-hydrate (C-S-H) gel in Portland cement pastes rarely represent single phases. Essential experimental requirements are summarised and new procedures for interpreting the data are described. These include, notably, plots of Si/Ca against other atom ratios, 3D plots to allow three such ratios to be correlated and solution of linear simultaneous equations to test and quantify hypotheses regarding the phases contributing to individual microanalyses. Application of these methods to the C-S-H gel of a 1-day-old mortar identified a phase with Al/Ca = 0.67 and S/Ca = 0.33, which we consider to be a highly substituted ettringite of probable composition $C_6A_2\bar{S}_2H_{34}$ or $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}(SO_4)_2[Al(OH)_4]_2$. If this is true for Portland cements in general, it might explain observed discrepancies between observed and calculated aluminate concentrations in the pore solution. The C-S-H gel of a similar mortar aged 600 days contained unsubstituted ettringite and an AFm phase with S/Ca = 0.125.

Keywords: Hydration; Early product; Calcium-silicate-hydrate (C-S-H); Ettringite; EDX

1. Introduction

Many investigations on cement pastes by energy-dispersive X-ray microanalyses of polished sections have been reported, among the more extensive being those of Harrisson et al. [1], Richardson and Groves [2], Bonen and Diamond [3] and Escalante-Garcia and Sharp [4]. They have provided information on the compositions of residual clinker phases, calcium-silicate-hydrate (C-S-H) and (to a lesser extent) hydrated aluminate or sulfoaluminate phases.

The hydrated material in cement pastes is conventionally divided into inner and outer products, defined approximately as those formed in space initially occupied by clinker grains and by water, respectively. Inner product is, in general, easily recognised in a backscattered electron (BSE) image in the scanning electron microscope (SEM), but the material commonly called outer product includes inner product of clinker grains too small to be distinguished at the level of resolution that can be obtained on a polished section. It is convenient to use the term "C-S-H" for the single phase and "C-S-H gel" for material that appears on a BSE image to be C-S-H but which may or may not also contain other phases admixed on a submicrometre scale. Both inner and outer products may include small quantities of other phases mixed with the C-S-H to form C-S-H gel.

For quantitative microanalysis in the SEM of phases in cement pastes or mortars, it is essential to use polished sections, to apply proper matrix corrections by the ZAF or other methods and to determine absolute contents of elements, which entails the use of standards and maintenance of a constant beam current. Although modern instrumentation permits the detection of oxygen, the results are insufficiently quantitative in the present context and oxygen is best calculated by stoichiometry. Microanalyses giving totals

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above 80–85% can then be rejected as probably including substantial contributions from anhydrous phases, although significant quantities of anhydrous material may still be present even for analysis totals lower than this figure. Normalised microanalyses are unsatisfactory because they do not allow this test to be made. Analysis totals below 80–85% usually indicate the absence of significant proportions of anhydrous material, but for the hydrated silicate, aluminate and sulfoaluminate phases in cement pastes, their values cannot be simply interpreted because partial dehydration of the hydrated phases occurs in the high vacuum and because X-ray output is reduced as a result of micro or nanoporosity [5,6]. It is therefore usual to work with atomic ratios, most often relative to Ca, since most of the phases have sufficient Ca to allow robust normalisation.

The interpretation of data for the outer C-S-H gel is not altogether straightforward because most microanalyses are of mixtures of up to four or even more phases. Plots of Al/Ca vs. Si/Ca [1] and S/Ca vs. Al/Ca have been widely used. Although such plots are useful, each represents a projection of a 3D space having as its axes the principal ratios, namely Si/Ca, Al/Ca and S/Ca, and it can be difficult to obtain from them a clear picture of the 3D distribution of data points. To a lesser extent, these problems can occur also with microanalyses of the inner product, as this tends to contain small proportions of phases other than C-S-H [2]. Triangular diagrams have also been used [3].

In this paper, we describe some methods (apparently new to analysis of cement hydration products) that we have developed in the course of work on mortars cured at 20 °C. These mortars were reference materials, which formed part of a wider study of delayed ettringite formation in mortars cured at higher temperatures. The microanalyses were made in the SEM on material characterised as C-S-H gel in the inner or outer product, i.e., material that from BSE images could have been C-S-H. Material clearly consisting of other phases, such as CH or sulfoaluminate phases, was, as much as possible, avoided.

2. Experimental

The cement used was high in Al_2O_3, SO_3 and alkalis: CaO 65.5, SiO_2 21.9, Al_2O_3 5.4, Fe_2O_3 2.2, K_2O 1.1, Na_2O 0.1, MgO 1.3, SO_3 3.9%, specific surface area (Blaine) 337 $m^2\ kg^{-1}$. X-ray microanalyses of the clinker showed minor arcanite ($K\bar{S}$) and calcium langbeinite ($KC_2\bar{S}_3$) in addition to the four major phases. Details of the preparation of the mortars, curing conditions and SEM techniques are given elsewhere [7,8]. The SEM microanalyses were made on polished sections from the cores of the prisms using an energy-dispersive X-ray analyser and an accelerating voltage of 15 kV. Analysed mineral standards (Microanalysis Consultants, St. Ives, Cambridgeshire, UK) were used and matrix corrections were applied using the ZAF procedure. Atomic ratios relative to Ca of elements other than Si, Al and S were with few exceptions (< 0.1). In a total of 214 microanalyses, Fe/Ca and Mg/Ca exceeded 0.05 in only 15 and 18 microanalyses, respectively, and the ratios for other elements were insignificant. Oxygen was calculated by stoichiometry and microanalyses giving totals >80% were rejected. The specimens were also examined by BSE imaging and, after rough grinding and sieving to remove most of the aggregate, by X-ray diffraction (XRD) and ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (NMR) [7].

3. Methods used for interpreting the microanalytical data

3.1. 2D plots

We have found plots of Si/Ca vs. Al/Ca and Si/Ca vs. S/Ca particularly helpful for determining C-S-H compositions. Fig. 1 shows these for the outer C-S-H gel of the 1-day-old

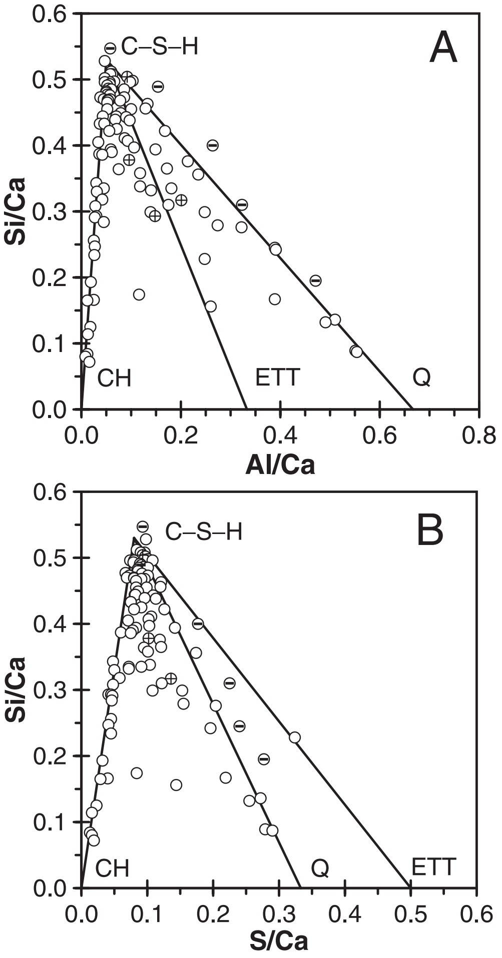

Fig. 1. Atom ratio plots of (A) Si/Ca vs. Al/Ca and (B) Si/Ca vs. S/Ca for the outer C-S-H gel of the 1-day-old mortar. Horizontal bars mark microanalyses for which significant silica contamination was suspected. Crosses mark microanalyses with Mg/Ca>0.1 or Fe/Ca>0.1 or both (not used in the calculations). ETT = ettringite; Q = AFt phase with Al/Ca = 0.667 and S/Ca = 0.333 (see text).

mortar. A few microanalyses had Si/Ca>0.6 and are not shown in the figures. We attribute these microanalyses to positions in which a substantial proportion of aggregate was present in the analysis volume. Subsequent calculations indicated that some other microanalyses probably included minor contributions from this source. These microanalyses are indicated in the figures.

The C-S-H has a higher Si/Ca ratio than any other hydrated phase present, so that in theory, at least, this ratio is the highest of all the observed values not invalidated by silica contamination. In reality, it is necessary to take into account the likelihood of experimental scatter, which will tend to make the true value lower than this maximum, and that none of the microanalyses represents pure C-S-H, which will tend to make it higher. For a mortar, silica contamination will tend to make it lower. There is no simple answer to these problems, which limit the precision with which the ratio can be determined and introduce an element of subjectivity into the interpretation. It is doubtful whether the Si/Ca or any other ratio relative to Ca can be reliably estimated to more closely than ± 0.01 (± 0.03 for Ca/Si). Microanalyses relating to mixtures of C-S-H with CH are valuable aids in determining the Si/Ca ratio, as they can be expected to lie close to a straight line on the plot that passes through the C-S-H and CH compositions. The data for the outer C-S-H gel were obtained before we realised the value of such microanalyses. Those of mixtures of C-S-H with sulfoaluminate phases can be used in the same way, even if the nature of the sulfoaluminate phase or phases has not been established, but are generally less useful due to the greater scatter of the data points.

When the Si/Ca ratio of the C-S-H and the line joining the C-S-H and CH compositions have been established, the other ratios are apparent from the appropriate plots.

3.2. 3D plots

As an aid to determining the nature and compositions of the sulfoaluminate and other phases, 3D plots are useful, since with the use of suitable software it is possible quickly to view the data from many angles. (We use the Surfer extension supplied with Igor Pro, Wavemetrics, Lake Oswego, OR, USA (http://www.wavemetrics.com)). This is equivalent to viewing multiple 2D projections. On a 3D plot, useful projections can be selected visually without the need for calculations.

Fig. 2A is a projection of a 3D plot of the microanalyses for the 1-day-old outer C-S-H gel. Si/Ca ratios are represented vertically, S/Ca ratios increase to the left and Al/Ca ratios increase into the plane of the figure. Four phases are identified. CH is represented by the open circle at the origin, and the plane containing it, C-S-H, and phase Q are seen edge on; nearly all the microanalyses lie on or close to this plane and are thus of material consisting essentially of one, two or all three of these phases. The nature of phase Q, a substituted ettringite, is discussed in Section 5.1.1. The fourth phase, unsubstituted ettringite, lies on the high sulfur side of this plane, and only one microanalysis could be of material in which it is a major constituent. Two microanalyses with Si/Ca ratios of approximately 0.7, mentioned in Section 3.1, are omitted from the plot, since they probably represent material containing substantial proportions of aggregate.

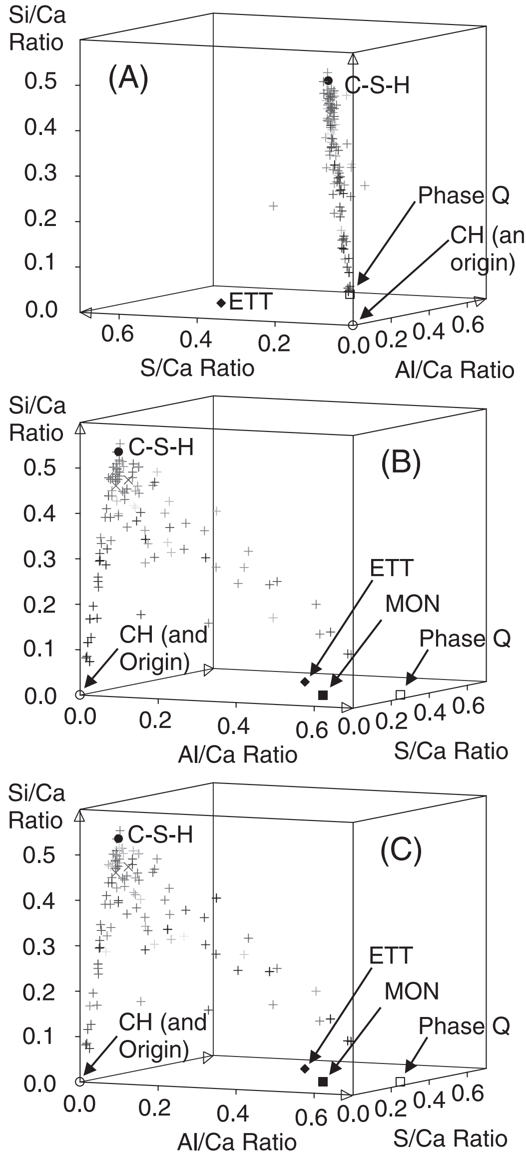

Fig. 2. 2D projections of 3D atom ratio plot for the outer C-S-H gel of the 1-day-old mortar. ETT = ettringite; Q = AFt phase with Al/Ca = 0.667 and S/Ca = 0.333 (see text); MON = monosulfate with Al/Ca = 0.5 and S/Ca = 0.25. (A) Projection viewed parallel to the CH, C-S-H and phase Q plane. (B) Projection viewed perpendicular to this plane, with Fe/Ca ratios indicated by grey levels ranging from black (0) to palest grey (≥ 0.02). (C) As in (B), but with grey levels indicating the Mg/Ca ratios.

Fig. 2B shows the same set of microanalyses after rotation by 90° about the (vertical) Si/Ca axis, so that Al/Ca ratios increase to the right and S/Ca ratios increase into the paper. We can now observe two subsets of points. A vertical series of points, on the left of the figure, represents mixtures of CH and C-S-H, while the more diffuse diagonal series of points running from top left to bottom right represents mixtures of C-S-H with a sulfoaluminate phase. On this projection, we also show monosulfate, another possible sulfoaluminate phase for which Al/Ca = 0.5 and S/Ca = 0.25. However, the points in this series do not extrapolate to monosulfate but rather to the position noted for phase Q. Most of the points in both series cluster towards C-S-H, indicating the presence of small quantities of the other phases embedded in the C-S-H.

A further development of 3D plots is also illustrated by Fig. 2, in that the grey level of the points is made to track a fourth compositional ratio. In Fig. 2B, this is scaled so that points with Fe/Ca = 0 are black while points with Fe/Ca $\geq$ 0.02 are grey, with intermediate values having intermediate grey levels. This can be more clearly demonstrated in colour, if available. The points close to CH are largely black, indicating that Fe does not associate with CH. Some Fe is associated with the C-S-H, with many points in this region being grey rather than black. This could arise either from the presence of Fe in the C-S-H, from admixture of the latter with a phase relatively high in this element, or from a combination of the two. The highest Fe/Ca ratios seem to be found for microanalyses containing mixtures of C-S-H and phase Q, which are lightest. Fig. 2A has similar grey levels shown, although the projection is such that these are not so easily observed.

Fig. 2C shows the same data set, but with the grey scale now indicating the Mg/Ca ratios using the same procedure and values as for Fe in Fig. 2B. In this case, the Mg appears to be randomly distributed, showing no association with any particular compositions. In principle, a fifth ratio can be represented by the size of the marker, but in practice the larger markers become visually dominant and so this procedure is not advised.

The 3D plots can also be used to select interesting or useful 2D projections, which can then be plotted analytically using normal graphing software. An example of this is described in Section 4.2.

3.3. Solution of simultaneous equations

A hypothesis regarding the nature and compositions of the phases present may be tested by setting up a set of linear simultaneous equations for each microanalysis. In the simplest case, there is one equation for each of the four principal elements (Ca, Si, Al and S), having the form

$$\Sigma a_{ij}x_j = b_i \qquad (1)$$

where the summation is for four phases assumed to be present, the coefficient a_{ij} is the atomic ratio relative to Ca of element i in phase j, x_j is the fraction of the total Ca that is present in phase j and b_i is the atomic ratio of element i to Ca in the microanalysis. The equations may be solved by inverting the matrix of a_{ij} coefficients by an elimination method [9] and the x_j's are then calculated using set of expressions of the type

$$x_j = \Sigma a_{ij}^{-1} b_i \qquad (2)$$

where there is one equation for each phase, the summations are for the chemical elements and a_{ij}^{-1}'s are the appropriate elements of the inverse matrix. Using a spreadsheet program, this second step can be carried out rapidly for a large number of microanalyses. The main tests of the starting assumptions are that they should be chemically reasonable both theoretically and in relation to the data and that none of the calculated x_j's should be significantly negative. This is equivalent to stating that in a 3D plot all the points lie within or close to the edge of the volume with apices at the pure phases chosen. Where two phases have similar compositions, the calculated x_j values may be very sensitive to small changes in composition of the analysed data point. The complete procedure may be repeated for various sets of starting assumptions, each represented by a set of a_{ij} coefficients, and that best satisfying these tests selected as the most probably correct. Comparison of the results for different input assumptions may suggest changes in the atomic ratios assumed for the C-S-H. In these and other calculations, microanalyses with either Mg/Ca>0.1 or Fe/Ca>0.1 were not used because we do not know how best to deal with them. We find no grounds for regarding more than a minor fraction of the Fe as being equivalent to Al. Microanalyses in which silica contamination was suspected were also not used. They comprise those with Si/Ca>0.06 and those indicated in Figs. 1 and 5.

3.4. Least-squares procedures

If the number of useful atom ratios exceeds the number of phases, a least-squares procedure may be used. As an example, we may consider the estimation of ettringite in a mixture assumed to contain ettringite, CH and C-S-H. All quantities are expressed in atoms per atom of Ca in the mixture. The Si is assumed to be present entirely in the C-S-H, and the quantities of Ca, Al and S in this phase are thereby calculated. By deducting the quantities of Al and S in the C-S-H from the observed Al/Ca and S/Ca ratios, the quantities in the ettringite are obtained, represented as a and s, respectively, and x as the quantity of Ca present in ettringite, which has to be estimated. The errors, Äa and Äc, in the Al and S contents are $a - x/3$ and $s - x/2$, respectively. Squaring each of these quantities, adding the results together, differentiating with respect to x and setting the result to zero gives the result

$$x = 6(2a + 3s)/13 \qquad (3)$$

The Ca not present in C-S-H or ettringite is assumed to be present in CH.

4. Results

4.1. The outer C-S-H gel in the 1-day-old mortar

The plots of Si/Ca vs. Al/Ca and S/Ca (Fig. 1) indicated that the C-S-H had Si/Ca = 0.53, Al/Ca = 0.05 and S/Ca = 0.08. The very high value for S/Ca was surprising but was strongly supported by the microanalyses of mixtures of C-S-H with CH, which on the Si/Ca vs. S/Ca plot lay close to a line passing through the C-S-H composition stated above. We think it possible that the C-S-H in this mortar was closely mixed with an approximately constant proportion of a calcium sulfate phase. This hypothesis requires further investigation, but for the present purpose, it is convenient to treat any such calcium sulfate as being part of the C-S-H. Some of the sulfate in the C-S-H can be attributed to evaporation of the pore solution, but calculations based on the probable quantity and composition of this constituent showed that it must be an almost negligible proportion.

We expected that this 1-day-old mortar would have contained unsubstituted ettringite, but the plot of Si/Ca vs. S/Ca shows only one microanalysis that clearly suggests the presence of this phase and that of Si/Ca vs. Al/Ca showed many microanalyses too high in Si or Al to be compatible with its presence. The possibility that the data could be explained by the presence of strätlingite (C_2ASH_8) was considered, but trial calculations showed that neither this nor any other AFm phase could be present as a major constituent. On the other hand, examination of the plots suggested the presence of a phase having Al/Ca ~0.67 and S/Ca ~0.33, which was tentatively called “Q.” This was also apparent on a plot of S/Ca vs. Al/Ca (Fig. 3). As is shown later, these ratios are consistent with the hypothesis that Q is a highly substituted ettringite or AFt phase. Calculations by solving simultaneous equations showed that most of the microanalyses could be explained reasonably satisfactorily, assuming the phases present to be CH, C-S-H, phase Q and ettringite, though only one microanalysis indicated any substantial proportion of this last phase. Six microanalyses gave significantly negative values for the fraction of the Ca present in ettringite (as low as −0.103 in one case). For these microanalyses, much better results were obtained by substituting an AFm phase with Al/Ca = 0.5 and S/Ca = 0 for the ettringite; this could possibly have been mono- or hemicarbonate. The microanalyses in question were all ones showing S/Ca ratios significantly below the general trend, which is apparent on Fig. 3. They are also visible on the 3D plot (Fig. 2A) where they lie to the right of the plane containing C-S-H, CH and phase Q. Fig. 4 shows the results of the calculations.

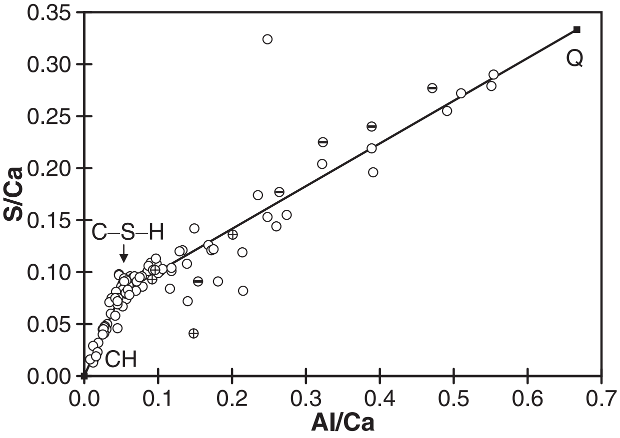

Fig. 3. Atom ratio plot of S/Ca vs. Al/Ca for the outer C-S-H gel of the 1-day-old mortar. Conventions as in Fig. 1.

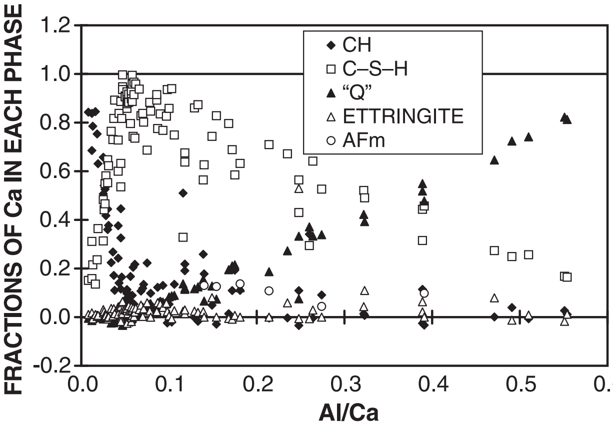

Fig. 4. Fractions of the Ca assigned to each phase in the outer C-S-H gel of the 1-day-old mortar. Q = AFt phase with Al/Ca = 0.667 and S/Ca = 0.333 (see text). The AFm phase has Al/Ca = 0.5 and S/Ca = 0.

XRD of the mortar, using a fraction from which the aggregate had been largely removed, showed peaks compatible with ettringite [7]. ^{27}Al NMR showed peaks compatible with ettringite and with tetrahedrally coordinated Al [7]. The BSE image showed the presence of ettringite [7]. It must be noted that the XRD and NMR results relate to the entire cement paste, whereas the microanalyses relate only to the C-S-H gel.

4.2. The outer C-S-H gel in the 600-day-old mortar

The plots of Si/Ca vs. Al/Ca or S/Ca (Fig. 5) suggest that the C-S-H has Si/Ca, Al/Ca and S/Ca ratios of 0.55, 0.04 and 0.05, respectively. Both 3D plots and solution of equations showed that the microanalyses correspond most closely to mixtures in varying proportions of C-S-H of this composition with CH, unsubstituted ettringite and an AFm phase with Al/Ca = 0.5 and S/Ca = 0.125. The AFm phase was not unsubstituted monosulfate ($C_4A\bar{S}H_{12}$). Fig. 6 shows the results of the calculations. Trial calculations and 3D plots viewed from various angles gave no indication that the S/Al ratio of the AFm phase varied with the Al/Ca ratio of the region analysed.

Three earlier studies on pure systems have shown that a silicate analogue of monosulfate can be prepared and that its

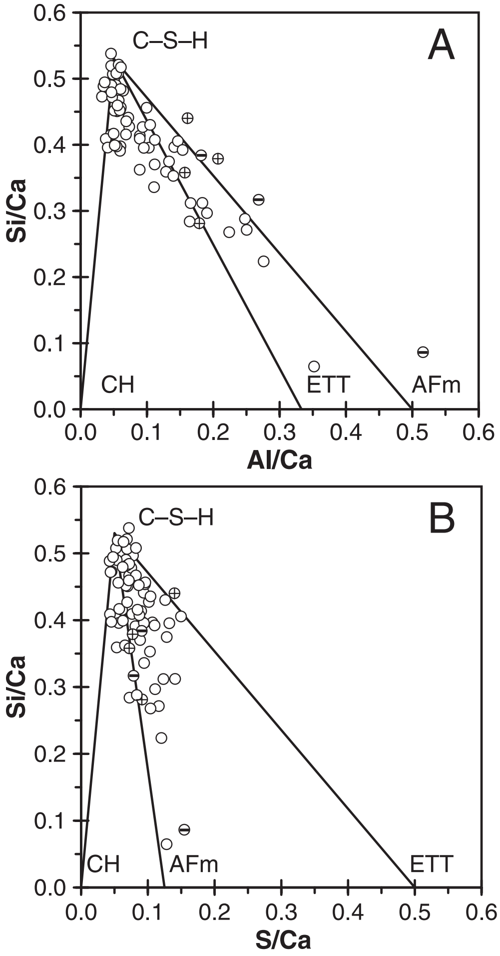

Fig. 5. Atom ratio plots of (A) Si/Ca vs. Al/Ca and (B) Si/Ca vs. S/Ca for the outer C-S-H gel of the 600-day-old mortar. The AFm phase has Al/Ca = 0.5 and S/Ca = 0.125. Conventions as in Fig. 1.

cell parameters are similar to those of monosulfate [10–12], but one showed it to be unstable at ordinary temperatures [12]. We considered the alternative hypothesis that the AFm phase was monosulfate in which the sulfate was partly replaced by silicate, with S/Ca = 0.15 and Si/Ca = 0.10. Fig. 7 is a projection of a 3D plot chosen to differentiate between the two hypotheses. All microanalyses representing combinations of C-S-H, CH and ettringite lie on or close to the plane containing the Si/Ca axis and normal to that of the paper and those in which the AFm phase is also present lie to the right of it. The silicate-free composition with S/Ca = 0.125 for the AFm phase provides the more satisfactory explanation of the microanalyses.

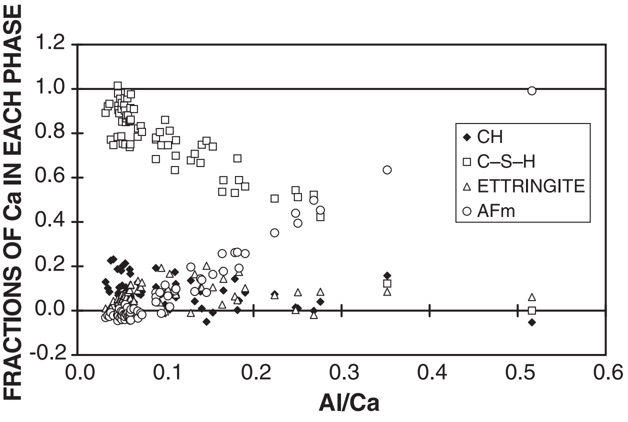

Fig. 6. Fractions of the Ca assigned to each phase in the outer C-S-H gel of the 600-day-old mortar. The AFm phase has Al/Ca = 0.5 and S/Ca = 0.125.

These conclusions are consistent with the evidence from XRD, NMR and BSE imaging [7]. XRD showed the presence of ettringite at 400 days, and ^{27}Al NMR showed peaks attributable to octahedrally coordinated Al in both ettringite and an AFm phase and to tetrahedrally coordinated Al, which could have been largely present in C-S-H. The AFm phase was evidently too poorly crystalline for detection by XRD. Ettringite was also observed in BSE images. As with the 1-day-old mortar, the XRD, NMR and BSE examinations relate to the cement paste as a whole, whereas the microanalyses relate only to the C-S-H gel as defined earlier.

4.3. The inner C-S-H gel (1- and 600-day-old mortars)

In contrast to the outer C-S-H gel, the inner C-S-H gel approximates to being C-S-H free from other phases. However, inner C-S-H gel contains minor inclusions of other phases [2] and in the case of the 1-day-old material the rims around the clinker grains are too narrow to ensure that microanalyses that exclude anhydrous residues do not include outer product. Therefore, the microanalyses were processed by the same methods as were used for the outer C-S-H gels.

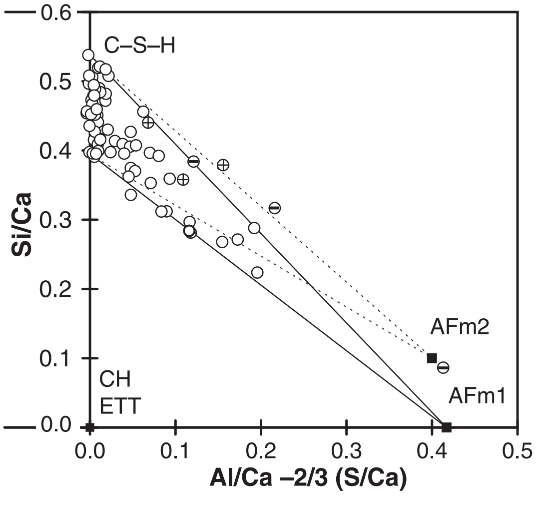

Fig. 7. Projection of a 3D plot onto a plane having as its axes [Al/Ca – 2/3 (S/Ca)] and Si/Ca. The C-S-H, CH and ettringite compositions all lie on or close to the plane containing the Si/Ca axis and normal to that of the paper. AFm1 has Al/Ca = 0.5, S/Ca = 0.125 and Si/Ca = 0. AFm2 has Al/Ca = 0.5, S/Ca = 0.15 and Si/Ca = 0.10.

The plots for the 1-day-old mortar (Fig. 8) showed C-S-H, with CH and a sulfoaluminate phase that could not be precisely identified. They indicated that the C-S-H had Si/Ca = 0.50, Al/Ca = 0.06 and S/Ca = 0.06. The relatively low value for Si/Ca is suspect, as even the highest observed values in this mortar could have represented mixtures with CH. Least-squares calculations were made as described in Section 3.4, assuming the phases present to be C-S-H, CH and ettringite or C-S-H, CH and Q. Both gave satisfactory results, so that it was not possible to prefer one hypothesis to the other. The calculations confirmed that all the 13 microanalyses were predominantly of C-S-H; the contents of CH were 0.00–0.23, and those of Q or ettringite were 0.00–0.10, each expressed as Ca/total Ca. The contents of CH decreased with increasing bulk Al/Ca ratio and those of Q or ettringite increased.

Plots of Si/Ca vs. Al/Ca and S/Ca for the 600-day-old mortar (Fig. 9) show mainly C-S-H with Si/Ca = 0.53, Al/Ca = 0.045 and S/Ca = 0.035. The C-S-H appears to be mixed in some cases with CH or a sulfoaluminate phase or both. Equations were set up and solved to test various hypotheses regarding the sulfoaluminate phases. A reasonable solution was obtained assuming the presence of C-S-H, CH, ettringite and AFm phase, assuming the latter to have S/Ca = 0.125 as in the outer C-S-H gel. Of the 25 microanalyses, 3 showed significant contents of CH (0.24–0.40 Ca/total Ca) and 2 showed barely significant contents of ettringite (~0.05 Ca/total Ca); little or no AFm phase was indicated.

4.4. Iron and magnesium

The Fe/Ca ratios in the outer C-S-H gel were ~0.01 for particles high in C-S-H or in the AFt phase, Q, rising irregularly to 0.05 for those high in AFm phase in the 600-day-old mortar. These results suggest that the mean Fe/Al ratio is ~0.1 in the AFm and much below 0.1 in the AFt phase. Qualitatively, at least, this is compatible with prior observations that most particles of both these types contain little or no Fe, though in a few the Fe/Al ratios may be substantial. The results further suggest that only a small proportion of the Fe released from the clinker phases enters either AFm or AFt phase. A few particles had relatively high Fe/Ca ratios (up to ~0.2). Typically, these had Al/Ca = 0.1–0.2, Si/Ca = 0.3–0.4 and S/Ca = ~0.1. These data are too scattered to justify detailed interpretation but suggest the presence of a hydrogarnet phase. This supports the observations of Copeland et al. [13] and Rodger and Groves [14] that a hydrogarnet or hydrogarnet precursor is a major hydration product of the ferrite phase.

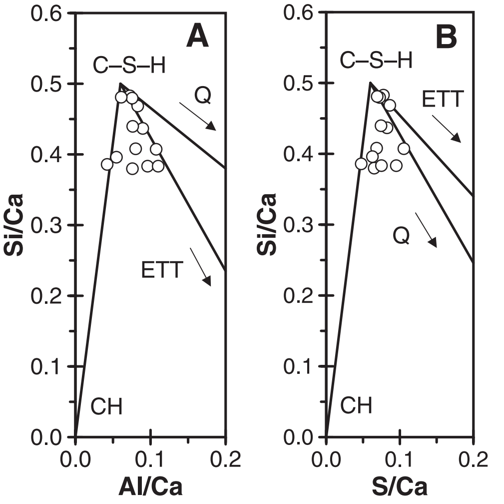

Fig. 8. Atom ratio plots of (A) Si/Ca vs. Al/Ca and (B) Si/Ca vs. S/Ca for the inner C-S-H gel of the 1-day-old mortar. ETT = ettringite; Q = AFt phase with Al/Ca = 0.667 and S/Ca = 0.333 (see text).

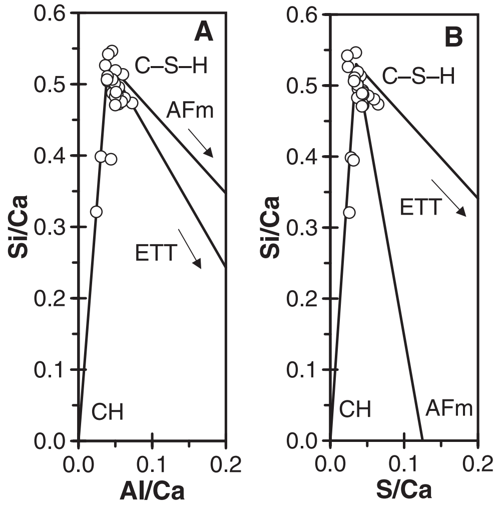

Fig. 9. Atom ratio plots of (A) Si/Ca vs. Al/Ca and (B) Si/Ca vs. S/Ca for the inner C-S-H gel of the 600-day-old mortar. ETT = ettringite; AFm has Al/Ca = 0.5 and S/Ca = 0.125.

The mean Mg/Ca ratios for the outer C-S-H gel were ~0.02. Most were ~0.01, but a few were higher (up to 0.14). In agreement with the observations of Richardson and Groves [2], the mean ratios for the inner gels were higher (0.04 ± 0.02), some exceeding the Al/Ca ratios (Mg/Al = 0.08–0.94 at 1 day and 0.42–1.15 at 600 days). We are uncertain as to the implications of this for the interpretation of the microanalyses. Richardson and Groves [2] reported that small amounts of a Mg-Al phase, presumably of hydrotalcite type, occurred in the inner product. Our own results, for both 1- and 600-day-old mortars, showed some correlation between the Mg/Ca and the Al/Ca ratios, with slopes indicating Mg/Al ratios of ~2, which might suggest that all of the Mg is present in such a phase. If this is correct, a substantial proportion of the Al that we have assumed to be in the C-S-H is really in the hydrotalcite-type phase. Against this hypothesis, ^{29}Si NMR results, which will be submitted for publication in a subsequent paper, suggest that the Al/Si ratios assigned to the C-S-H from microanalytical data are low rather than high. This matter requires further investigation.

5. Discussion

5.1. AFt phases

5.1.1. General

The composition of the phase described above as "Q" is consistent with an AFt phase in which one half of the channel sites are occupied by sulfate and the others by hydroxoaluminate, giving the ionic constitution $\{Ca_6[Al(OH)_6]_2{\cdot}24H_2O\}(SO_4)_2[Al(OH)_4]_2$ and the oxide formula $C_6A_{22}\bar{S}_2H_{34}$.

Such a phase would give an XRD pattern closely similar to that of ettringite and probably indistinguishable from it in a cement paste or mortar, and the chemical shift of the octahedral Al peak in the ^{27}Al NMR spectrum would probably be close to that of ettringite. AFt phases containing $Al(OH)_4^-$ in the channel sites do not appear to have been previously reported, but ones containing the analogous $B(OH)_4^-$ ion are well established [15–17].

For approximately 50 years, it has been widely supposed that the hydrated sulfoaluminate phase formed during the first days of Portland cement hydration is ettringite ($C_6A\bar{S}H_{32}$). Examination of the literature shows, however, that while the evidence for an AFt phase is convincing the evidence for its composition is scanty. The AFt structure admits of substantial variations in composition that have only minor effects on XRD patterns and other properties on which the identifications have been based. The composition assigned to it in cement pastes at early ages has been based almost entirely on the similarities in properties to the unsubstituted phase of natural or synthetic origin for which the composition is well established rather than on direct microanalyses of the paste phase itself.

5.1.2. Previous microanalyses

Only a few previous microanalyses of the AFt phase in Portland cement pastes appear to have been reported. Lachowski et al. [18], Diamond and Lachowski [19] and Taylor et al. [20] reported transmission electron microscopy (TEM) microanalyses of particles present in ground and redispersed cement pastes and characterised as AFt. In general, the microanalyses indicated compositions near to that of unsubstituted ettringite, but usually with significant deficiencies in S and sometimes in Al. Si was often found, but Fe contents were low. These results are suspect, because the particles could have contained C-S-H and because beam damage could have caused some loss of material.

Richardson and Groves [2] reported TEM microanalyses of the AFt phase in Portland cement pastes aged 24 h to 3.5 years obtained on ion-thinned sections. Various precautions were taken to minimise damage during thinning and subsequent examination. Most of the microanalyses corresponded to mixtures of partially dehydrated AFt phase with varying proportions of C-S-H. In general, the AFt phase was not significantly deficient in sulfate relative to ettringite and did not contain Si. Only about 30% of the microanalyses showed a detectable Fe content; for these, the Fe/Al ratio was 1:3.

Bonen and Diamond [3] reported SEM microanalyses of a 3-day-old cement paste studied on a polished section. They characterised eight areas of hydration products as mixtures of ettringite, with varying deficiencies of sulfate, together with C-S-H. Recalculation from their data indicates that while four of the microanalyses can be thus explained, the others would require also the presence of CH. All could be explained assuming them to be mixtures of C-S-H, CH and Q, with either ettringite or an AFm phase.

5.1.3. Other relevant data

Midgely and Rosaman [21] were probably the first to question that the AFt phase in cement pastes has the ettringite composition. They concluded from thermal analysis data that its composition was essentially that of unsubstituted ettringite at early ages but that over a period of weeks or months the sulfate was progressively substituted by hydroxyl. Bailey and Hampson [22] discussed and extended earlier works [23–25] on the reactions between C_3A, gypsum and water. Their approach was based on TEM, solution compositions and thermodynamic reasoning. They concluded that the ettringite formed was highly deficient in both calcium and sulfate and that it had a limiting composition of approximately $Ca_4[Al(OH)_6]_2SO_4{\cdot}xH_2O$. The solubility product of the AFt phase formed at pH 12.5 was substantially higher than that of the phase formed at pH 11.5. The Al/Ca and S/Ca ratios implied by this formula are 0.5 and 0.25, respectively, which are relatively near those of 0.67 and 0.33 that we have found for Q.

Damidot and Glasser [26] noted that the invariant concentrations calculated from thermodynamic data for the CaO-Al_2O_3-$CaSO_4$-K_2O-H_2O system generally agreed well with experimentally determined values, except in the case of Al_2O_3 for which the observed concentrations were consistently higher. Kelzenberg et al. [27] found that this was also true for the pore solutions in Portland cement pastes during the first 2 h after mixing. During the latter part of this period, when the solid phases included calcium hydroxide, ettringite and gypsum, the observed Al_2O_3 concentrations were several orders of magnitude higher than those calculated. If, as our results suggest, the AFt phase formed in the early hydration product is at least in part Q and not ettringite, this might account for the discrepancy between observed and calculated concentrations.

Several investigations on the early hydration reactions of C_3A–gypsum mixtures or Portland cement have given indications of the formation of an initial product, formed before ettringite [23,28–31]. The most detailed results are those of Christensen et al. [31], who followed the reaction of C_3A, $C_{12}A_7$ or CA with deutero-gypsum and D_2O using a neutron diffraction method that allowed the wet paste to be studied in real time. A precursor phase to ettringite was found mainly in products formed at 50 or 60 °C but also in short runs at temperatures up to 120 °C. The neutron diffraction powder pattern was not unequivocally indexed, but the authors considered it possible that the phase was a metastable modification of ettringite with different positions for the OD^- and D_2O groups. This and other reported ettringite precursors could possibly be identified with Q, and further investigation of them would be of much interest.

5.2. AFm phases

Only a few previous investigations on the composition of the AFm phases in normally cured cement pastes have been reported. Harrisson et al. [1] reported 31 SEM microanalyses of the AFm phase in Portland cement pastes, alone or mixed with C-S-H. Most had S/Ca ratios significantly below that of monosulfate, with minor contents of Si and a mean Fe/Ca ratio of 0.02; four microanalyses approximated to monosulfate. Several subsequent investigations of mature cement pastes by this method [4,32,33] have shown the monosulfate in them to be substantially free from replacements of the sulfate or other constituent ions. In contrast, Bonen and Diamond [3] found the AFm phase in a 3-day-old paste to be monosulfate markedly deficient in sulfate, with a mean S/Ca ratio of 0.13. Its mean Fe/Al ratio was 0.07.

Lachowski et al. [18] and Taylor et al. [20] made TEM microanalyses of AFm phases in ground and redispersed material. They reported that these had monosulfate compositions substantially modified by substitutions of sulfate by hydroxide and by Si- and Al-containing anions and that varying proportions of K, Mg and Fe could also be present. As with the corresponding studies on AFt phases, these results are suspect.

Richardson and Groves [2] reported EPMA and TEM microanalyses of relatively large crystals of AFm phases in Portland cement pastes aged from 1 day to 3.5 years. The TEM microanalyses were made on ion-thinned sections. There did not appear to be any relationship between composition and age. All were deficient in sulfate relative to monosulfate, the S/(Al + Fe) ratios being 0–0.15 or 0–0.08 as found by TEM and microprobe analyses, respectively; the corresponding ranges of Fe/(Al + Fe) ratio were 0–0.31 and 0–0.36.

These results do not show any clear pattern of variation in the S/Ca ratio either with age or with cement composition. The deficiencies in sulfate relative to the monosulfate composition, also observed in the present work, could most simply be attributed to solid solution with C_4AH_x, equivalent to substitution by hydroxide. Carbonate substitution is another possibility and could explain both the absence of any apparent relation to cement composition or age and the otherwise puzzling coexistence in the present case of ettringite with an AFm phase relatively low in sulfate; small amounts of carbonate have a disproportionate effect in replacing monosulfate by ettringite and carbonate-containing AFm phases [34]. XRD gave no evidence of either mono- or hemicarbonate, but the low degree of crystallinity of the AFm phase could be consistent with a disordered structure in which interlayers containing sulfate, hydroxide and carbonate were all present. While the detector used had a thin window and could thus detect carbon, the samples were stabilised in an epoxy resin of high carbon content and also coated with carbon; thus, it was not possible to test if phases were carbonated.

6. Conclusions

1. New procedures that we have found useful in the interpretation of X-ray microanalyses of Portland cement pastes include (a) plots of Si/Ca vs. Al/Ca, S/Ca and other ratios, (b) 3D plots having as their axes Si/Ca, Al/Ca and S/Ca, (c) addition of colour to plots to allow correlation with an extra interatomic ratio, (d) solutions of four equations for four unknowns to test and quantify hypotheses regarding the hydrated phases contributing to a given microanalysis and (e) least-squares calculations having the same objective in cases where only three phases are present.
2. In a 1-day-old mortar, the hydration products detected by X-ray microanalysis in the outer C-S-H gel were C-S-H, CH, ettringite (minor) and a phase with Al/Ca = 0.67 and S/Ca = 0.33, which we call Q and consider to be a highly substituted ettringite of probable composition $C_6A_2\bar{S}_2H_{34}$ or $\{Ca_6[Al(OH)_6]_2\cdot 24H_2O\}(SO_4)_2[Al(OH)_4]_2$, i.e., of ettringite structure but with sulfate and hydroxoaluminate ions in the channel sites. Much of the phase commonly described as ettringite that is present at early ages may really be of this composition. This hypothesis might explain discrepancies between observed alumina concentrations in the pore solution and those calculated from phase equilibria, reports of major variations in ettringite composition and properties with pH of formation and observations of a phase formed as a precursor to ettringite.
3. In a 600-day-old mortar of the same cement, the hydration products found in the outer C-S-H gel by X-ray microanalysis were C-S-H, CH, ettringite and an AFm phase similar to monosulfate but deficient in S (S/Ca = 0.125). The deficiency in interlayer anions could have been made good by hydroxyl or carbonate or both. In the literature, there appears to be no relation between S/Ca ratio of the AFm phase and either age or cement composition. This tends to favour the hypothesis that the sulfate deficiency is at least partly balanced by carbonate, a hypothesis that might also account for the otherwise puzzling coexistence of ettringite with an AFm phase low in sulfate.
4. The mean Fe/Al ratio in the AFm phase was found to be ~ 0.1 and that in the AFt phases was much below 0.1. Only a small proportion of the Fe in the hydration products enters either of these products; more may enter a hydrogarnet-type phase.

5. Our results were obtained on mortars made from a single cement. Caution is needed in generalising from them in the absence of further data.

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