JOURNAL OF MATERIALS SCIENCE 20 (1985) 2853–2860

High strength cement pastes

Part 2 *Reactions during setting*

S. A. RODGER, S. A. BROOKS, W. SINCLAIR[†], G. W. GROVES
D. D. DOUBLE[*]
Department of Metallurgy and Science of Materials, Oxford University, Parks Road, Oxford, UK

A study of the chemical reactions occurring in high strength cements is presented with particular reference to the cement–polymer interaction. The addition of small amounts (1.6%) of polyvinyl (alcohol/acetate) to the high alumina cement Secar 71 significantly retards the normal hydration reactions. At much larger doses (10% PVA) the crystalline hydrates are completely suppressed and the polymer reacts with the cement solution to form calcium acetate and a crosslinked polymeric product. In the case of high strength OPC/polyacrylamide pastes, the high pH of the cement solution converts the polymer to polyacrylic acid which reacts with the cations from the hydrated cement to form a crosslinked metal–polyacrylate. This latter system is analogous to reactions which occur in certain polyacrylic acid-based dental cements.

1. Introduction

The production of high strength cement pastes, often known as MDF (macro-defect-free) pastes, following the methods first reported by Birchall *et al.* [1, 2], involves the addition of a water-soluble polymer to cement and water. A major function of the polymer is to permit the development of a plastic mass from a mixture containing relatively little water, during a process of high-shear mixing. However, the polymer must also be expected to interact in some way with the hydration process. Following the study of the microstructure of typical MDF pastes described in a previous paper, we here study the evidence of polymer–cement interactions provided by calorimetry, solution chemistry and infrared spectroscopy. Of primary interest is the system of a high alumina cement, Secar 71, with polyvinyl alcohol/acetate which can produce a paste with a strength in bending ~ 150 MPa; infra-red studies are also reported for ordinary Portland cement (OPC)–polyacrylamide, C_3S[‡]–polyacrylamide and CA–polyvinylalcohol/acetate systems. The results indicate that strong interactions occur between polymer and cement in these systems.

2. Experimental details

2.1. Materials

Cement powders used in this study were a typical Blue Circle Northfleet ordinary Portland cement (OPC) and Lafarge Secar 71 high alumina cement. Secar 71 is composed chiefly of Al_2O_3 (72.32%) and CaO (26.2%) plus several minor oxides such as SiO_2 (0.5%), Na_2O (0.21%), Fe_2O_3 (0.23%), K_2O (0.2%) and MgO (0.2%). The principal phases of this cement are CA and CA_2. In addition, small amounts of α-Al_2O_3 and $Na_2Al_{22}O_{34}$ have also been identified.

Monocalcium aluminate was prepared by reacting the appropriate amount of $CaCO_3$ and Al_2O_3 powder together in a platinum crucible at 1450° C. After 12 h heat treatment the pellet was air-quenched, ground and then checked for purity by powder X-ray diffraction XRD. Only peaks of CA were present in the X-ray pattern. Preparation of C_3S powder followed the procedure outlined by LeSueur [3].

---

[*] *Present address*: Cemcon Research Associates Inc, 9901 George Palmer Highway, Lanham, Maryland 20706, USA.
[†] *Present address*: BHP Melbourne Research Laboratories, PO Box 264, Clayton, Victoria 3168, Australia.
[‡] Cement chemistry notation is used: C = CaO, S = SiO_2, A = Al_2O_3.

0022–2461/85 $03.00 + .12

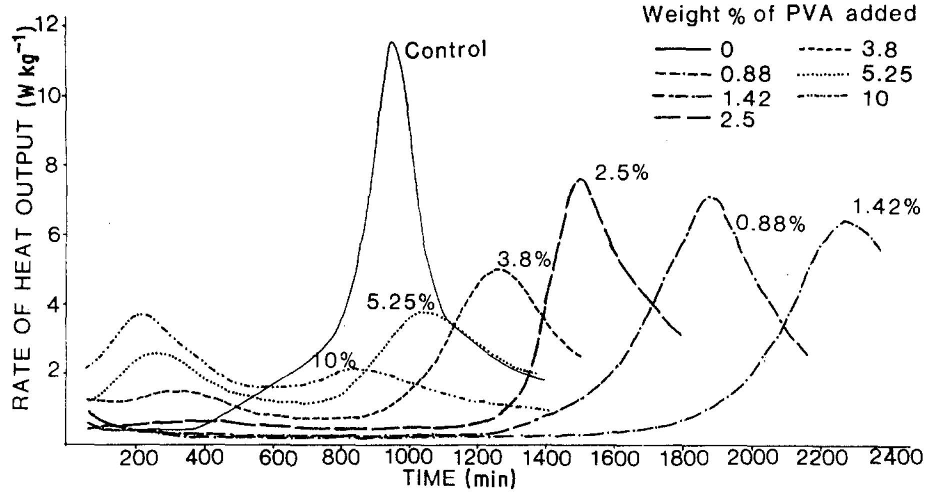

Figure 1 Heat evolution against time curves for control and Secar 71 pastes treated with polyvinyl alcohol/acetate. w/c = 0.5.

Mixed with these cements are water soluble polymers. Polyacrylamide is typically added as a gel (20% wt/wt polymer/water) to OPC while poly (vinyl alcohol/acetate) (PVA), approximately 79 mol% hydrolysed, is used in powdered form with Secar 71 based cements. Both of these polymers are commercially available, the PVA under the trade name "Gohsenol" and the polyacrylamide as "Separan".

2.2. Methods

Heat evolution curves for cement + polymer, hydrated at a water/cement ratio of 0.5, were recorded at 27° C using a conduction calorimeter. Details of the apparatus and the method have been previously described [4].

Solution chemistry of Secar 71 treated with Gohsenol was carried out on the aqueous filtrate of cement slurries made up with a water/solid ratio of 4. The mixture was agitated using a magnetic stirrer and then filtrated at prescribed time intervals to extract the aqueous solution. Mixing and filtering were undertaken in plastic apparatus under a nitrogen atmosphere at 22 ± 2° C. The concentrations of calcium and aluminium in the aqueous phases were determined by EDTA titration and colorimetric analysis, respectively. Details of the apparatus and method for analysing the solutions are given in previous publications [5, 6].

Pastes prepared for infra-red spectroscopic measurements contained a larger quantity of polymer than normally used in high strength cements. 20% Gohsenol was mixed with Secar 71 and CA powders while 11 and 17% of polyacrylamide was added to OPC and C_3S respectively. Cement powders were also reacted with 20% of polymer and 23% deuterium oxide. The parent polymers, cement powders, and cement pastes were ground and sieved to a size of less than 53 μm, mixed with KBr and pressed into thin discs. Transmission infra-red spectra of these materials were recorded over the frequency range 4000 to 600 cm^{-1}.

3. Results

3.1. Calorimetry

Fig. 1 shows the heat evolution curves obtained from a hydrating mix of Secar 71 with freshly distilled water in the presence of various wt% polyvinyl alcohol/acetate. The control curve from Secar 71 hydrated with water shows a single exotherm with a maximum at about 950 min. Small additions of polymer (< 3 wt%) produce a retardation of the exotherm to a maximum of 2400 min for a 1.6 wt% addition. However, when larger quantities of polymer are added an extra exotherm appears at short times which increases as the amount of PVA added increases and at the same time the original exotherm becomes progressively less retarded and decreases substantially in size.

XRD traces of hydrating paste containing 5 wt% PVA show no evidence of the crystalline hydrates, CAH_{10} or C_2AH_8, after the first exotherm (i.e. at 600 min). However, after the second

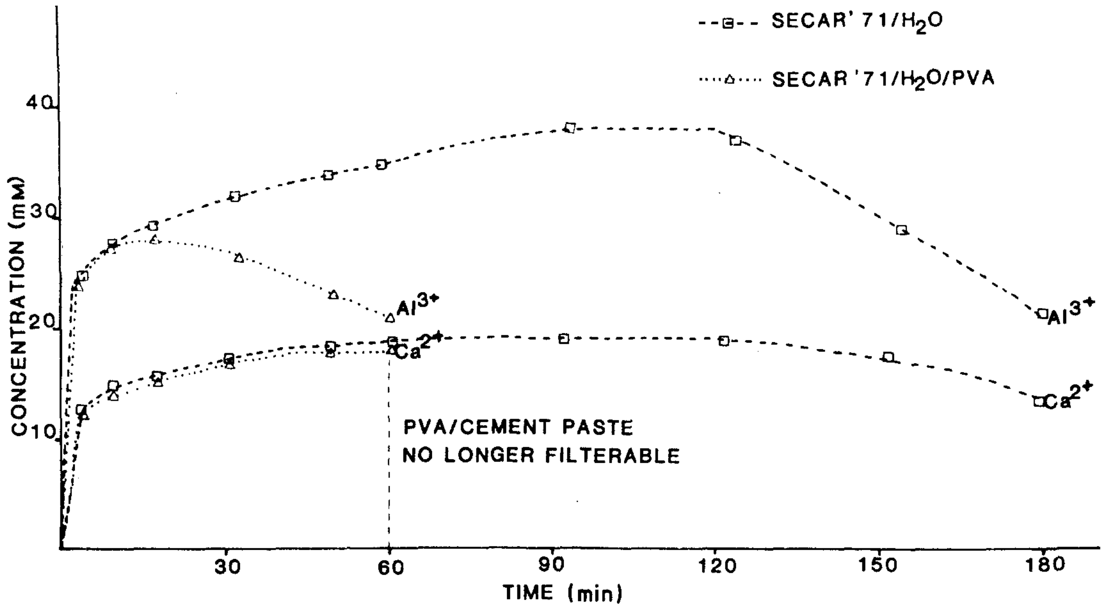

Figure 2 Concentration against time curves for solutions filtered from Secar 71 + water and Secar 71 + water + polyvinyl alcohol/acetate. w/s = 4.

isotherm (at 1500 min) peaks corresponding to C_2AH_8 appear. Thus the second isotherm may be identified as due to the formation of calcium aluminate hydrates whilst the first may correspond to the interaction between the polymer addition and the cement. It is also notable that, as expected, XRD shows the amount of crystalline hydrate material formed to decrease rapidly as the second exotherm decreases in size.

3.2. Solution chemistry

Secar 71 consists of an approximately equimolar mix of CA and CA_2 the latter being less reactive and of little hydraulic value. Hence the composition of the solution phase of a Secar 71 paste is largely due to the congruent dissolution of CA. Fig. 2 shows how the calcium and aluminium concentrations in solution vary with time. When Secar 71 is hydrated with freshly distilled water the calcium and aluminium concentrations rise concurrently the C:A ratio being approximately unity. After 2 h the concentrations begin to drop but again the C:A ratio remains at ~ 1 suggesting the precipitation of CAH_{10}. However, when the polyvinyl acetate/alcohol is added to the cement although the calcium and aluminium concentrations initially rise together, C:A = 1, after about 10 min the calcium concentration continues to rise whilst the aluminium concentration begins to drop, suggesting that aluminium is being removed from solution, e.g. in the form of an insoluble complex. After 1 h the PVA/cement mix becomes unfilterable as the paste has become a solid rubbery mass.

3.3. Infrared spectra

Infrared spectra of the anhydrous clinkers and organic polymers, PVA and polyacrylamide, are shown in Fig. 3. The spectra of cement pastes and the pastes of CA and C_3S formed with the polymers are shown in Fig. 4. Band assignments for these figures have been collected in Tables I and II and are based on standard texts such as Bellamy [7] and also on the previous infrared studies of Crisp *et al.* [8]. The absorptions of most interest in this study are those arising from the asymmetric and symmetric stretching vibrations of the metal carboxylates which occur in the regions of 1530 to 1610 and 1390 to 1420 cm^{-1}. Because of a possible interference from a water band at 1630 cm^{-1}, infrared spectra were also obtained from samples hydrated using D_2O. The spectra from these experiments revealed similar patterns to those obtained from hydration with water although the amount of reaction between OPC + polyacrylamide and C_3S + polyacrylamide hydrated with D_2O was much reduced.

The most notable features in both CA + PVA and Secar 71 + PVA infrared patterns is the almost complete absence of the carbonyl (C=O) band of the acetate group at 1720 cm^{-1} and the emergence

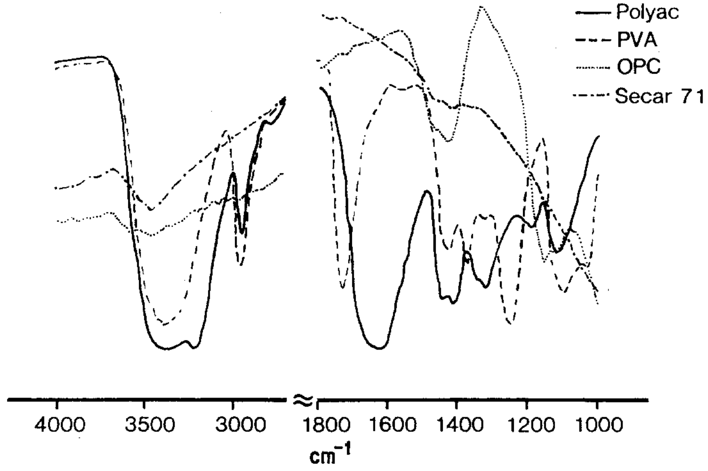

Figure 3 Infrared spectra of polyvinyl alcohol/acetate (PVA) and polyacrylamide (polyac) films and anhydrous OPC and 71 powders in KBr discs.

of the two metal carboxylate absorbances at 1570 and 1415 cm^{-1}. In the case of OPC and C_3S + polyacrylamide the situation is more complicated. Spectra from these pastes show the disappearance of bands due to N–H stretching at 3200 and ~ 1630 cm^{-1} and also a reduction and slight shift of the C=O (amide I) band at 1650 to 1680 cm^{-1}. The NH stretching band at 3360 cm^{-1} would also be lost, but is replaced by the strong broad O–H stretching band, which overlaps this region, resulting from the water of hydration. The appearance of two bands at 1570 and 1410 cm^{-1} is charateristic of the asymmetric and symmetric stretching vibrations of a carboxylate salt and indicates a reaction between polymer and anhydrous cement.

4. Discussion

4.1. High alumina based MDF cements

The calorimetric results show that at low concentrations PVA acts as a typical long chain organic compound in that it retards the setting of the cement. It has been reported [9] that PVA may be used successfully to prevent or slow down the growth of crystals in silver halide solutions thus the mechanism of retardation is probably poisoning of nucleation sites or adsorption on to grain surfaces preventing further hydration.

As the concentrations of PVA added increases the retarding effect is reduced and an earlier peak begins to appear. This early peak increases in height as the PVA addition increases whilst the later peak which corresponds to calcium aluminate hydrate formation decreases. If a similar quantity of PVA is mixed with an inert filler, e.g. sand, neither peak occurs so we can conclude that this early peak is due to the interaction between the polymer and ions released from the cement.

Solution chemistry results suggest that in the presence of PVA, alumina ions are being removed from solution, i.e. forming an insoluble complex or compound. The calcium ion concentration,

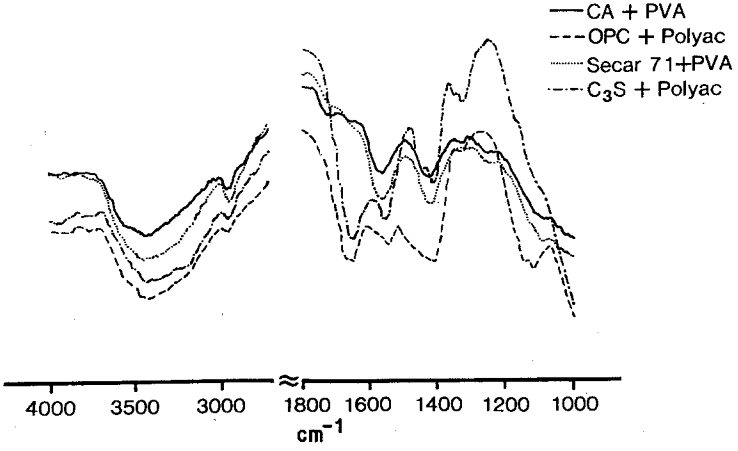

Figure 4 Infrared spectra of cements and cement minerals formed with polyvinyl alcohol/acetate (PVA) and polyacrylamide (polyac).

TABLE I Infrared absorptions of PVA and polyacrylamide (Fig. 3). Frequencies in cm^{-1}

PVA	Assignment	Polyacrylamide	Assignment
3360vsb	OHstr	3360vsb	N–Hstr
2930m	CHstr	3200vs	N–Hstr
1720s	C=Ostr (acetate)	2940m	CHstr
1430m	CH, CH_2, OH bend	1600–1640vsb	C=Ostr, NH bend
1370m	CH bend	1445m	CH bend
1245s	C–Ostr	1415m	
1096mb	C–Ostr, OH bend	1350m	
		1320m	

s = strong, m = medium, b = broad, str = stretch.

however, remains very similar to that in the control. EDS measurements in the electron microscope also suggest that the gel phase between the anhydrous cement grains is aluminium rich, the C:A ratio being 1:1.2 to 2 for a typical HAC/PVA mix [10]. It is well known that the borate ion $[B(OH)_4]^-$ is able to form complexes with certain polyhydroxy compounds such as glycerol, mannitol or sugars [11] and it is known [9] that orthoboric acid H_3BO_3 reacts with polyvinyl alcohol in the presence of a base to form a completely glassy crosslinked polymer phase as shown in Fig. 5. The aluminate ion $[Al(OH)_4]^-$ has a very similar tetrahedral structure and may react in an analogous fashion.

Infrared measurements indicate that on mixing PVA with the cement a metal carboxylate is formed and X-ray evidence suggests that it is calcium acetate ($C_4H_6CaO_4(H_2O)_{0.5}$). This will be formed by the reaction of calcium ions released from the cement with the acetate ions liberated by the hydrolysis of the polyvinyl acetate in the alkaline environments thus leaving pure polyvinyl alcohol in solution. This step is important since pure polyvinyl alcohol will not dissolve directly in cold water due to the extremely strong hydrogen bonding between the polymer chains.

Thus we postulate the following reaction scheme, shown diagramatically in Fig. 6. When water is added to the cement mixed with the partially hydrolysed polyvinyl acetate the rising pH causes the hydrolysis of the acetate groups leaving polyvinyl alcohol in solution with acetate ions which subsequently react with calcium ions to form calcium acetate. The metal ions in solution will then crosslink the polyvinyl alcohol chains; this causes the polymer matrix to become rubbery and thus allows the physical processing to continue as the cement/polymer mix attains a plasticine like consistency. The polymer will also coordinate with metal ions on the surface of the cement grains producing a cohesive matrix which links the anhydrous particles.

The material remains in this rubbery state for about 7 h after which the polymer matrix begins to become more rigid due to dehydration caused by the formation of a very small amount of amorphous hydrate material. This will remove the coordination spheres of water from the crosslinked polymer and impart stiffness. The process is not simply one of drying by evaporation since an MDF cement will set at a high relative humidity. An additional loss of water is achieved when the set cement is heated at 80° C for several hours and about 2% by weight is lost in this process. Birchall [2] suggests that this process causes a further reduction of porosity as a result of polymer contraction.

4.2. OPC based MDF cements

An MDF type cement with flexural strengths of about 50 to 80 MPa may be made using the same

TABLE II Infrared spectra of cements (Fig. 4). Frequencies in cm^{-1}

CA + PVA	OPC + Polyac	Secar 71 + PVA	C_3S + Polyac	Assignment
3450s	3430s	3460s	3430s	OHstr
2940w	2940w	2940w	2940w	CHstr
1670vw	1680s	1670vw	1670s	C=Ostr
1570s	1570m	1570s	1560m	C–Ostr (salt)
	1450s		1450s	CH_2 bend
1415sb	1410sb	1415sb	1410m	C–Ostr (salt)

s = strong, w = weak, m = medium, sh = shoulder, b = broad, str = stretch.

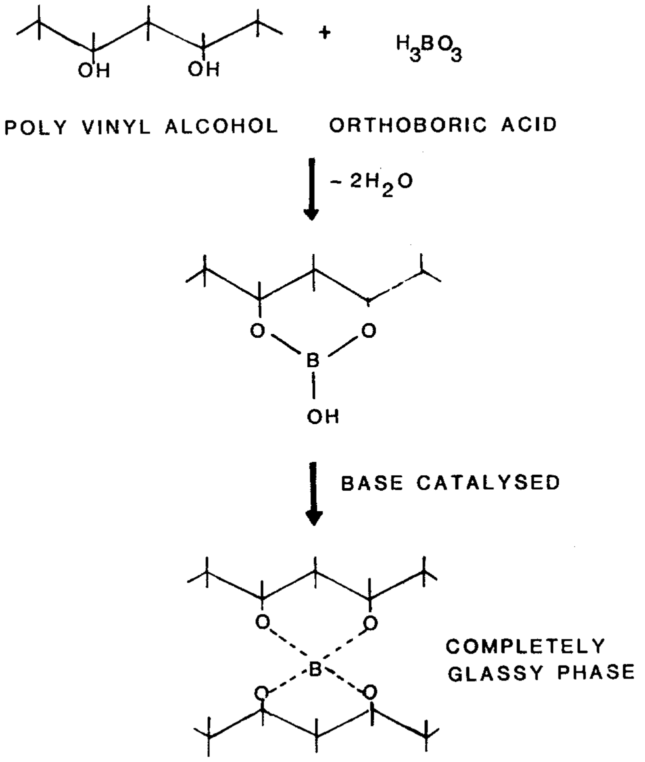

Figure 5 Reaction of PVA with orthoboric acid to produce a boron crosslinked polymer (after Pritchard [9]).

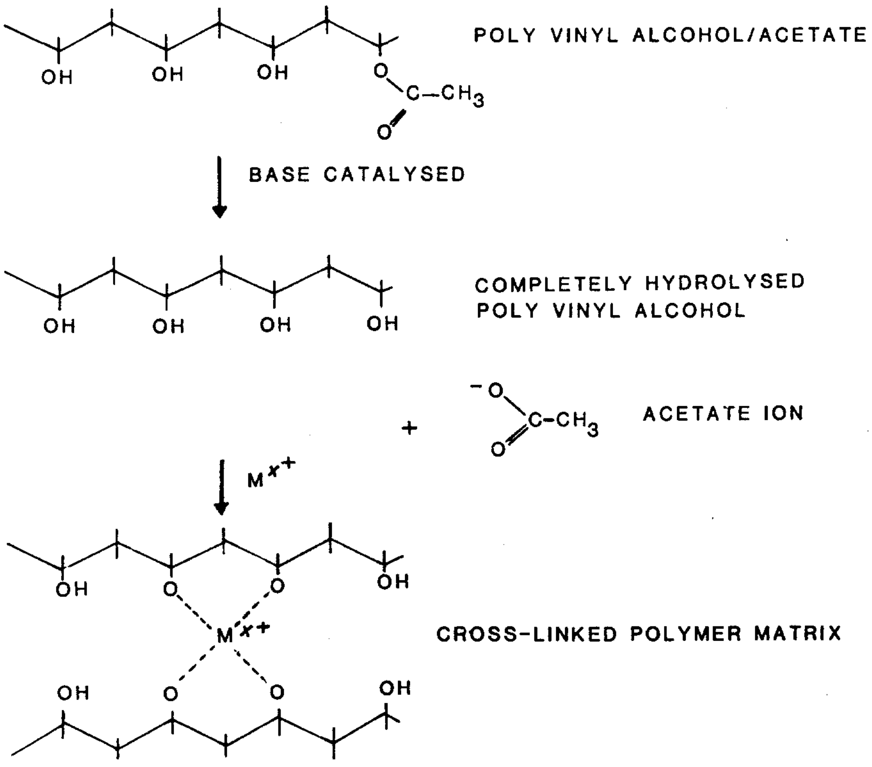

Figure 6 Reaction of polyvinyl alcohol/acetate with hydrated Secar 71.

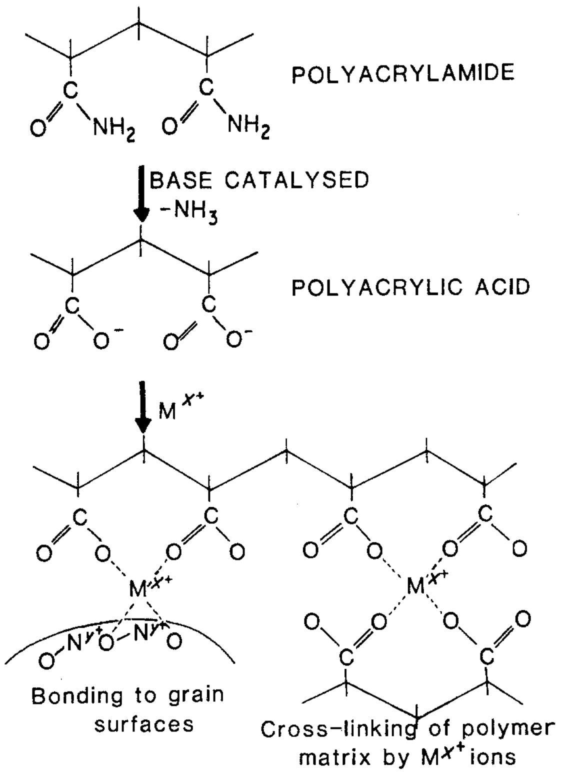

Figure 7 Reaction between polyacrylamide and OPC showing the bonding between cement and polymer and crosslinking of the polymer by cations from cement hydration.

processing method as for the HAC based system with OPC and polyacrylamide. Here the cement system bears a striking resemblance to glass-ionomer cements which are formed by reacting special calcium alumino-silicate glasses with aqueous solutions of polyalkenoic acids. The reactions involved in these cements which are widely used as dental filling materials have been fully described by Crisp *et al.* [8]. This work shows that when metal oxides are mixed with polyacrylic acid the hydrogen on the carboxyl group of the acid becomes replaced by the metal ions released by the oxides. Setting and hardening then results from the crosslinking of the polyacrylate chains by the cations.

The reaction can be extremely rapid depending on the oxide used which for the MDF cement processing method is undesirable since the product becomes a crumbly mass. By using the precursor polyacrylamide, this reaction is retarded by the necessity to convert the amide to an acid group. This occurs readily at the pHs in cement solutions with the accompanying liberation of ammonia, thus allowing sufficient working time to physically remove the porosity.

Evidence for the proposed reaction scheme shown in Fig. 7 lies both in the infrared results and the EDS measurements described in a previous paper [10]. From the infrared we can see the disappearance of the amide groups and the appearance of bands corresponsing to the formation of both carboxylic acid groups and metal carboxylate salts. EDS measurements show the presence of calcium in the polymer gel matrix between the anhydrous particles and so we can conclude that the cement grains are linked by a calcium cross-linked, polymer matrix in addition to cement hydration products.

5. Conclusions

Polymer additions used in the fabrication of MDF cement have significant effects on the hydration of the cement and themselves undergo reactions with the cement solution. In the case of the high alumina cement Secar 71 the normal hydration reactions are strongly suppressed by polyvinyl acetate/alcohol addition and the polymer reacts with Ca^{2+} and Al^{3+} ions from the cement to form calcium acetate and a crosslinked product. In the case of OPC with polyacrylamide, crosslinking by Ca^{2+} ions is proposed to occur analogous to reactions in polyacrylic acid-based dental cements. The behaviour of the polymer in each case is more complex than that of an inert rheological aid.

Acknowledgements

We wish to thank Dr H. Prosser (Laboratory of the Government Chemist, London) for advice on the interpretation of infrared spectra. Financial support from the Science and Engineering Research Council is acknowledged.

References

1. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Nature* 289 (1981) 388.
2. J. D. BIRCHALL, *Phil. Trans. Roy. Soc.* A310 (1983) 31.
3. P. J. LESUEUR, D. D. DOUBLE and G. W. GROVES, *Proc. Brit. Ceram. Soc.* **35** (1984) 177.
4. D. D. DOUBLE, A. HELLAWELL and S. J. PERRY, *Proc. Roy. Soc.* A359 (1978) 435.
5. N. L. THOMAS and D. D. DOUBLE, *Cem. Conc. Res.* 11 (1981) 675.
6. S. A. RODGER and D. D. DOUBLE, *ibid.* 14 (1984) 73.

7. L. J. BELLAMY, "The Infra-Red Spectra of Complex Molecules" (Methuen, London, 1954).
8. S. CRISP, H. J. PROSSER and A. D. WILSON, *J. Mater. Sci.* 11 (1976) 36.
9. J. F. PRITCHARD, "Polyvinyl alcohol" (Gordon and Breach, London, 1970).
10. W. SINCLAIR and G. W. GROVES, *J. Mater. Sci.* 20 (1985) 2846.
11. J. F. YOUNG, *Cem. Conc. Res.* 2 (1972) 415.

Received 29 August
and accepted 13 September 1984