

The hydration of an aluminous cement with added polyvinyl alcohol-acetate

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We have studied the hydration of Secar 71 high alumina cement with added poly(vinyl alcohol-acetate). These materials are used in production of macro-defect-free cements. The polymer has considerable effects on the cement chemistry; the heat output profile measured by conduction calorimetry is significantly altered and few crystalline hydrates are produced. Where hydrate crystals do occur, the calcium-rich compounds are preferred. There are some differences in behaviour between pure polyvinyl alcohol and polymers containing acetate groups. Evidence is presented for polymer complexes in which metal ions from the cement crosslink the polymer chains. Such complexes are formed most readily by aluminium ions, so the cement grains are left with a relative surplus of calcium on their hydrating surfaces.

1. Introduction

The hydration of calcium aluminate cements with suitable polymer additives can produce a so-called macro-defect-free (MDF) material of superior tensile strength and fracture toughness [1, 2]. The addition of a water-soluble polymer such as partially hydrolysed polyvinyl acetate permits the formation of a workable paste containing very little water; the polymer acts as a lubricant facilitating close packing of the cement grains, which are then held tightly together as the polymer-water gel dehydrates. It is thus possible to explain the observed mechanical properties of MDF cements in terms of a purely physical interaction between cement and polymer producing a dense microstructure of very low porosity [2]. It is clear, however, that the increased strength does not arise simply from a lack of voids in the microstructure [3, 4], and it is possible that chemical reactions involving the polymer are to some degree responsible for the observed MDF properties [5, 6]. We have investigated this possibility by using the techniques of conduction calorimetry, X-ray diffraction, electron probe microanalysis and infrared spectroscopy to study in detail the hydration of a calcium aluminate cement with various types of poly(vinyl alcohol-acetate) added, and we find evidence for a chemical reaction between cement and polymer in these systems. In order to amplify the chemical changes we added more water than is normally used in the manufacture of MDF cements, but the chemical reactions which we observe will also be significant in the hydration of the MDF material.

This paper uses cement chemistry notation; C = CaO, A = Al₂O₃, H = H₂O.

2. Experimental

2.1. Materials

"Secar 71" aluminous cement supplied by the Lafarge Aluminous Cement Co was analysed by quantitative

X-ray diffraction and found to consist of 54% CA₂, 45% CA and 1% C₁₂A₇. "Gohsenol" polymers were supplied in powdered form by Nippon Gohsei. Four types of polymer were used; three partially hydrolysed polyvinyl acetates and one polyvinyl alcohol (Table I). The manufacturer's grade symbols are abbreviated in this paper to KH, GH, GL and NH. The first three are partially hydrolysed polyvinyl acetates; NH is almost pure polyvinyl alcohol. KH, GH and NH are long-chain polymers of about 2000 units while GL has about 600 units per chain.

Mixtures of 10 + 1, 20 + 1 and 50 + 1 Secar + polymer by mass were prepared in a shaking apparatus. Conduction calorimeter samples and those for X-ray analysis were hydrated under nitrogen at 20 or 40°C, using distilled water at a water to cement ratio of 0.5. Samples for electron probe microanalysis were hydrated for 3 days at 20°C. The partially hydrolysed acetates KH, GH and GL all mix readily with water at room temperature to form gels. Freshly prepared cement pastes containing these polymers were therefore very sticky and viscous. Polyvinyl alcohol (NH) is not readily soluble in cold water; pastes containing NH polymer were more like typical cement pastes.

2.2. Methods

The course of the hydration reaction was followed using conduction calorimetry and X-ray diffraction. X-ray measurements were made on a Siemens D500 diffractometer using copper K α radiation at 40 kV.

TABLE I Classification of polymers used

Symbol	Molecular weight	Hydrolysis (%)
KH17S	111 000	80
GH17S	98 000	88
GL05S	29 000	88
NH18S	80 000	99

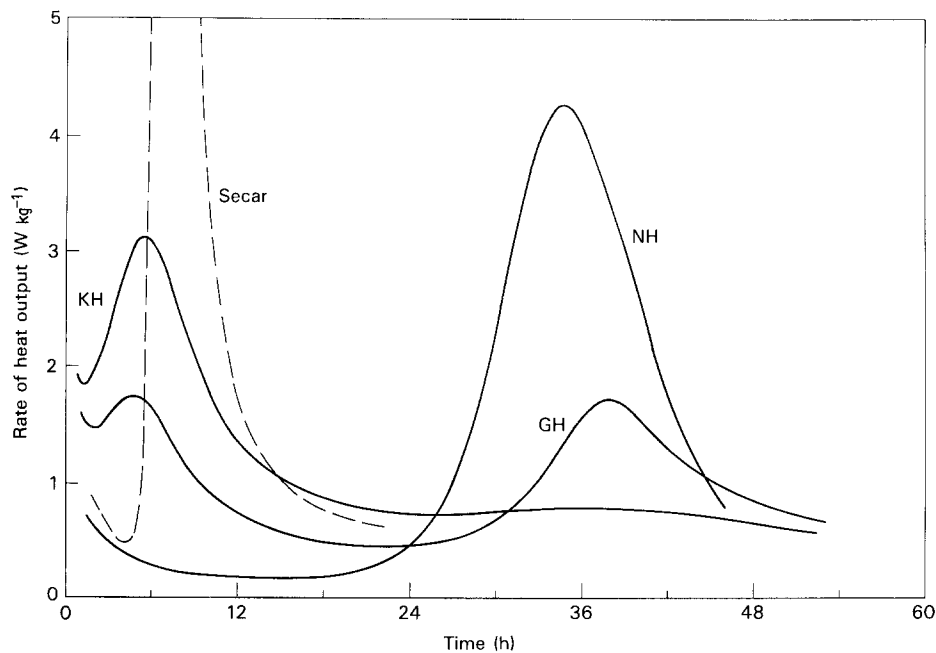


Figure 1 Conduction calorimeter output from 10 + 1 Secar + polymer mixes and from pure Secar, at 20°C.

Details of the conduction calorimetry experiment and of our quantitative X-ray diffraction analysis (QXDA) method are given elsewhere [7]. For infrared measurements samples of the hydrated polymer cements were mixed with potassium bromide and compressed into discs. Spectra were recorded using a Grubb Parsons double beam spectrometer. It was also possible to extract small amounts of polymer from the hydrated cements by density separation; the powdered material was shaken with chloroform and centrifuged. These polymer extracts were examined using infrared and X-ray fluorescence spectroscopy.

Electron probe microanalysis (EPMA) measurements were made on a Cambridge Microscan 9 crystal spectrometer electron probe microanalyser. Analyses were made of calcium and aluminium; it was also possible to determine carbon and oxygen by using an Ovonix multilayer detector crystal.

Differential thermal analysis (DTA) measurements were made on a DuPont 900 instrument.

3. Results

3.1. Calorimetry

Fig. 1 shows the conduction calorimeter output from pure Secar and from 10 + 1 Secar + polymer mixtures using KH, GH and NH polymers, hydrated at 20°C. The polymer mixtures give much lower, broader peaks than the pure Secar, and the total heat output is reduced from 270 to about 220 kJ per kilogram of dry solid. With the partially hydrolysed acetates KH and GH, there are two calorimeter peaks at about 6 and 36 h. With KH the first peak is the stronger one, while with GH the two are about equal in intensity. Between these times, the hydrating material was flexible, with a dry, rubbery texture. After the second peak it was brittle. The fully hydrated NH polymer

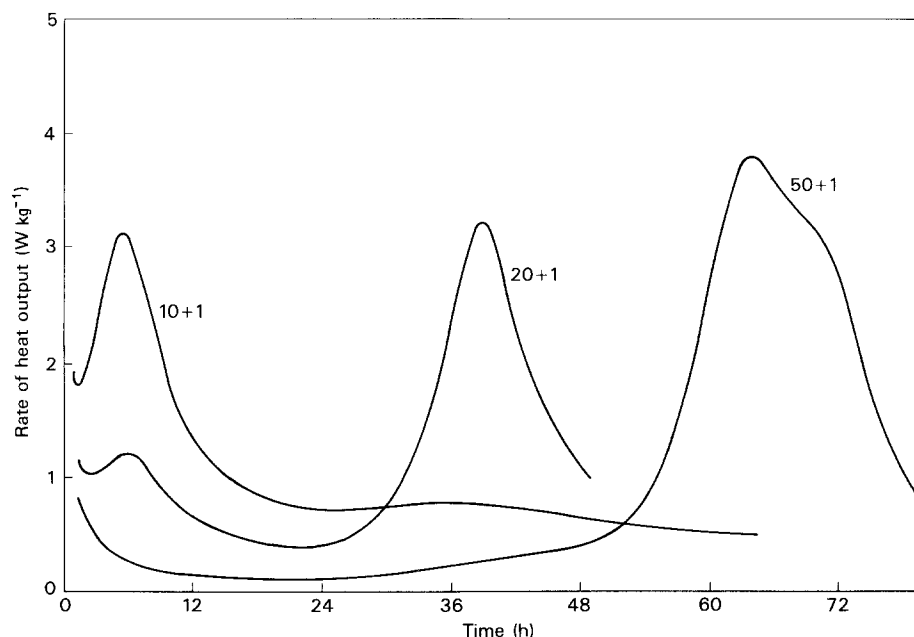


Figure 2 Conduction calorimeter output from 10 + 1, 20 + 1 and 50 + 1 mixes of Secar + KH polymer at 20°C.

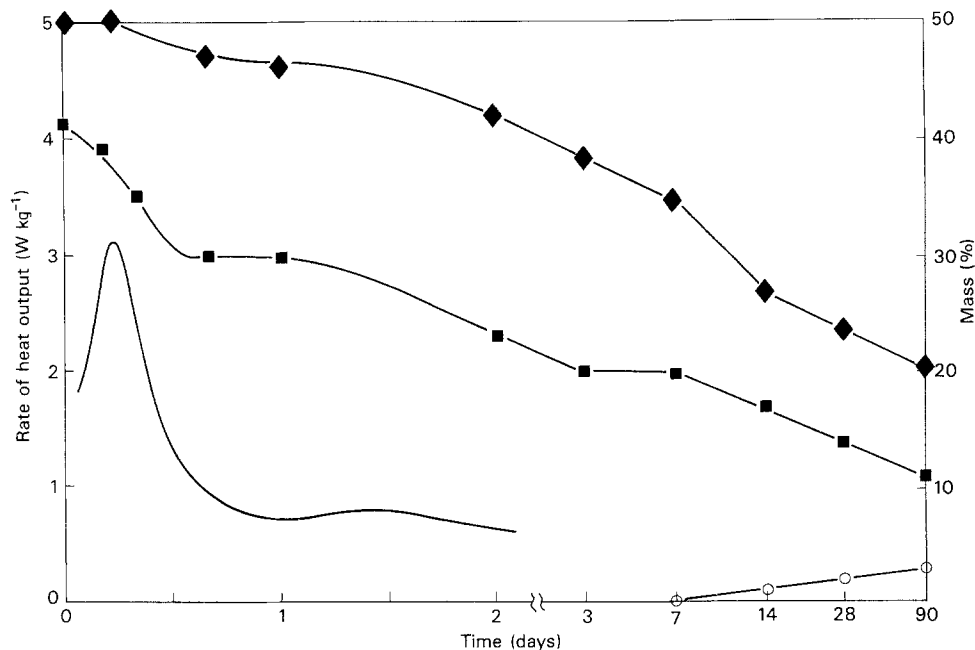


Figure 3 Conduction calorimeter output and phase composition of 10 + 1 Secar + KH polymer mixture hydrated at 20°C. (◆ CA₂, ■ CA, ○ C₃AH₆).

gave only the second peak and did not go through a flexible phase. At 40°C a similar pattern was observed, but accelerated with the peaks occurring at about 1½ and 4 h. The short chain GL polymer behaved similarly to GH.

Fig. 2 illustrates the effect of varying the polymer concentration; it shows the output at 20°C from, 10 + 1, 20 + 1 and 50 + 1 mixes using KH polymer. The 10 + 1 and 20 + 1 mixes give two peaks of heat output, but in the 20 + 1 mix the second peak is the larger of the two. Hydration of the 50 + 1 mix took considerably longer; the single peak at 60 to 72 h represents a heat output similar to that from pure Secar. A similar pattern was seen with GH polymer. The NH polymer gave only a single peak irrespective of concentration, but unlike KH and GH the peak occurred soonest at low polymer concentration; the

50 + 1 NH mix gave a peak at 9 h similar to that from pure Secar.

3.2. X-ray diffraction

Fig. 3 shows the variation with time of the amounts of crystalline materials in a hydrating mixture of 10 + 1 Secar + KH polymer at 20°C, together with the calorimeter output. Fig. 4 gives the same information for the NH polymer; the behaviour of GH was intermediate between the two and GL was similar to GH. In each case the calorimeter peaks correspond to reductions in the CA mass fraction; thus with KH the CA is consumed in two stages while with NH there is only one. The hydration of CA₂ begins after about 36 h; the slight reduction in CA₂ mass fraction corresponding to the first calorimeter peak with KH is due only to the increase in total solid mass as CA reacts

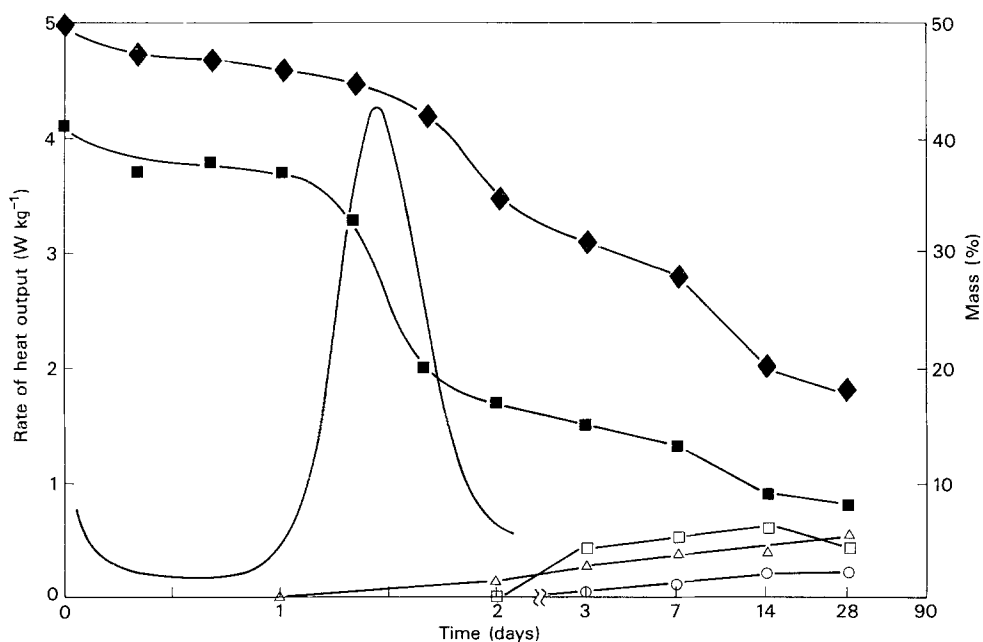


Figure 4 Conduction calorimeter output and phase composition of 10 + 1 Secar + NH polymer mixture hydrated at 20°C. (◆ CA₂, ■ CA, □ CAH₁₀, △ C₂AH₈, ○ C₃AH₆).

TABLE II Composition (%) of 10 + 1 Secar + polymer mixes hydrated for 3 days at 20°C

	CA	CA ₂	C ₂ AH ₈	C ₃ AH ₆	CAH ₁₀
KH	20	38	0	0	0
GH	16	33	0	1	0
NH	15	31	3	1	4
pure Secar*	14	30	0	0	24

*Hydrated for 24 h

with water. The most interesting feature of the X-ray results is that crystalline hydrates are formed only very slowly and in small quantities. With pure Secar, slightly more CA and CA₂ are consumed and a large quantity of CAH₁₀ is produced. Such crystalline hydrates as do form in the polymer mixes tend to be calcium-rich; thus the KH mix gave C₃AH₆ but no CAH₁₀ and the NH mix gave CAH₁₀, C₂AH₈ and C₃AH₆. With pure Secar C₂AH₈ is not formed at 20°C and C₃AH₆ is produced only after long periods by conversion of CAH₁₀ [7]. Table II shows the composition of 10 + 1 polymer mixes after 3 days hydration.

With lower polymer concentrations, slightly more CA and CA₂ were consumed and more crystalline hydrates were produced. The KH and GH mixtures produced C₂AH₈; the NH mixture gave a little C₂AH₈ but mainly CAH₁₀.

At 40°C the hydration was much more rapid but similar trends were observed. Thus the KH 10 + 1 mix gave only C₃AH₆ (12% at 28 days). The NH 10 + 1 mix gave initially C₂AH₈, which reached a maximum at about 12 h and then declined, and finally C₃AH₆ (26% at 28 days).

It is possible to identify a number of trends from the X-ray results. The effects of polymer on the hydration decrease in the order KH > GH > NH and with decreasing concentration. The main effects are as follows.

(i) The polymer restricts the consumption of CA and CA₂ and lowers the heat output.

(ii) Polymer mixes yield only small amounts of crystalline hydrates, and C₂AH₈ and C₃AH₆ are preferred to CAH₁₀.

There is no corresponding simple trend governing the number and timing of the calorimeter peaks (see above).

3.3. Infrared spectra

Infrared measurements were made on the pure polymers, on hydrated Secar + polymer mixtures and on the polymer extracts obtained by density separation of these mixtures in a centrifuge. The main absorptions in the polymers are the OH stretch at 3400 cm⁻¹, the CH stretch at 2940 cm⁻¹ and the ester carbonyl group resonance at 1730 cm⁻¹; the latter is absent from the NH polymer. In the KH polymer extract after reaction with cement, the OH signal was weaker and there was no ester resonance. Two new, sharp signals appeared at 1460 and 1380 cm⁻¹; the NH polymer extract gave only a weak spectrum and these two new signals were not observed. The hydrated Secar + polymer mixtures themselves showed a number of broad absorptions, most of which may be attributed to the cement. One signal at 1580 cm⁻¹ may be due to

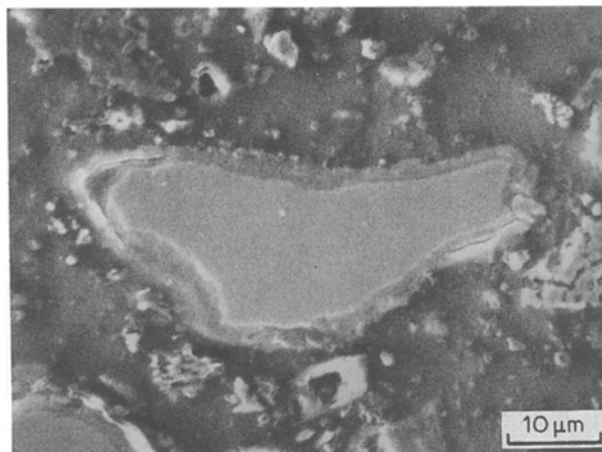


Figure 5 Electron micrograph of a hydrating grain in a 10 + 1 Secar + GH polymer mixture.

calcium acetate hydrate [6] but we found no X-ray evidence for this material. The second main resonance of the acetate ion at 1440 cm⁻¹ overlaps with signals of both the polymer and the hydrated cement. Hydrolysis of the acetate groups from the polymer is to be expected in the alkaline environment of the cement, and certainly occurs if the polymer is soaked in a supersaturated CA solution. Polymers so treated gave acetate ion infrared signals at 1580 and 1440 cm⁻¹.

3.4. Electron probe microanalysis

Samples of Secar and of the four types of polymer cement at ratios of 10 + 1 and 20 + 1 were investigated. All four polymers gave similar results. Grains of CA and CA₂ were surrounded by a matrix of amorphous hydrated material. Hydrate crystals were not observed; only a few are to be expected and these were presumably too small to see. Many KH, GH and GL samples contained small lumps of unmixed polymer, which must have coagulated from the polymer-water gel. NH samples had a very porous structure consistent with their weak, crumbly nature. The most visible effect of added polymer was the appearance of "hydration shells" around both CA and CA₂ grains (Fig. 5). These shells were clearer and more abundant in some samples than in others; they were up to 3 μm thick and were usually rich in calcium with molar C to A ratio (CaO to Al₂O₃ ratio) between 1 and 2. Such shells were not seen in Secar samples without polymer, although there were some calcium-rich areas in the hydrated material both near to grain edges and remote from clinker grains. The hydrated material in the polymer cements had C to A ratio between 0.3 and 1.0; although its composition was very variable it seemed on average to contain more aluminium than the hydrated phase from pure Secar. There were significant concentrations of carbon arising from polymer in the hydrated material of KH, GH and GL cubes (up to 20% carbon in some regions in the 10 + 1 samples) but little if any in the hydration shells of the clinker grains. The NH samples had much less polymer in their hydrated material, but no obvious lumps of unmixed polymer. The NH polymer appears to be less strongly bound to the cement than are the acetate polymers, so it is possible that polymer is lost

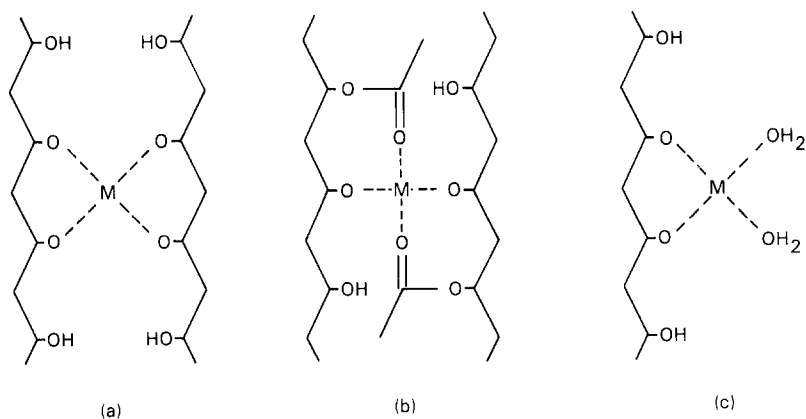


Figure 6 Polymer complexing of metal ions: (a), (b) cross-linking of polymer chains through ester or hydroxyl groups; (c) a hydrated complex involving a single polymer chain.

from the surface of NH samples either during sample preparation or under the electron beam. Samples with lower polymer concentration (20 + 1) gave similar results to the 10 + 1 samples except that, as expected, the hydrated material contained less carbon.

3.5. Other results

As mentioned above, we were able to extract small amounts of polymer from powdered hydrated polymer cements by density separation in a centrifuge. X-ray fluorescence analysis revealed the presence of varying amounts of both calcium and aluminium. It was only possible to extract small quantities of polymer (about 10% of the total) so the extracted material probably represents weakly bound polymer which may not be representative of the whole.

Differential thermal analysis of the polymer cements gave two main signals. A broad endotherm extending from 50 to 300°C represented dehydration and decomposition of the amorphous hydrated material; small peaks due to C_2AH_8 , C_3AH_6 and AH_3 were superimposed on this broad signal when these crystalline hydrates were present. Combustion of the polymer produced an exotherm at about 350°C; in NH samples the oxidation occurred in two stages with a second exotherm at 450°C.

4. Discussion

It is clear from the calorimetry and X-ray diffraction results that all four types of polymer have significant effects on the hydration of Secar. The KH, GH and GL polymers which contain acetate groups and form gels with water produce broadly similar effects; there are some differences between these and the pure polyvinyl alcohol (NH) which is sparingly soluble and does not form a gel. The acetate polymers give two peaks in their calorimeter output; the first peak must be due to the presence of ester groups rather than to gel-forming ability since it is stronger in KH than in GH or GL which are more extensively hydrolysed. This first peak is significant only at high polymer concentration (10 + 1 ratio) and we believe it is due to cross-linking of polymer chains through complexing of metal ions by either ester or hydroxyl groups (Figs 6a and 6b). The structure will also contain water molecules bound to the metal ions and polymer chains. This cross-linked material represents the flexible, rubbery phase which exists in the time between the two calorimeter peaks. At lower polymer concentrations there is much

less cross-linking of chains, so the initial calorimeter peak is small or absent and the flexible material is not produced. The second peak, corresponding to the single calorimeter signal of NH samples, represents the further reaction of calcium aluminates with water and with the hydroxyl groups of the polymer (Fig. 6c). This reaction may or may not involve cross-linking of chains; in any case extensive hydration occurs and a brittle material results. The metal ions seem to complex more readily with the acetate polymers, giving an early calorimeter peak and finally producing a reasonably strong material. The fully hydrolysed NH polymer produces only a weak, crumbly polymer cement which, according to the EPMA results, readily loses polymer from its hydrated material.

It is uncertain to what extent the acetate groups are hydrolysed from the acetate polymers in the cement. As noted above, we found no X-ray evidence for inorganic acetates in the hydrated cements. Infrared measurements on the mixtures gave a signal at 1580 cm^{-1} which could be due either to acetate ions, or to an ester group resonance lowered in frequency by complexing to a metal ion. The two new infrared signals in the KH polymer extract are probably due to metal-oxygen bonds in the polymer complex. Complete hydrolysis of the acetates would leave pure polyvinyl alcohol in solution, thus explaining why the acetate polymers react more quickly than the polyvinyl alcohol itself which takes much longer to dissolve. However, it is only the first of the two calorimeter peaks which is accelerated; the second occurs at the same time as the peak in the NH mixture (Fig. 1). If the only effect of the acetate groups is to produce a dissolved polyvinyl alcohol, then all the polymer mixes ought to show similar hydration behaviour, but delayed in the case of NH by the limited solubility. As it is, only the acetate polymers appear to promote cross-linking of polymer chains to give a flexible intermediate phase. Furthermore, the initial calorimeter peak corresponding to formation of this phase is strongest in the KH polymer which contains most acetate groups (Fig. 1). Thus if the acetate groups are hydrolysed off, this must occur during rather than before the first reaction with the metal ions, since the ester groups clearly determine the extent of this initial metal-polymer reaction.

The presence of polymer inhibits the formation of crystalline calcium aluminate hydrates. The heat output from the hydration of polymer cements was

slightly less than from pure Secar, so the crystallisation of the amorphous hydrated material would be an exothermic process; it is prevented by the loss in entropy which would accompany crystallisation and separation of the polymer from the inorganic material. The NH polymer which is least strongly bound to the hydrated material is less effective than the others at suppressing the formation of hydrate crystals.

Both X-ray and EPMA results indicate that the polymers complex more readily with aluminium than with calcium ions. This leaves a relative surplus of calcium so that when crystalline hydrates do form, C_2AH_8 and C_3AH_6 are preferred to CAH_{10} . The calcium-rich hydration shells around CA and CA_2 grains suggest that the hydration involves first the removal of aluminium ions from the grain surfaces, followed later by the calcium ions. Thus around each grain there is always a thin, calcium-rich perimeter, and beyond this in the hydrated material a slight surplus of aluminium in accordance with the preference of the polymer. The detection by EPMA of carbon in the hydrated material does not necessarily mean that the polymer is chemically bound there, but the infrared, X-ray and calorimetry results supply ample evidence that this is the case. The lower polymer concentrations measured in NH samples are consistent with the weaker complexing associated with the fully hydrolysed polymer.

There is good agreement between our results and those of Rodger *et al.* [6], who used a partially hydrolysed polyvinyl acetate. We agree with their observation of a double calorimeter peak, of which the first component is strongest at high polymer concentration, but our X-ray results show only very small quantities of crystalline hydrates even after the second calorimeter peak. It is clear that the polymer complexes more readily with aluminium ions; both our EPMA and X-ray results and the solution chemistry experiments and electron microscope measurements of Rodger *et al.* support this conclusion. We are not certain to what extent the acetate groups are hydrolysed from the polymer chains; our infrared results seem inconclusive and we do not see X-ray signals from calcium acetate.

5. Conclusions

Both polyvinyl alcohol and partially hydrolysed poly-

vinyl acetate react chemically with Secar cement in the presence of water, affecting the course of the cement hydration and thus the microstructure and strength. The polymers form complexes with the metal ions from the cement, preferring aluminium to calcium. Polymers containing ester groups react most readily, cross-linking through metal ions to produce a flexible intermediate phase. Further reaction involving water molecules and polymer hydroxyl groups then produces a hard hydrated material. Polyvinyl alcohol itself, which is not readily soluble in water, does not give a flexible intermediate phase and the final hydrated material is weak, porous and brittle.

The hydrating calcium aluminate grains are surrounded by shells of calcium-rich material; in the presence of polymer the aluminium ions are more readily removed leaving a relative surplus of calcium behind. The polymer is not present in these shells but was detected in the outlying hydrated material.

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