JOURNAL OF MATERIALS SCIENCE **30** (1995) 3856–3862

The formation, stability and microstructure of calcium sulpoaluminate hydrates present in hydrated cement pastes, using *in situ* synchrotron energy-dispersive diffraction

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Synchrotron radiation–energy dispersive diffraction has been used for the first time to study the formation and stability of the calcium sulphoaluminate hydrates in hydrated Portland cement pastes. By using this technique it has also been possible to investigate microstructural and compositional characteristics of the ettringite (AFt) phase. The longer term slow development of the monosulphate (AFm) phase has also been monitored, although the characterized content is quite low. Differences were detected between the microstructural characteristics of the AFt phase formed in the high ferrite sulphate-resisting-type cement pastes, as compared with the equivalent phase formed from the ordinary Portland cements. These differences were especially significant at later hydration times and have been ascribed to compositional differences between the ettringite (AFt) formed from the two different types of cement.

1. Introduction

As part of a more general collaborative project between Norway and Sweden the hydration behaviour of four works' Portland cement has been studied. We here report results obtained using synchrotron radiation–energy dispersive diffraction (SR–EDD) to investigate the formation behaviour, stability and compositional changes, etc., of the ettringite (in cement chemistry, Ca = C, AL – A, Fe = F, Si = S) (AFt) and monosulphate (AFm) phases present in the still hydrating, wet cement pastes. (The term ettringite has come to be used in a generic sense to represent the AFt phases formed as a result of C_3A or C_4AF hydration with gypsum in water. This same nomenclature is also used to describe the AFt phase(s) formed in Portland cement [1]. It is, however, incorrect in the strictest sense to define any phase as ettringite, other than one with the structural formula $[Ca_3Al(OH)_6 \cdot 12H_2O]_2(SO_4^{2-})_3 \cdot 2H_2O$, or more simply $C_3A \cdot 3CaSO_4 \cdot 32H_2O$. The AFt phase in cement pastes contains additional substitutional ions, such as Fe^{3+}, Si^{4+} and OH^- [1]. The term monosulphate (AFm) is similarly the generic term for the less sulphated phase formed as a result of C_3A or C_4AF hydration with gypsum in water, and in the strict sense should only be the phase with the structural formula $Ca_4[Al(OH)_6]_2SO_4^{2-} \cdot 6H_2O$. In Portland cement pastes, the AFm phase probably contains additional substitutional ions, such as Fe^{3+}, Si^{4+} and OH^-, etc. [2].) The particular advantage of this technique is bulk, ~1 cm^3, transmission X-ray diffraction (XRD) equivalent data can be obtained [3–5]. Of potentially equal importance, the sample does not require further processing before examination, as could be required for conventional XRD, or thermal techniques, such as thermogravimetry (TG). Such treatment has been found to affect, and partially decompose, labile phases of interest [6, 7]. Copeland and Kantro [6] have found the degree of drying of cement pastes can affect the character and intensity of the XRD reflections due to the AFm phase.

The formation and stability, etc., of the above calcium sulphoaluminate hydrates is of importance in relation to the overall durability of mortars and concretes. The stability of these phases is known to be important in the potentially deleterious expansive behaviour of certain cements, used in the production of heat-cured concretes [8–10]. The ettringite (AFt) phase has also been associated with deterioration of concrete due to the "alkali aggregate reaction", one of the most widespread problems restricting the design life of concrete structures [11–13]. In addition, the stability of Portland cement to "sulphate attack" is apparently related to the characteristics of these sulphoaluminates, although details of the mechanism remain uncertain [14, 15]. More detailed investigations of the overall behaviour and nature of the AFt and AFm phases in Portland cement pastes are therefore necessary, to characterize more fully the important factors contributing to the deterioration of cementitious materials.

We here report for the first time SR–EDD *in situ* bulk XRD equivalent analysis of the formation, stability and compositional details of the calcium sulphoaluminate hydrates present in conventional cement pastes.

2. Experimental procedure

In the present investigation the hydration behaviour of four standard works' Portland cements was studied by SR–EDD. The full chemical analysis and physical-chemical properties of these cements are presented in Table I. From the chemical analysis, these cements can be separated into two types: the ANL, a high ferrite (C_4AF) cement, is a typical sulphate-resisting Portland cement (srpc), whilst the remainder, containing C_3A and C_4AF, are basically ordinary Portland cements (opc). All pastes were prepared by mixing for 1 min the cement and deionized-distilled water, at a conventional weight ratio of solid to H_2O of 0.50. The paste was then poured into the cylindrical perspex SR–EDD sample holders, 35 mm long and 10 mm internal diameter, and finally sealed using a rubber bung to minimize evaporation. After 1 d this was removed and the surface sealed using clear varnish. Various samples were prepared to cover the hydration period of 7–326 d and the availability of beam time at the SR–EDD facility at the Daresbury Laboratory.

The details of the SR–EDD technique are covered elsewhere [5, 16]. In summary, the technique exploits the intense parallel beams of white radiation available from a synchrotron source, in combination with an energy-dispersive (ED) detector. By irradiating a polycrystalline sample with such radiation, diffraction occurs over a continuous range of wavelengths, λ, and Bragg angles, θ, satisfying the Bragg equation. However, the ED-detector collimation system deliberately allows only a small "subset" of these diffracted X-ray photons to enter the detector, just those which are diffracted by a specific angle, θ. The ED-detector sorts out these diffracted photons into their respective energies using a multi-channel analyser, the resulting energy spectrum is the required EDD pattern. Because energy, E, and wavelength are reciprocally related, the Bragg equation can be rewritten as $Ed \sin\theta =$ constant. In the present investigations, the collimator is set at the pre-determined angle necessary to cover the range of d_{hkl} reflections considered appropriate of close to 0.25–2 nm. At the angle used the total volume swept by the diffracting lozenge would be $\sim 1\ \text{cm}^3$ per sample revolution. Each SR–EDD spectrum was collected over a period of 4 min.

TABLE I Chemical analysis of cements

Content (%)	ANL	SLSH	P30	P38
CaO	64.0	63.2	63.5	62.2
SiO_2	22.6	20.5	20.7	19.7
Al_2O_3	3.50	4.39	4.78	4.91
Fe_2O_3	4.91	2.28	3.68	3.65
MgO	0.95	3.68	2.73	2.79
K_2O	0.68	1.33	1.07	1.05
Na_2O	0.08	0.28	0.46	0.45
SO_3	1.98	0.04	3.17	3.37
K_2O (sol)	0.37	1.06	0.81	0.79
Na_2O (sol)	0.07	0.18	0.27	0.28
SO_3 (sol)	1.64	2.06	1.63	1.65
Free CaO	0.83	1.11	0.92	0.99
Bogue[a]				
C_3S	48.9	60.2	49.9	50.7
C_2S	27.9	13.4	21.7	18.1
C_3A	1.0	8.7	6.4	6.8
C_4AF	14.9	6.9	11.2	11.1
SSA ($m^2 kg^{-1}$)	305	461	330	438

[a] Estimated phase content using Bogue calculation (see [4] but Vol. 2, Appendix 2).

In certain additional experiments, synthetic ettringites were prepared by suspension hydration of pure C_3A and C_4AF in the presence of the stoichiometric amounts of $CaSO_4 \cdot 2H_2O$ required completely to form ettringite, as $C_3A \cdot 3CaSO_4 \cdot 32H_2O$. The water to solid ratio of 5 was used and the suspensions were continuously shaken for 60 d. After this period, each suspension was filtered, washed with acetone and then placed in a sealed container. The synthetic ettringites were interblended with 5% rutile (TiO_2) and then examined by conventional XRD, using a Siemens D500 diffractometer.

3. Results and discussion

3.1. Formation and character of the ettringite (AFt) phase

3.1.1. Formation and stability

The overall SR–EDD intensity data from two d_{hkl} reflections due to the AFt phase in the hydrating pastes are presented in Fig. 1. This summarizes the effect of cement type and hydration time on the formation and stability of this important hydrate. If, for the present, the intensity data for the 0.565 nm reflection are considered to be representative of the overall AFt content, then preliminary estimates can be undertaken, utilizing data from the one reliable SR–EDD run on ANL paste, where there is comparable DSC analysis of the AFt content [17]. The results obtained are presented in Table II. These estimates clearly show the presence of a significant ettringite (AFt) content in all pastes for at least 326 d. Only in the instance of the SLSH pastes is there any consistent and measurable decrease in content during the first 60 d, of some 15%. Between 60 d and the longer hydration times there is a decrease in the estimated content in all the cement pastes of close to 22%, see Table II. These results clearly show a significant proportion of the original SO_3 content is still incorporated within an ettringite-like phase for at least 326 d. Assuming for the present the ettringite (AFt) phase has the same molecular composition as synthetic ettringite of $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (mol wt 1555), then the proportion of the original cement SO_3 content still incorporated within such a lattice, was

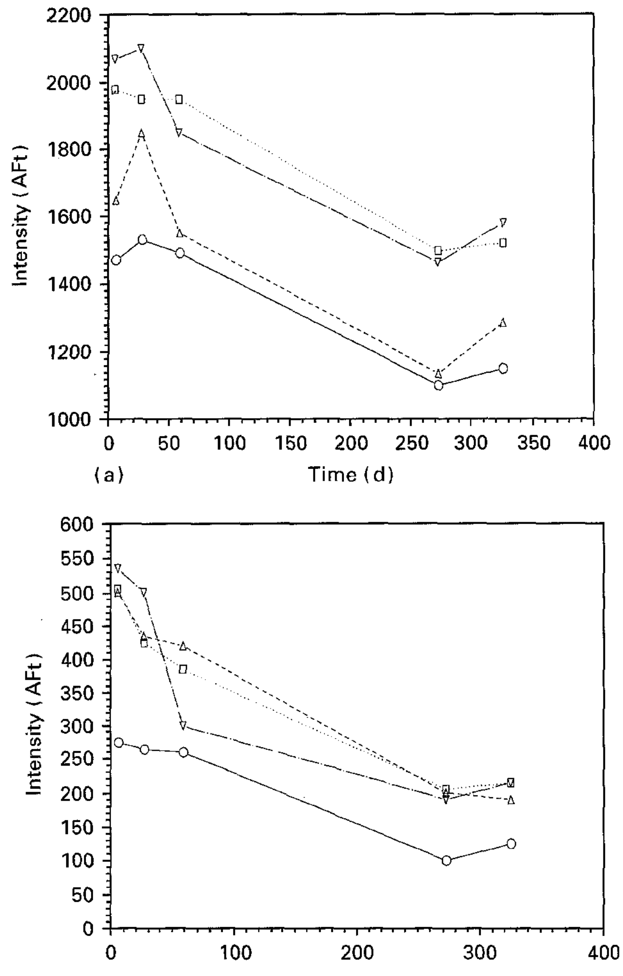

Figure 1 Changes in intensity of two d_{hkl} reflections due to the ettringite (AFt) phase, as a function of the hydration time and cement: (a) 0.565 nm, (b) 0.77 nm. (○) ANL, (△) SLSH, (▽) P30, (□) P38.

TABLE II Estimated AFt content in pastes: from intensity SR–EDD 0.565 nm AFt reflection, relative to DSC content in ANL paste at 1 h hydration

Time (d)	ANL	SLSH	P30	P38
1 h	2.7[a]	–	–	–
7	7.0	8.9	9.8	9.6
28	7.5	8.0	10.0	9.4
60	7.2	7.2	9.0	9.4
273	5.7	5.3	7.5	7.3
326	6.4	5.8	7.7	7.9

[a] DSC AFt content at 1 h of 2.7%, SR–EDD 0.565 nm intensity in equivalent paste of 210 units, additional estimates from intensity data in Fig. 1.

estimated to range from ~75% in ANL pastes, down to ~50% in a SLSH paste at 60 d hydration. At later ages this decreases to close to ~55% in ANL pastes, compared to approximately 40% in the other cement pastes. It would therefore appear that the ettringite (AFt) phase in the ANL high ferrite cement pastes is somewhat more stable compared to the equivalent phase in pastes prepared from the remaining high C_3A cements, if the original SO_3 content of the various cements is included in the calculations. However, if the averaged early age contents (to 60 d) are simply compared to the meaned late age values, then the percentage decrease is very similar in all the cement pastes, at ~25%. Clearly the percentage decomposition of the ettringite (AFt) phase after nearly 1 y is relatively small and surprisingly similar, considering the range of cement pastes studied. More detailed relationships between the intensity of the individual d_{hkl} reflections and experimental variables, such as cement type and hydration time are more difficult to ascertain. These difficulties are probably associated with the absence of an internal standard and the problems of preparing standardized pastes.

3.1.2. Changes in peak intensity ratio: microstructural characteristics

The ratio of the intensity of observed AFt d_{hkl} reflections has been calculated, the values obtained as a function of cement type and hydration time are presented in Fig. 2. The ratio of the 0.97/0.565 nm peaks (I_{100}/I_{110} reflections) clearly shows the difference between the AFt in the ANL pastes, compared to that in all the other cement pastes, although the divergence is somewhat less by 60 d hydration in the instance of the P30 and P38 pastes. In addition, there are smaller differences in this ratio for the AFt phase present in the pastes prepared from the other three cements. After the first 7 d hydration, the 0.97/0.565 nm intensity ratio for AFt phase, in each of the cement pastes remains constant to within the probable experimental error for at least 326 d. It would therefore appear that the AFt crystals are formed within these pastes, with particular characteristics, dependent on the cement type from which they are formed and these remain the same for at least 326 d.

In all the cement pastes studied the greatest difference in the SR–EDD characteristics of the AFt phase, is between that formed in the ANL pastes, compared to the equivalent AFt formed in pastes prepared with

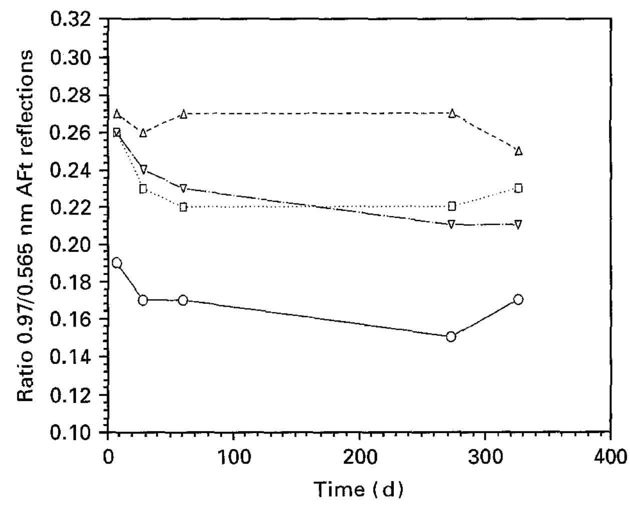

Figure 2 Changes in the peak intensity ratio of two ettringite (AFt) reflections, as a function of hydration time and cement. (○) ANL, (△) SLSH, (▽) P30, (□) P38.

the remaining cements. In relation to the types of cements studied, the differences are in broad terms consistent with the ANL being different from the others; this is a typical sulphate-resisting high ferrite cement, whilst the remaining are opcs, containing both C_3A and the ferrite phase, see Table I. However, this purely descriptive exposition does not explain, what the differences and changes in the intensity ratios signify in relation to the overall microstructural characteristics of the developing AFt phase in various cement pastes.

At the present time it is uncertain which, if any, of the following hypotheses can be used to explain the observed variations:

1. differences in the morphology and preferential crystallinity of the ettringite (AFt) phase. At early hydration times ettringite crystals some 1 μm x 10 μm in size have been observed [18]. Furthermore, ettringite has a highly orientated structure [19], which could be affected by the local aqueous environment during the formation stage. It is a frequent problem in powder diffraction that changes in crystal morphology can produce large changes in relative peak intensities, due to the crystal morphology affecting packing and the resultant preferred orientation effects;
2. changes in the X-ray absorption and the density of the cement pastes with time. Because, with SR–EDD the various peaks are expressed at different X-ray photon energies, they are therefore also subject to varying X-ray absorptions by the sample. If the overall density remains constant, then there will be no changes in the absorption and, consequently, no change in the relative peak intensities. However, if the density does change, as could occur at early hydration times, then these absorption factors will be modified, especially at low energy, and affect the intensity ratios.

Without further experimental investigations it is uncertain which of these hypotheses is the most important. However, previous cement hydration studies have found the ettringite (AFt) phase can have a range of morphologies at later ages [20]. In addition, Older and Gasser [14] have proposed the morphology of the ettringite (AFt) formed from the high-ferrite srpc, is different from that present in opc pastes. We therefore tentatively suggest this is perhaps the most important factor contributing to the observed differences in the 0.97/0.565 nm peak intensity ratio.

3.1.3. Differences in d-spacing: compositional changes

The d_{100} spacing has been determined for the ettringite (AFt) phase present in all the cement pastes studied. The values obtained and the observed changes with cement type and hydration time are presented in Fig. 3. These results are limited to the AFt d_{100} reflection at 0.97 nm and are probably of greater relative accuracy, than absolute, because no reference was used. However, the differences observed appear to be greater than the accuracy quoted for SR–EDD, of close to 7 in 10^4 [4]. The d-values quoted below are the calculated means from the experimental data, with the appropriate standard deviation (± 1 S.D.). In addition to d_{100} spacings obtained from pastes hydrated for more than 7 d, preliminary data obtained after only 1 and 8 h hydration are also included. The results obtained indicate a consistent difference, except for during the first few hours hydration, between the d_{100} spacing of the AFt phase in ANL pastes, compared to that formed in the remaining cement pastes. It would therefore appear there is a difference in at least one of the cell dimensions of the AFt formed from the ferrite phase present in ANL, compared to that formed mainly from C_3A, the more reactive, of the calcium aluminate phases present in the remaining cements [21].

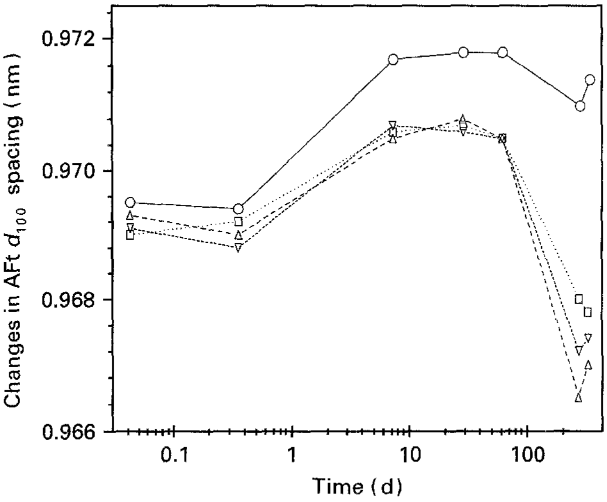

Figure 3 Changes in the d_{100} spacing of the ettringite (AFt) phase, as a function of the hydration time and cement. (○) ANL, (△) SLSH, (▽) P30, (□) P38.

3.1.3.1. Early ages: first few hours. The observed overall similarity in the d_{100} spacing during the first few hours is probably because the initial AFt phase is formed from the hydration of the same basic C_3A-like phase present in all the cements. In the instance of the high-ferrite ANL cement, the Bogue C_3A content is ~1%, see Table I. In this cement, the AFt content by DSC analysis at 8 h is only 3.5% [17], well below the maximum possible assuming a $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ molecular formula for the AFt phase.

Equivalent SR–EDD runs of ANL cement interblended with synthetic ettringite and rutile were undertaken. Compared to the rutile internal standard, the d_{100}-spacing for the ettringite was found to be 0.9725 ± 0.0008 nm, whilst the meaned value of this reflection for the AFt phase in the cement pastes at 1 and 8 h hydration was found to be 0.9692 ± 0.0003 nm.. It would therefore appear that the AFt phase formed in cement pastes at early times is not the same as synthetic ettringite. Muhamad *et al.* [2] have studied the formation of ettringite using SR–EDD and found the *a*-cell parameter was smaller than that for a pure synthetic ettringite at early ages. They ascribed the observed differences to a deficiency of SO_4^{2-} ions in the lattice. We therefore tentatively suggest, the similar decrease in the d_{100} spacing of the AFt phase in our pastes, at early ages, compared to that for pure ettringite, is also as a consequence of an equivalent deficiency in the SO_4^{2-} content.

3.1.3.2. Later ages: 7–326 d. In the hydration period between the first few hours and 7–60 d, the ettringite (AFt) d_{100} spacing was found to have increased in value, in all pastes, see Fig. 3. In this later hydration period, the d_{100}-spacing for the AFt phase in ANL pastes is now different from that in all the remaining cement pastes, see Fig. 3. The d_{100}-spacing of AFt in ANL pastes is 0.9718 ± 0.0001 nm, as compared to 0.9706 ± 0.0001 nm in the other cement pastes. At the longest hydration ages of 273 and 326 d, the meaned d_{100}-spacing of AFt in the ANL pastes appears to remain the same, as during the 7–60 d period, to within the likely experimental error at 0.9712 ± 0.0002 nm, whilst the AFt d_{100}-spacing in the remaining pastes decreases to 0.9673 ± 0.0006 nm, see Fig. 3.

The most obvious difference between the cements is that ANL is a typical high-ferrite, low-heat, sulphate-resisting-type cement, whilst the remainder are ordinary Portland cements containing both C_3A and the ferrite phase, see Table I. In simple terms, it would appear the observed differences in the d_{100}-spacing are directly related to the high ferrite content in the ANL cement. However, synthetic preparations of ettringite (AFt) from pure C_3A and C_4AF were found by conventional XRD to be surprisingly similar, see Table III. Struble [22] has also found Al^{3+} and Fe^{3+} containing synthetic ettringites are crystallographically very similar. In our conventional XRD, for instance, no difference was observed between the d_{100}-spacing of the ettringite (AFt) phase formed from C_3A or C_4AF. In contrast, a definite difference in this spacing was observed in the SR–EDD studies, in cement pastes containing different relative proportions of these calcium aluminates. It would therefore appear there are clear differences between the ettringite (AFt) formed from the synthetic phases and the apparently equivalent phase present in cement pastes.

Lachowski *et al.* [2] have used electron microscopy to analyse the composition of hydrates in cements pastes. In their studies the AFt phase was found to have a range of compositions; however, the main impurity ion detected was silicon, although iron was also found to be present in specific analyses. From an examination of the overall data, it was also considered likely that certain sites in the lattice could also be occupied by OH^- or CO_3^{2-} ions. Similar suggestions were earlier made by Midgley and Rosaman [23] from DTA and XRD studies of cement pastes. More recently, Pöllmann [24] have found the cell dimensions of synthetic solid solutions of ettringites depends on the relative concentrations of SO_4^{2-}, OH^- and CO_3^{2-} in the lattice.

If our results are compared with the only available apparently similar cement paste data presented by Midgley and Rosaman [23], there appears to be general areas of agreement, as well as differences in some of the details. In general terms, they found the AFt formed in pastes prepared from high ferrite cement, was different from that formed in the hydration of cements containing C_3A and ferrite, in agreement with our findings. However, we have found the d_{100} spacing of the AFt phase in ANL, the high ferrite cement, to remain basically constant throughout the 7–326 d period, whilst Midgley and Rosaman [23] found the same spacing for the AFt formed from this type of cement to be the more rapidly changing. It is uncertain why the two sets of results are inconsistent; however, no information on the cements used was included in their paper, to enable a more critical evaluation of the data. In view of the well-known stability of high-ferrite cements to sulphate attack, etc. [15], compared to opc, it would appear that our results, are, at least superficially, more consistent with such behaviour.

From the available experimental evidence it is uncertain what, if any, compositional variations, within the AFt lattice are responsible for the observed changes in the d_{100}-spacing. However, possible changes include variations in the relative proportions of such additional ions, as OH^-, Fe^{3-} and Si^{4+}. An increase in the OH^- content of the AFt formed from the higher alkali SLSH, P30 and P38 cements, is consistent with not only Bailey and Hampson [25] calculations, but also with changes in the cell dimensions observed by Pöllmann and co-worker [24, 26] in their XRD studies of synthetic ettringites. Differences in the pore-fluid chemistry could not only affect the morphology of the developing AFt crystallites, but also the lattice composition. The solubilities of alkalies and sulphates are considerably lower in the ANL cement, compared to the remaining cements, see Table I. These, and the later consequential, differences in the pore-fluid OH^- concentration [27], could well be important factors affecting the lattice composition of the AFt phase in the various cement pastes.

TABLE III Conventional XRD of synthetic ettringites

Ettringite (from $C_3A/CaSO_4 \cdot 2H_2O$ paste)		Ettringite (from $C_4AF/CaSO_4 \cdot 2H_2O$ paste)	
d_{hkl}-spacing[a] (nm)	Relative intensity	d_{hkl}-spacing[a] (nm)	Relative intensity
0.9728	100	0.9726	100
0.5662	57	0.5616	52
0.4702	41	0.4710	25
0.3883	59	0.3883	45
0.2565	48	0.2566	39

[a] Values relative to rutile as the internal standard.

3.2. Monosulphate (AFm) phase

The other important calcium sulpho-aluminate hydrate present in cement pastes is the monosulphate (AFm) phase. Within the present SR–EDD investigation, the d_{0002} reflection at 0.45 nm has been used to monitor the presence of this phase. The overall changes in the intensity with cement type and hydration time are shown in Fig. 4. The development of this phase with increasing hydration time appears to be basically independent of the cement type, within the

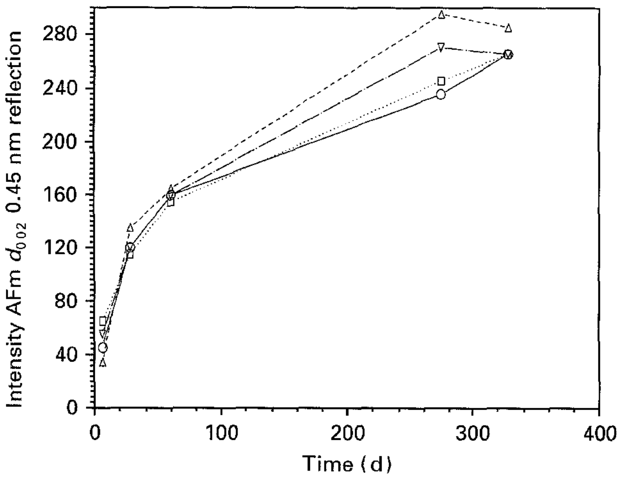

Figure 4 Development of the detected monosulphate (AFm) phase, as a function of hydration time and cement. (○) ANL, (△) SLSH, (▽) P30, (□) P38.

TABLE IV Estimate of AFm content in paste: from XRD and SR–EDD data

Technique: sample	Ettringite (AFt) 0.56 nm reflection (intensity)	Monosulphate (AFm) 0.45 nm reflection (intensity)
XRD:		
10% ettringite	150	–
10% monosulphate	–	330
SR–EDD:		
ANL-326 d (6.4%AFt, Table II)	1150	260

ANL paste, 326 d: % AFm, by combining the XRD and SR–EDD data: equals 150/330 × 260/1150 × 6.4% = 0.6%.

likely error in the intensity measurements. Unfortunately, we have no direct SR–EDD data on the content. However, previous conventional XRD of standard mixes of synthetic ettringite and monosulphate can be used to estimate the content, see Table IV. Compared to the X-ray intensity of the crystalline synthetic phase, the overall content would appear to be only 0.6% at 326 d. This should not, however, be taken as a direct indication of the actual content in these pastes.

Skibsted *et al.* [28] have found this phase to be undetectable by XRD, and barely so by DSC; in contrast, they found ^{27}Al MAS NMR spectroscopy was capable of detecting a significant amount of AFm, to such an extent that in the chemically dried paste examined, there appeared to be more AFm than AFt. This paste was prepared from a Swedish cement similar to the SLSH used in the present SR–EDD investigations. Taylor [29] has suggested that the AFm is incorporated within the developing amorphous calcium silicate hydrate, perhaps being interstratified within or near the disordered silicate layers. The AFm phase is, consequently, considerably disordered, to such an extent that neither diffraction, nor thermally based techniques appear to be capable of analysing the actual content of this phase in cement pastes. Even in the present investigation, where the pastes still contain unbound water and are not chemically dried, which could affect the stability [6, 7], the technique is probably still not fully monitoring the actual AFm content.

4. Conclusion

The SR–EDD technique has been shown to be capable of not only monitoring the overall content of the AFt phase in cement pastes, but also more detailed microstructural and compositional characteristics. The most significant differences in the characteristics of the AFt phase, are those between this phase forming in pastes prepared from the typical C_3A containing ordinary Portland cements, compared to the ferrite containing srpc. There appear to be differences in the morphology of the AFt crystals at all ages, and at later ages (⩾ 273 d) probable compositional changes within the phase formed in opc pastes, as compared to the apparently compositionally more stable analogue present in the high-ferrite cement pastes.

The technique is also capable of monitoring the AFm phase, although probably not the actual content, due to the disorganized nature of this phase in the cement paste system. The peak intensity was found to increase with increasing hydration time; no significant differences were observed between the four cements.

Acknowledgements

One of the authors (E.H.) thanks Cementa AB, Sweden, for funding the basic experimental investigations, carried out under contract at the Daresbury Laboratory, Warrington, UK, and Euroc Research AB, for further funding and both companies for permission to publish. Thanks are also due to Johan Eriksson, Euroc Research AB, for the conventional XRD experiments.

References

1. RILEM Committee 68-MMH, Task Group 3., "The hydration of tricalcium aluminate and tetracalcium aluminoferrite in the presence of calcium sulphate", *Mater. Construct.* **19** (1986) 137.
2. E. E. LACHOWSKI, K. MOHAN, H. F. W. TAYLOR and A. E. MOORE, *J. Am. Ceram. Soc.* **63** (1980) 447.
3. S. RESHID, P. BARNES and X. TURRILLAS, *Adv. Cem. Res.* **4** (1991/92) 61.
4. M. N. MUHAMAD, P. BARNES, C. H. FENTIMAN, D. HÄUSERMANN, PÖLLMANN and S. RESHID, *Cem. Concr. Res.* **23** (1993) 267.
5. P. BARNES, S. M. CLARK, D. HÄUSERMANN, E. HENDERSON, C. H. FENTIMAN, M. N. MUHAMAD and S. RESHID, *Phase Transitions* **39** (1992) 117.
6. L. E. COPELAND and D. L. KANTRO, in "The Chemistry of Cements", Vol. 1, edited by H. F. W. Taylor (Academic Press, London, 1968), Ch. 8.
7. A. XU, S. L. SARKAR and L. O. NILSSON, *Mater. Struct.* **26** (1993) 414.
8. D. HEINZ and U. LUDWIG, in "Proceedings 8th International Congress on the Chemistry of Cement", Rio de Janeiro, Vol. V (1986) p. 189.
9. P. TEPPONEN and Bo-E. ERIKSSON, *Nordic Concr. Res. Publ.* **6** (1987) 199.
10. R. L. DAY, Portland Research Association, R and D Publication RD 108T, "The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Analysis" (Portland Cement Association, Skokie, IL, 1992).

11. V. JOHANSEN, N. THAULOW and J. SKALNY, *Adv. Cem. Res.* **5** (1993) 23.
12. T. N. JONES and A. B. POOLE, in "Proceedings of the 7th International Conference on AAR in Concrete", Ottawa (Nayes Publishers, Park Ridge, NJ, 1986) p. 446.
13. A. SHAYAN and G. W. QUICK, in "Proceedings of the 14th International Conference of the Cement Microscopy Association" (Costa Mesa, CA, 1992) p. 11.
14. I. ODLER and M. GASSER, *J. Am. Ceram. Soc.* **71** (1988) 1015.
15. P.K. MEHTA, in "Materials Science of Concrete III", edited by J. Skalny (American Ceramic Society, Westerville, OH, 1993) p. 105.
16. D. HÄUSERMANN and P. BARNES, *Phase Transit.* **39** (1992) 99.
17. E. HENDERSON, unpublished data.
18. I. JAWED, J. SKALNY and J. F. YOUNG, "Structure & Preformance of Cements", edited by P. Barnes (Applied Science, London, 1983) Ch. 7.
19. A. MOORE and H. F. W. TAYLOR, *Acta. Crystallogr. B* **26** (1970) 386.
20. S. DIAMOND, in "Proceedings of the 8th International Congress on the Chemistry of Cement", Vol. 1, Rio de Janeiro (1986) p. 122.
21. J. BENSTED, in "Advances in Cement Technology", edited by S. N. Ghosh (Pergamon Press, Oxford, 1983) p. 307.
22. L. J. STRUBLE, in "Proceedings of the 8th International Congress on the Chemistry of Cement", Vol. IV, Rio de Janeiro (1986) p. 582.
23. H. G. MIDGLEY and D. ROSAMAN, in "Proceedings of the 4th International Symposium Chemistry of Cement", Vol. I, Washington (1960) p. 259.
24. H. PÖLLMANN, in "Proceedings of the 9th International Conference Cement Microscopy", Reno, Nevada (1987) p. 426.
25. J. E. BAILEY and C. J. HAMPSON, in "International Seminar on Calcium Aluminates", Turin, (1982) p. 199.
26. H.-J. KUZEL and H. PÖLLMANN, *Cem. Concr. Res.* **21** (1991) 885.
27. J. J. KOLLEK, in Proceedings of the 3rd International Conference "Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete", Vol. 1, Trondheim, Norway (1989) p. 373.
28. J. SKIBSTED, E. HENDERSON and H. J. JAKOBSEN, *Inorg. Chem.* **32** (1993) 1013.
29. H. F. W. TAYLOR, in "Advances in Cement Manufacture and Use", edited by E. Gartner (Potosi, Missouri, 1988) p. 295.

Received 15 July 1994
and accepted 21 February 1995