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Influence of organic additives on the morphology and X-ray diffraction line profiles of synthetic calcium hydroxide

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Scanning electron microscopy and X-ray diffraction techniques have been used to characterize pure synthetic calcium hydroxide (CH) and CH doped with selective additives. From scanning electron microscopy (SEM) observations the plasticizers and Melment additives appear to restrict growth in the *c* crystallographic direction resulting in a "plate"-type morphology, which may be due to chemisorption, as there are no significant changes in the lattice parameters.

1. Introduction

When Portland cement undergoes hydration under normal conditions, the two major products are colloidal calcium silicate hydrates (C–S–H) and calcium hydroxide (CH). In a fully hydrated sample, the CH accounts for 20% of the weight of the solid material [1]. To what extent this phase contributes to the compressive strength of cured cement is uncertain, but clearly changes in its morphology are likely to modify the mechanical properties. Studies [2–4] of the effects of (a) temperature and (b) water–solid ratio on the growth and morphology of CH in cement pastes have been reviewed in a recent paper [5].

Admixtures are now used in concrete to control the setting times and particularly the workability of fresh mixes. It has been shown that the presence of organic additives can significantly influence the morphology of CH formed by the hydration of tricalcium silicate (C_3S) and Portland cement pastes [6–16]. In 1972, Berger and McGregor [6], using optical microscopy, evaluated the effect of 62 admixtures on CH morphology. They classified the crystal morphology which developed during the hydration of the doped C_3S into three distinct morphological groups based on the ratios of the *c* to *a* crystallographic axes and a fourth group displaying an irregular morphology which resembled radial aggregates. They found that the addition of organic esters resulted in the formation of a hexagonal morphology with c/a in the range 0.5 to 1.5, whereas addition of organic acids resulted in an irregular morphology.

In this paper the effect of organic additives on the morphology, lattice parameters and X-ray line profiles of synthetic CH is examined.

2. Experimental work

Stoichiometric and doped CH crystals were prepared by a diffusion process first described by Johnson [17], using solutions of $CaCl_2 \cdot 6H_2O$ ($0.6\,kg\,l^{-1}$) and KOH ($0.316\,kg\,l^{-1}$) [18]. The organic additives (Fig. 1) used were: (a) two superplasticizers: Melment (the sodium salt of a sulphonated melamine formaldehyde condensate) and SP1 (sulphonated naphthalene formaldehyde condensate), (b) two placticizers CCP1 and CCP6 (modified lignosulphonates), (c) acetic acid. The crystals were allowed to grow for a minimum of three weeks then removed from solution, washed several times in distilled water, alcohol and oven dried at 100° C before storing in a desiccator over soda asbestos.

Samples of stoichiometric and doped CH crystals were crushed to a fine powder (< 300 mesh B.S. sieve) using an agate pestle and mortar and were then examined by X-ray diffraction. A Philips PW1050/25 goniometer and PW1730/10 generator employing monochromated Cu$K\alpha$ radiation were used to step-scan a range of reflections from powder samples of the hydroxide. Each peak was scanned over two or three °2θ at a rate of 0.01 °$2\theta\,min^{-1}$ using a forty second count rate except for the 2 0 . 0 reflection, where a 100 sec count rate was necessary because of the low intensity of the line profile. Representative crystals were splutter-coated with gold (approximately 20 nm). Electron micrographs of the pure and doped crystals were taken on a Philips PSEM 500 electron microscope.

3. Results and discussion

$Ca(OH)_2$ crystals in the form of hexagonal plates and prisms were obtained from the inner surfaces of the beakers. A description of the effect that the distinct addition of the various organic dopants had on the habit of the CH crystals is given in Table I. The introduction of the two superplasticizers and the two plasticizers caused a diversity in the morphology of the CH crystals ranging from irregular concretionary

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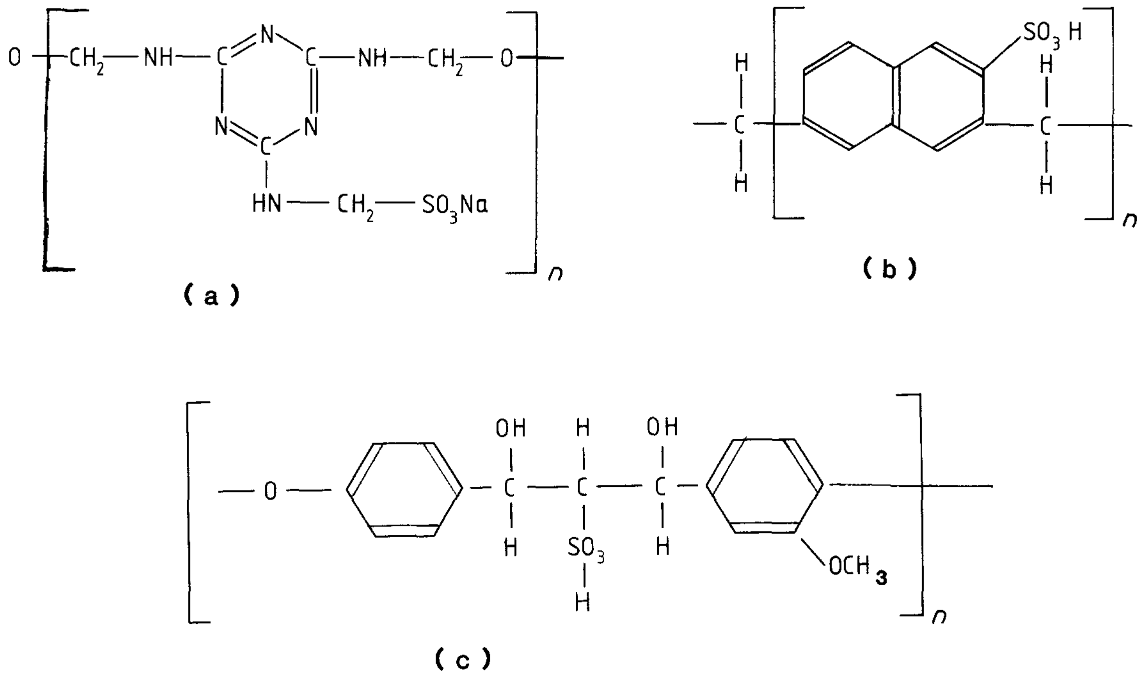

Figure 1 The chemical structure of the four organic dopants: (a) Melment, (b) SP1, (c) CCP1 and CCP6.

TABLE I Observations on pure CH and CH doped with organic additives

Organic additive	Description of the crystal morphology of the synthetic CH
Control	$CaCl_2$ and KOH solutions: the crystals were in the form of hexagonal plates and prisms the latter showing perfect cleavage perpendicular to the *c* crystallographic axis. Irregular overgrowths were common. A higher concentration of crystals was observed around the top of the inner surface of the beaker which contained the $CaCl_2$ solution.
Acetic acid	Colourless tabular or platey crystals were formed
Super plasticizer SP1	(i) Beaker containing the $CaCl_2$ solution originally: the crystals occurred as individual nodules or irregular concretionary aggregates. These aggregates were a homogeneous yellow–beige colour, and each individual nodule was approximately 1 mm diameter. (ii) Beaker containing the KOH solution initially: "fan"-type intergrowths were observed as the characteristic habit of the CH crystals, which were mainly colourless except for a pale yellow diffuse band near the top 00.1 face. (iii) Base of the desiccator: pale yellow crystals were present as simple or complex intergrowths.
Concrete plasticizer CCP1	(i) $CaCl_2$ solution: crystals were fairly similar to those doped with SP1 from the same site except that sometimes the prism faces were elongated and ended in a nodule. These irregular aggregates were heterogeneously coloured in shades varying from orange–brown to dark brown. The organic additive appeared to be more strongly absorbed at the top of the crystal. (ii) KOH solution: simple or complex arborescent habit was the distinguishing feature of these CH crystals. These branching type crystals attained a length of up to 5 mm and were a pale golden-yellow shade. (iii) Base of the desiccator: pale yellow crystals were present as simple or complex intergrowths.
Concrete plasticizer CCP6	(i) $CaCl_2$ solution: the crystals occurred as single nodules, irregular concretionary aggregates or as nodules joined to form a radiating rosette-type structure. These nodular structures were heterogeneously coloured in shades varying from a yellow–beige at the base to a brownish purple at the top. (ii) KOH solution: simple or complex arborescent habit was the distinguishing feature of these CH crystals. These branching crystals attained a length of up to 5 mm, were slightly wider than those doped with CCP1 and a pale golden yellow shade. (iii) Base of the desiccator: pale yellow or colourless crystals occurring as simple or complex intergrowths were observed.
Melment at 0.6% and 1.2%	(i) $CaCl_2$ solution: few crystals with a pronounced tabular hexagonal morphology. The average width of the basal pinacoid face was 3 mm while the prism faces attained a length of 0.5 mm. The crystals doped with Melment at a 1.2% level had a more platey morphology. (ii) KOH solution: overlapping tabular crystals occurred around the top rim of the beaker.

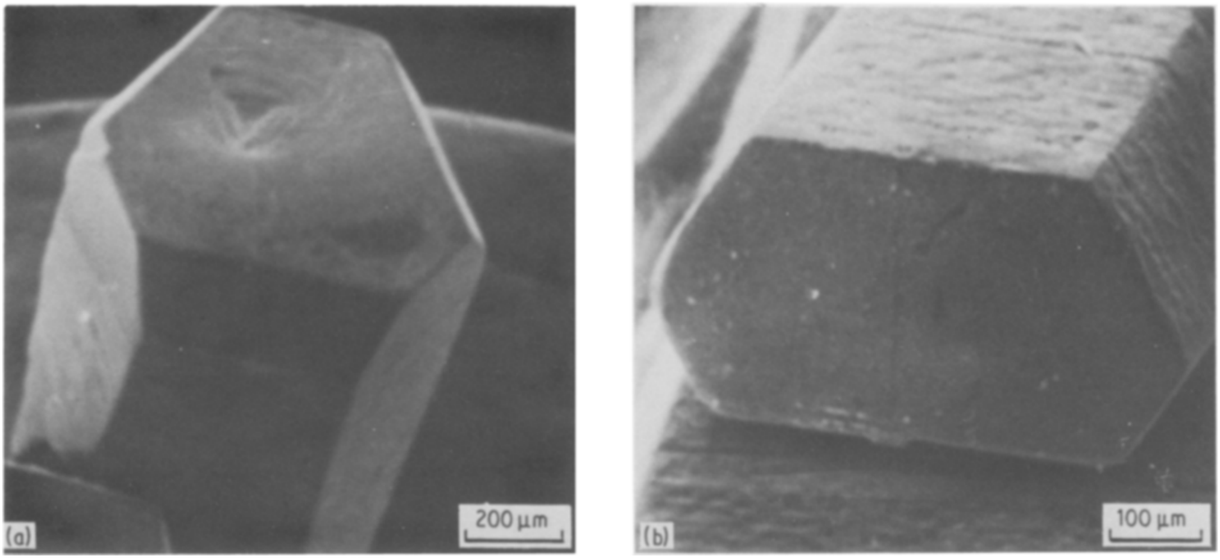

Figure 2 (a) Single crystal of CH displaying an etch pit on the 0 0 . 1 surface. (b) CH crystal displaying a pronounced hexagonal morphology.

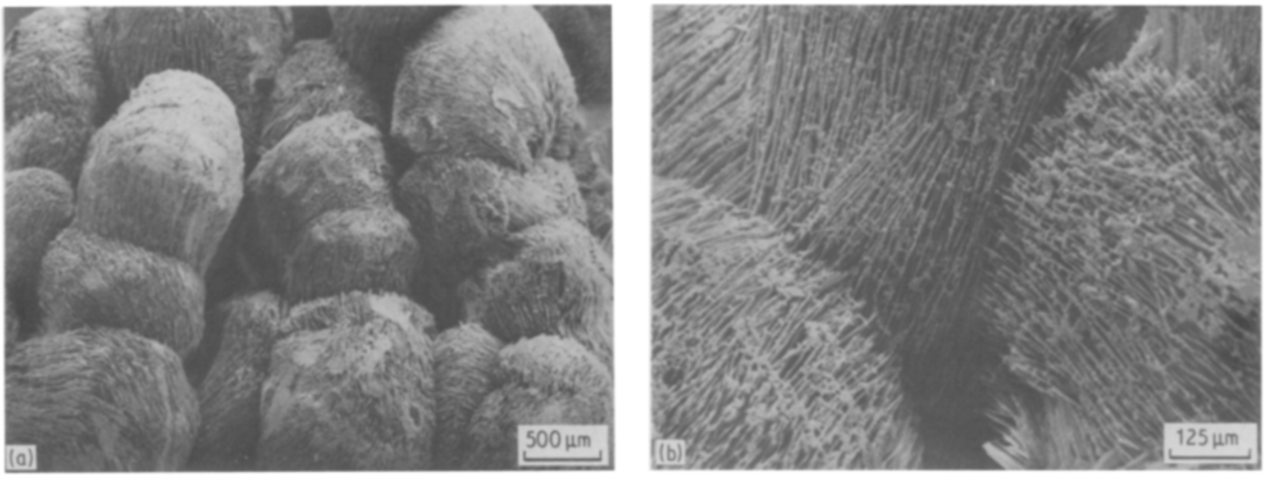

Figure 3 (a) CH + lignosulphate displaying an irregular nodular morphology. (b) As (a) but higher magnification reveals the nodules to be composed of aggregates of parallel plates.

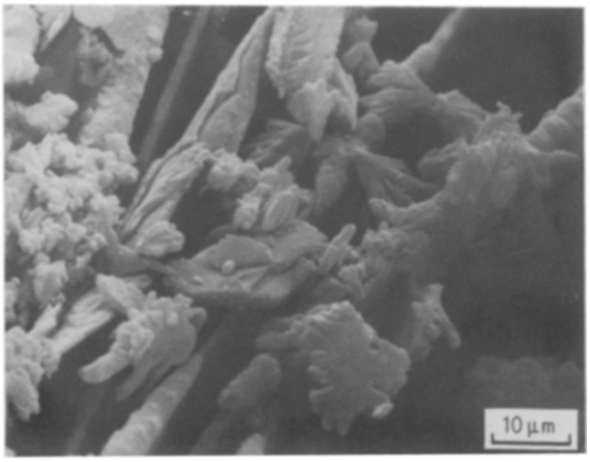

Figure 4 A secondary crystallization partially coating the plates of CH + lignosulphate.

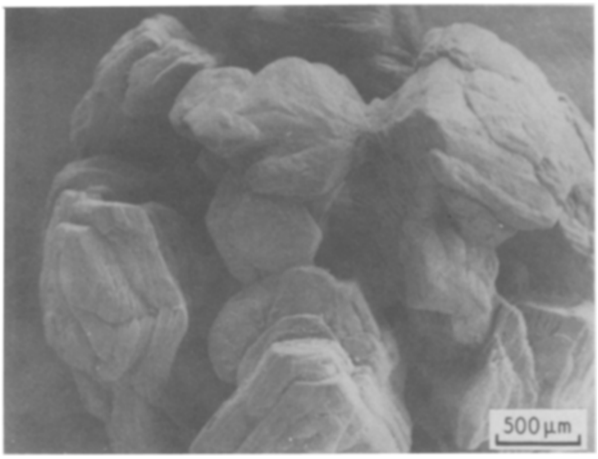

Figure 5 "Rosette"-type structure of CH + lignosulphate.

aggregates to simple intergrowths depending on the site of the crystal. These additives were originally present in the beaker containing the $CaCl_2$ solution and thus had the greatest effect on the crystals growing in the local environment. The heterogeneously coloured crystals probably reflect different surface absorption of the additives.

A sequence of micrographs of the pure and doped samples taken on the SEM illustrated a variation in the morphology of the crystals. The stoichiometric CH (Figs 2a and b) had a pronounced "blocky" hexagonal morphology and several of the crystals showed overgrowths on the *c* crystallographic axis. One of the crystals on the 00.1 surface contained an etch pit which could correspond to a site where a dislocation meets the surface; recent synchrotron topography research [19, 20] clearly reveals areas of defects and inclusion in CH crystals.

The CH synthesized from solutions to which the organic compounds were added showed three distinct habits. The irregular nodular structure of the CH + lignosulphate was observed (Figs 3a and b) to be composed of an aggregate of parallel plates aligned in the *a* crystallographic direction. A higher magnification reveals that a secondary crystallisation is in the form of radiating masses of crystals randomly oriented, Fig. 4. This habit was common to crystals with each of the three additives present. Another habit imparted by one of the lignosulphonate plasticizers was a "rosette" type stucture composed of thin plates forming branches radiating outwards from a central CH crystal, Fig. 5. The cleavage plates are delineated and their surfaces have a "scaley" appearance due to a variation in growth conditions. Some of the crystals extracted from the beaker that originally contained KOH solution exhibited an arborescent structure which is polycrystalline and elongated in the *c* crystallographic direction. The cleavage planes were partially and randomly delineated, Fig. 6. A secondary crystallization which sporadically encrusted the cleavage planes was seen at a higher magnification. Crystals doped with Melment at both the 0.6 and 1.2% level had a pronounced "platey" morphology such as that shown in Fig. 7a. In detail these crystals have a "scaley" appearance due to differential growth of the layers. Higher magnification and another crystal specimen showed that a variation occurred in the orientation of the CH plates which appear to be of unequal size, Fig. 7b. The localized curvature of individual plates is attributed to mechanical deformation probably caused when the crystals were extracted. At a higher magnification, viewed along the *a* axis, the top prism surfaces are slightly irregular in width due to perpendicular (to the layers) and non-uniform fractures, Figs 7c, d. The prism surface has an uneven "scaley" appearance. The introduction of acetic acid produced tabular CH crystals. Increasing the magnification reveals that the 00.1 basal surface has a micronodular texture cut by an irregular network of ridges.

3.1. X-ray line profile analysis

The line profiles obtained from a continuous and a step-scan of synthetic samples of stoichiometric CH showed little difference in shape except that the latter enhanced the α_2 peak separation and detected the low intensity 20.0 reflection. A description of the shape of both pure and doped CH line profiles obtained by step-scanning the main peaks is given in Table II. The main difference between the two sets of profiles is that the 00.3 and 00.4 reflections from the CH doped with the superplasticizer SP1 and the two plasticizers are less resolved than those of pure synthetic CH, Figs 8a and b. CH crystals doped with Melment had similar X-ray line profiles to that of stoichiometric CH. The lattice parameters obtained from a least squares analysis of the data from a Nelson–Riley graph [21] are given in Table III. No significant difference is seen in the values obtained for the pure and doped CH.

4. Further discussion

Four of the organic dopants caused a diversity in the morphology of CH. Before examining reasons for these differences, the growth of pure synthetic CH is described. When more than $1.14\,g\,l^{-1}$ calcium oxide is dissolved in water (at 25° C) a supersaturated solution of CH is formed. Hedin [22] found that CH crystals usually grew in all directions as long as the concentration of the solution was high. When the concentration was above $1.5\,g\;CaO\,l^{-1}$ the rate of growth normal to the basal pinacoid was greater than that normal to the hexagonal prism. Preponderant

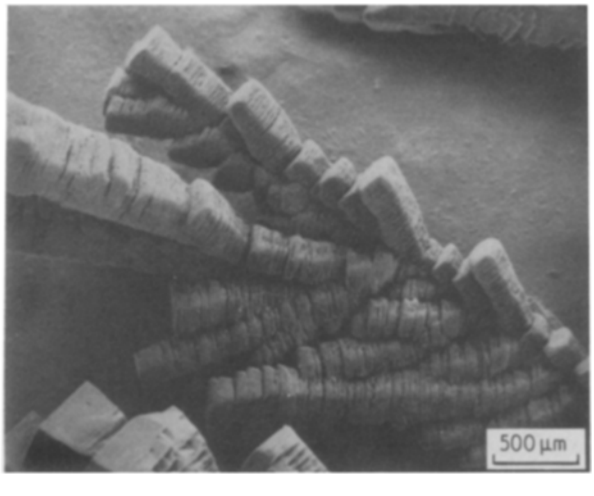

Figure 6 CH + lignosulphate exhibiting an "arborescent"-type morphology.

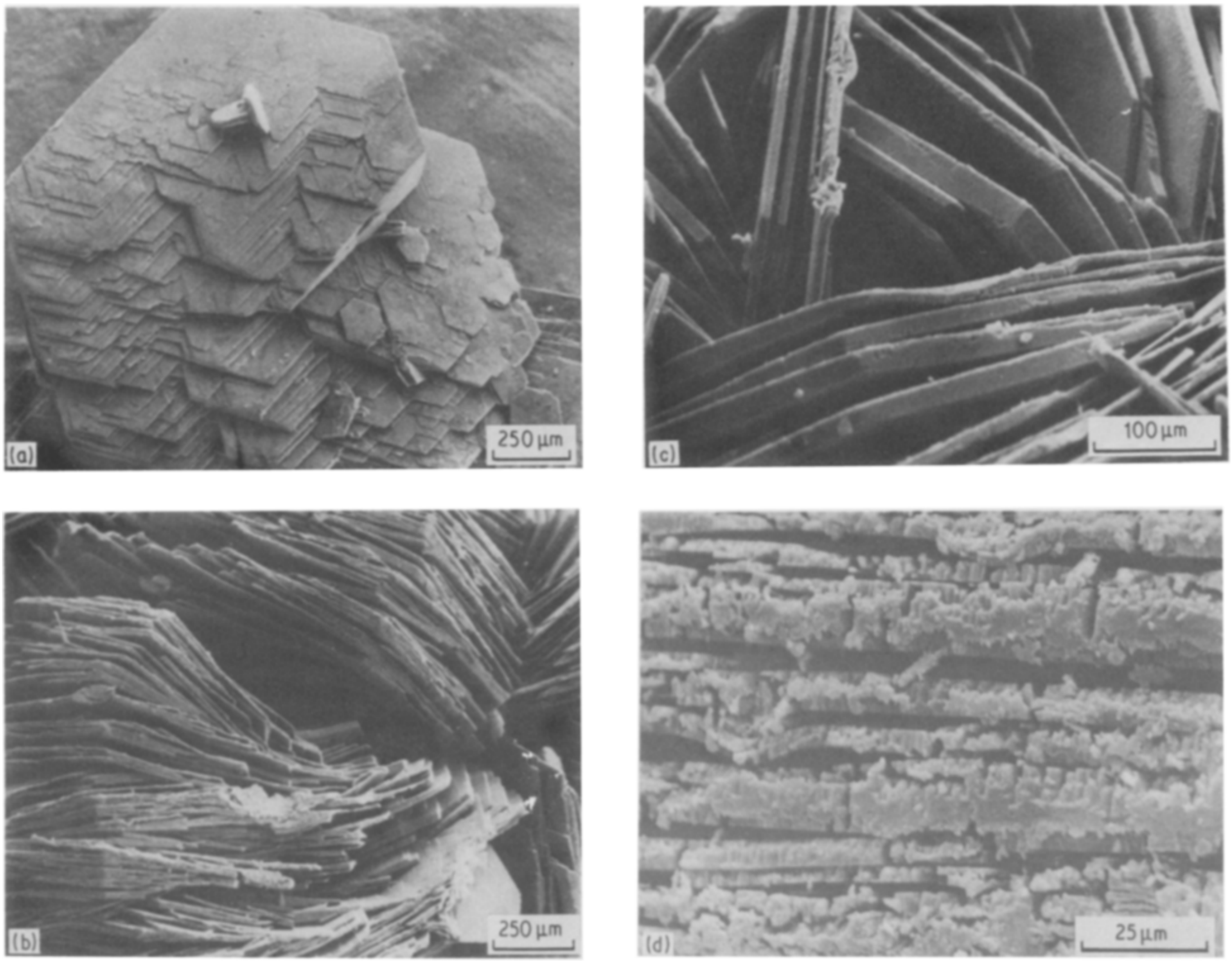

Figure 7 (a) "Platey" morphology of CH doped with Melment at the 1.2% level. (b) Irregular fractured scaley surface of the prism face of CH + 1.2% Melment. (c) The same sample × 320. (d) The same sample × 1280.

growth normal to the prism faces gave rise to flat tubular crystals.

CH crystals have ion absorption on the prism faces at all concentrations and molecular adsorption on the prism bases. Molecular adsorption does not begin until the concentration is relatively high, when the dissociation of the solution is lower and the molecular concentration is higher. However, once growth has started an increase in solution concentration causes a more rapid increase in the growth-rate on the basal surfaces than on the edges of the crystals.

The organic additives could influence the growth of CH crystals by: (i) effectively poisoning growth on various CH faces; (ii) influencing the solubility of the Ca^{2+} ions; (iii) being adsorbed on the surface of CH crystals as indicated by a change in zeta potential, or (iv) substituting for Ca^{2+} or OH^- ions within the crystal structure.

The structure of the organic additives is given in Fig. 1 and it can be seen that they have a sulphonate group in common. From a study of the absorption of dyes (several of which have the sulphonate group)

TABLE II The step-scan profiles of pure synthetic and doped CH

Reflection		Description of the shape of the line profiles	
hkl	2θ (deg)	(a) Pure synthetic CH	(b) Doped CH
00.1	18.10	Smooth profile no $\alpha_1\alpha_2$ separation	Smooth profile no $\alpha_1\alpha_2$ separation
10.0	28.65	Smooth profile no $\alpha_1\alpha_2$ separation	Smooth profile no $\alpha_1\alpha_2$ separation
00.2	36.75	Smooth profile no $\alpha_1\alpha_2$ separation	Smooth profile no $\alpha_1\alpha_2$ separation
11.0	50.84	Smooth profile no $\alpha_1\alpha_2$ separation	Smooth profile no $\alpha_1\alpha_2$ separation
00.3	56.20	Slight shoulder due to α_2 separation	No shoulder present with CH doped with the superplasticizer SP1 and the plasticizers CCP1 and CCP6
20.0	55.34	Very slight shoulder due to α_2 separation	Very slight shoulder due to α_2 separation
00.4	77.70	A pronounced peak due to α_2 separation	A slight shoulder is present with CH doped with the superplasticizer SP1 and one of the plasticizers, CCP1. No shoulder with the other plasticizer, CCP6

TABLE III Lattice parameters for CH and CH doped with organic additives from a least squares analysis applied to a Nelson–Riley plot

CH + dopant	Lattice parameter (nm)	
	a	*c*
Pure CH [21]	0.4909	0.3593
CH + SP1	0.4896 ± 0.0006	0.3590 ± 0.0007
CH + CCP1	0.4900 ± 0.0009	0.3595 ± 0.0008
CH + CCP6	0.4901 ± 0.0009	0.3584 ± 0.0008
CH + 0.6% Melment	0.4919 ± 0.0008	0.3595 ± 0.0005
CH + 1.2% Melment	0.4895 ± 0.0007	0.3587 ± 0.0007
CH + acetic acid	0.4898 ± 0.0006	0.3595 ± 0.0007

onto crystal surfaces, France [23] has concluded that certain polar groups in the dye ion are responsible for adhesion to the crystal surface and that of these the SO_3Na group is the most important; except where sterically hindered, this group renders potent any large organic molecule in which it occurs. Jawed *et al.* [12] found that sodium lignosulphonate delayed or completely inhibited the growth of CH from a supersaturated solution. At a lignosulphonate concentration of 2.5 p.p.m. no effect on crystal growth was observed. At concentrations above 200 p.p.m. the growth and also the nucleation of CH was completely inhibited. When crystal growth did occur at a higher supersaturation level it occurred as numerous small crystals; however, a description of the morphology of the CH was not presented. Many commercial lignosulphonates contain sugars and sugar acids such as xylonic and gluconic acids which may act as Ca^{2+} binders. The zeta potential of CH crystals (measured in a saturated solution) was found to be 33.5 mV [24]. Roy and Daimon [24] found that the presence of admixtures such as sulphonated naphthalene (containing a retarder) caused the zeta potential of CH crystals to change from a positive to a negative value, indicating that the admixture is adsorbed on the surface of the CH particles.

Hayek and Dierkes [8, 9] have studied the effect of Melment on hydrating cement pastes and found that the CH reflections were strongly suppressed from which they suggested that the Melment strongly interferes with the crystallization of CH permitting its separation in more or less amorphous states.

From SEM observations, the organic additives appear to restrict growth along the *x*-axis resulting in a "platey" morphology. Thus it is suggested that these selective additives are chemisorbed on to specific faces and are not taken into the structure because there is no significant change in the lattice parameters from those of pure synthetic CH.

5. Conclusions

The addition of the organic dopants modifies the habit of the CH crystals, broadens the X-ray diffraction line profiles, but produces no significant change in the *a* and *c* lattice parameters.

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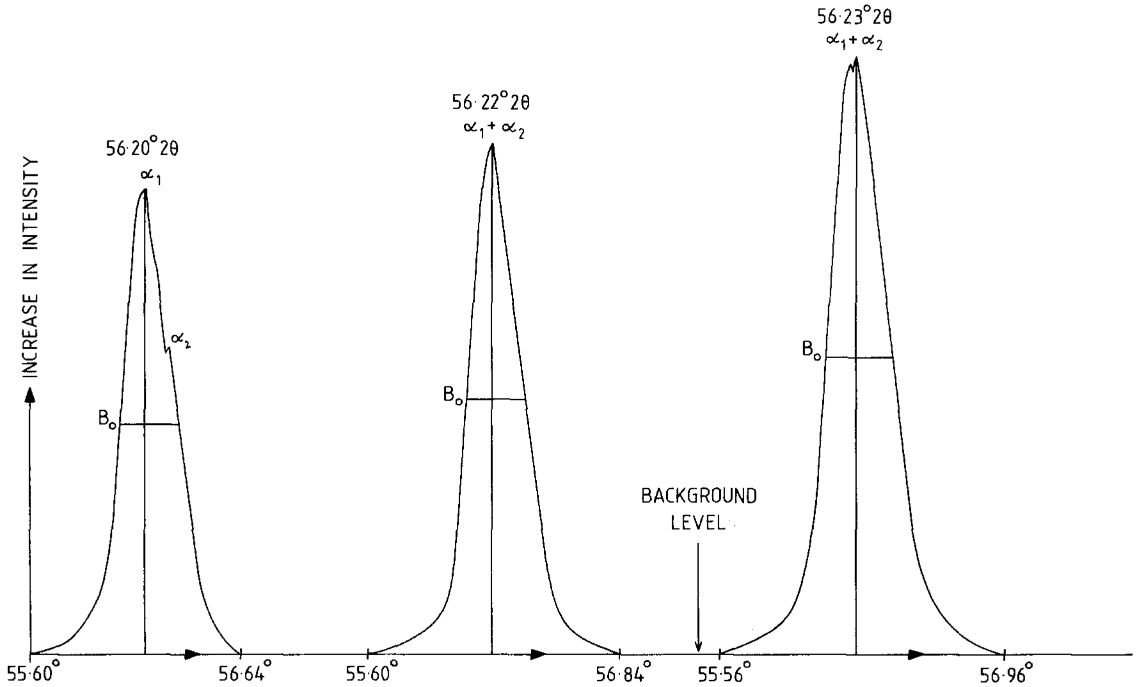

Figure 8 (a) The step-scan 00.3 line profiles of: (i) pure synthetic CH – small peak and slight shoulder due to α_2 separation; (ii) CH + SP1 – no $\alpha_1\alpha_2$ peak separation; (iii) CH + CCP1 – no $\alpha_1\alpha_2$ peak separation. (b) The step-scan 00.4 line profiles of: (i) pure synthetic CH – pronounced peak due to α_2 separation; (ii) CH + SP1 – slight shoulder due to α_2 separation; (iii) CH + CCP1 – slight shoulder arising from α_2 separation; (iv) CH + CCP6 – no $\alpha_1\alpha_2$ peak separation.

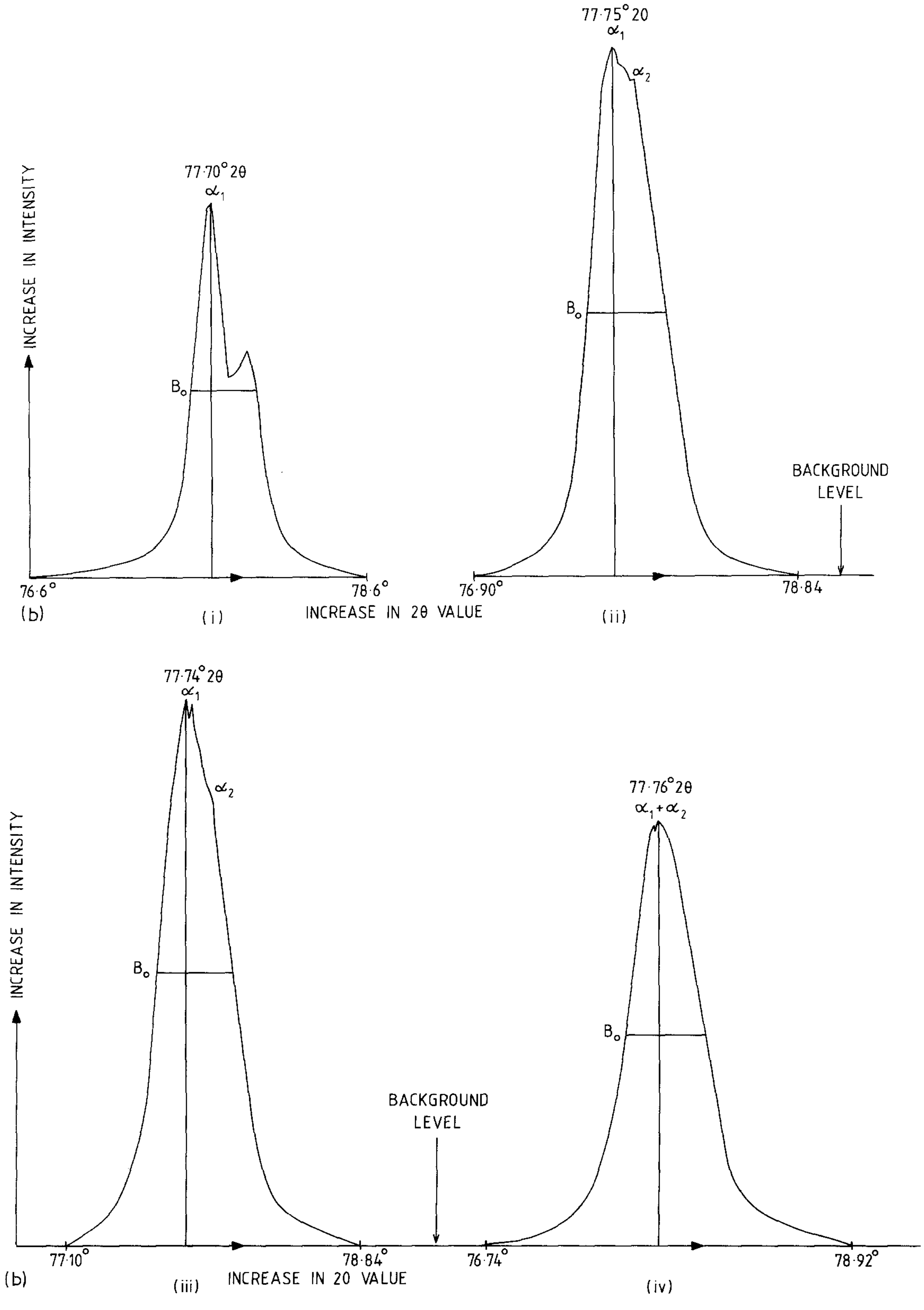

Figure 8 Continued.

References

1. S. DIAMOND, "Hydraulic cement pastes – their structure and properties", Proceedings of the Conference, University of Sheffield (Cement and Concrete Association, 1976) p. 2.
2. R. L. BERGER and J. D. McGREGOR, *J. Amer. Ceram. Soc.* **56** (2) (1973) 73.
3. N. GREENING, quoted by A. Grudemo, *Cem. Concr. Res.* **9** (1979) 19.
4. G. W. GROVES, *ibid.* **11** (1981) 713.
5. A. P. BARKER, *World Cem.* **15** (1) (1984) 25.
6. R. L. BERGER and J. D. McGREGOR, *Cem. Concr. Res.* **2** (1972) 43.
7. S. DIAMOND, *J. Amer. Ceram. Soc.* **56** (1973) 323.
8. E. HAYEK and P. DIERKES, Lecture at the Melment Symposium, Trostberg (1973).
9. P. DIERKES and E. HAYEK, *Chem-Kunst, Aktuell.* **29** (2) (1975) 71.
10. J. F. YOUNG, R. L. BERGER and F. V. LAWRENCE, *Cem. Concr. Res.* **3** (1973) 689.
11. N. B. MILESTONE, *J. Amer. Ceram. Soc.* **62** (1979) 321.
12. I. JAWED, A. W. KLEMM and J. SKALNY, *ibid.* **62** (1979) 461.
13. S. CHANDRA and L. BERNTSSON, *Cem. Concr. Res.* **11** (1981) 125.
14. T. SUGAMA and L. E. KUKACKA, *ibid.* **12** (1982) 789.
15. R. SH. MIKHAIL, M. SHATER and T. M. EL-

AKKED, *ibid.* **13** (1983) 207.
16. J. D. BIRCHALL and N. L. THOMAS, *Proc. Brit. Ceram. Soc.* **35** (1984) 305.
17. J. JOHNSON, *J. Amer. Chem. Soc.* **36** (1914) 16.
18. A. P. BARKER, N. H. BRETT and J. H. SHARP, Proceedings of the Eleventh Conference on Science Ceramics, edited by R. Carlsson and S. Karlsson (Swedish Ceramic Society, Gothenburg, 1981) p. 375.
19. P. BARNES and A. GHOSE, The Microscopy of Unhydrated Portland Cement, in "Structure and Performance of Cements", edited by P. Barnes (Applied Science, London, 1983) Ch. 4, p. 191.
20. A. P. BARKER and P. BARNES, unpublished results (1985).
21. ASTM, X-ray Powder Data File, Card No. 4-0733 2nd Printing (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1967).
22. R. HEDIN, *Swed. Forskringsinst. Cem. Betong. K. Tek. Hoegsk, Stockholm,* **33** (1962) 1.
23. W. G. FRANCE, *Colloid Chem.* **5** (1944) 443.
24. D. M. ROY and M. DAIMON, Proceedings of the Seventh International Conference on the Chemistry of Concrete, Paris, Vol. 2 (1980) II-242.

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