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Studies in the setting of polyelectrolyte cements

Part VII *The effect of divalent metal chlorides on the properties of zinc polycarboxylate and glass–ionomer dental cements*

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A study is reported in which a zinc polycarboxylate and a glass polyalkenoate dental cement, were prepared from aqueous solutions of divalent metal chlorides, namely $ZnCl_2$, $CaCl_2$, $MgCl_2$ and $SrCl_2$, all at 1.0 mol dm^{-3} concentration, as well as from pure water. Calcium chloride was employed at additional concentrations, i.e. 2.0, 0.5 and 0.1 mol dm^{-3}. As was previously found for monovalent salts, setting of the zinc polycarboxylate was speeded up and water uptake generally enhanced by the presence of the divalent metal salts. However, the divalent salts were found to reduce the compressive strength at 24 h (from 86 MPa to about 60 MPa). The glass polyalkenoate showed broadly similar effects to those observed in the presence of monovalent salts, with the setting time being increased, water uptake inhibited and compressive strength at 24 h reduced; however, by contrast, the working time was generally reduced. These results occur because the rate of the neutralization process is increased by the divalent salts, a consequence of the reduced pH of the poly(acrylic acid) caused by these salts. Infrared spectroscopy demonstrated interactions between the metal chlorides and poly(acrylic acid), with various chelate structures being apparent from the position of the asymmetric carbonyl stretch. © *1998 Chapman & Hall*

1. Introduction

This paper is the latest in a series aimed at extending our knowledge of the setting chemistry of zinc polycarboxylate and glass polyalkenoate cements through studying the effect of additives upon them. Both are well established materials for use in clinical dentistry [1] and belong to the general class of acid–base cements [2]. They are prepared by reaction of aqueous polyelectrolyte, typically poly(acrylic acid), with a powdered base. In the case of the zinc polycarboxylate, this base consists of heat-treated zinc oxide together with about 10% magnesium oxide; for the glass polyalkenoate, the base consists of a special acid-decomposable glass, typically a calcium aluminofluorosilicate that may also contain significant proportions of phosphate.

For a long time these cements were assumed to set by similar reactions and to have very similar microstructures [3]. More recently, however, studies have shown this assumption to be incorrect [4]. The differences in setting and microstructure lead to differences in the effect of additives. For example, the addition of sodium chloride to zinc polycarboxylate caused a significant increase in the setting rate, but made no difference to the strength [5, 6], whereas adding it to glass polyalkenoate made little or no difference to the setting rate but led to a marked reduction in compressive strength. Similarly diverse effects have been found with other sodium salts [5] and with potassium halides [7]. For the latter salts, glass polyalkenoate showed a systematic reduction in strength through the series $Cl^- > Br^- > I^-$, with chloride causing greatest reduction and iodide least.

The current work extends the study of additives to include divalent metal chlorides. Salts of this kind have previously been used in glass polyalkenoates, being added as dry powders to the glass at levels of 10%, prior to reaction with aqueous poly(acrylic acid) [8]. A large number of such salts were studied, both those of Main Group elements, such as calcium, barium or tin, and transition metals, such as copper, zirconium and zinc. The study was carried out in order to determine the effect of such compounds on the speed of the setting reaction of a specific glass polyalkenoate, in the hope that formulations could be found with setting characteristics suitable for a range of applications. For almost every compound examined, setting was faster when the salt was present. Apart from this discovery, and ranking compounds in order of effectiveness, the authors were not able to draw particularly profound conclusions from their study.

In the current work, a more detailed study is reported, in which the range of additives was limited to

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zinc, magnesium, calcium and strontium chlorides. These salts were incorporated into water-activated commercial cements based on poly(acrylic acid), one glass polyalkenoate (AquaCem) and one zinc polycarboxylate (PolyF Plus, both manufactured by Dentsply, Germany). The effect of these salts on working and setting times, and on the compressive strength and nett mass change at 24 h were determined. In addition, a complementary study was carried out on the interaction of the metal chlorides with poly(acrylic acid) using infrared spectroscopy.

2. Materials and methods

The materials employed were a zinc polycarboxylate, PolyFPlus, and a glass polyalkenoate, AquaCem (both Dentsply Ltd, Konstanz, Germany). The powder : liquid ratio was as recommended by the manufacturers, i.e. 5 : 1 by mass for the zinc polycarboxylate, 3.3 : 1 for the glass polyalkenoate. Samples were prepared by spatulating together the appropriate amount of powder (deactivated ZnO or glass plus dried polymer) with water or aqueous solution of divalent metal chloride on a ceramic tile using a metal mixing spatula. Details of the compounds used to prepare the aqueous solutions are given in Table I.

Compressive strengths at 24 h were determined for cements activated with water and with the halide solutions. Six specimens of each cement were prepared by placing freshly mixed cement paste in cylindrical moulds of dimensions 12 mm high × 6 mm diameter. Specimens were stored in their moulds for 1 h at 37 °C, then in water at the same temperature for a further 23 h. After storage, samples were tested for compressive strength using a universal testing machine (Type EU500, Howden, Leamington Spa, UK) at a crosshead speed of 0.1 cm min^{-1}. Loads at failure were converted to strength values, and means and standard deviations were determined for each cement composition. Differences in compressive strength were assessed for significance using one-way ANOVA.

Working and setting times were determined for cements set by water activation and by activation with each of the divalent metal chloride solutions. All determinations used the oscillating rheometer [5] at ambient temperature (21–23 °C), duplicate values being recorded. Working time was taken to be the point at which the amplitude of oscillation reached 95% of the initial (maximum) value; setting time as the point where amplitude was 5% of this value.

Poly(acrylic acid)–MCl_2 solutions were prepared by adding together equal volumes of aqueous 1 mol dm^{-3} metal chloride solution and 25% aqueous poly(acrylic acid) (Versicol E7, Allied Colloids, Bradford, UK). Specimens for infrared spectroscopy were prepared by applying small amounts of these solutions by brush to calcium fluoride plates. After allowing to dry at room temperature, their infrared spectra were recorded in transmission using a spectrophotometer (Type 983G, Perkin–Elmer, UK). The pH of the solutions was determined using a digital pH meter (Type PHA300, Whatman, UK); for comparison, a similar solution of sodium chloride and poly(acrylic acid) was prepared, and used in experiments on infrared spectroscopy and pH.

TABLE I Divalent metal chlorides used as additives

Halide	Grade	Supplier
$MgCl_2$	AnalaR Reagent	BDH, Poole, Dorset, UK
$CaCl_2$	Laboratory Reagent	BDH, Poole, Dorset, UK
$SrCl_2$	ACS Reagent	Aldrich, Gillingham, Dorset, UK
$ZnCl_2$	Specified Laboratory Reagent	Fisons, Loughborough, UK

3. Results

The values for working and setting time for each activating liquid are shown for zinc polycarboxylate and glass polyalkenoate, respectively, in Tables II and III.

From these figures, it can be seen that for the zinc polycarboxylate, the various dichloride solutions significantly speeded up the setting reaction. Surprisingly, all of the 1 mol dm^{-3} solutions except $SrCl_2$ also speeded up the setting of the glass polyalkenoate. This result contrasts strikingly with results obtained previously for monovalent metal halides.

The effect of these solutions on compressive strength is shown in Tables IV and V.

At the 1 mol dm^{-3} level, there were no significant differences between the results for the dichlorides in the zinc polycarboxylate, but all were significantly weaker than the cement prepared from pure water ($P < 0.01$). Differences between the varying concentrations of $CaCl_2$ were all significant ($P < 0.01$), but the difference between the 0.1 mol dm^{-3} $CaCl_2$ and pure water was not significant.

TABLE II The influence of divalent metal chlorides on the setting characteristics of zinc polycarboxylate

Liquid	Working time (min)	Setting time (min)
Water	3.0	7.9
1 M $MgCl_2$	1.4	2.7
1 M $CaCl_2$	1.0	2.7
1 M $SrCl_2$	1.5	2.9
1 M $ZnCl_2$	1.6	4.1
2 M $CaCl_2$	0.7	1.7
0.5 M $CaCl_2$	1.4	3.4
0.1 M $CaCl_2$	1.9	5.6

TABLE III The influence of divalent metal chlorides on the setting characteristics of glass polyalkenoate

Liquid	Working time (min)	Setting time (min)
Water	4.2	12.4
1 M $MgCl_2$	2.2	13.2
1 M $CaCl_2$	2.1	12.9
1 M $SrCl_2$	4.7	22.5
1 M $ZnCl_2$	2.1	11.2
2 M $CaCl_2$	2.5	12.9
0.5 M $CaCl_2$	2.3	10.6
0.1 M $CaCl_2$	2.0	8.3

TABLE IV Compressive strength at 24 h of zinc polycarboxylate cements with divalent metal chlorides (standard deviations in parentheses)

Liquid	Compressive strength (MPa)
Water	86.0 (13.8)
1 M $MgCl_2$	60.4 (1.3)
1 M $CaCl_2$	57.3 (6.6)
1 M $SrCl_2$	59.8 (5.1)
1 M $ZnCl_2$	64.2 (6.7)
2 M $CaCl_2$	15.9 (5.1)
0.5 M $CaCl_2$	53.6 (3.2)
0.1 M $CaCl_2$	74.4 (13.6)

TABLE V Compressive strength at 24 h of glass polyalkenoate cements with divalent metal chlorides (standard deviations in parentheses)

Liquid	Compressive strength (MPa)
Water	94.3 (8.3)
1 M $MgCl_2$	45.3 (11.8)
1 M $CaCl_2$	50.4 (6.7)
1 M $SrCl_2$	40.7 (5.5)
1 M $ZnCl_2$	63.8 (3.4)
2 M $CaCl_2$	26.3 (1.7)
0.5 M $CaCl_2$	56.7 (10.2)
0.1 M $CaCl_2$	91.1 (15.6)

TABLE VI Nett weight gain at 24 h for zinc polycarboxylate cements with divalent metal chlorides (standard deviations in parentheses)

Liquid	Weight gain (%)
Water	0.08 (0.11)
1 M $MgCl_2$	0.99 (0.21)
1 M $CaCl_2$	− 0.01 (0.37)
1 M $SrCl_2$	1.04 (0.57)
1 M $ZnCl_2$	1.02 (0.34)
2 M $CaCl_2$	− 0.28 (0.31)
0.5 M $CaCl_2$	0.53 (0.20)
0.1 M $CaCl_2$	0.69 (0.16)

TABLE VII Nett weight gain at 24 h for glass polyalkenoate cements with divalent metal chlorides (standard deviations in parentheses)

Liquid	Weight gain (%)
Water	1.77 (0.34)
1 M $MgCl_2$	− 1.05 (0.70)
1 M $CaCl_2$	1.20 (0.49)
1 M $SrCl_2$	1.04 (0.34)
1 M $ZnCl_2$	1.39 (0.15)
2 M $CaCl_2$	− 0.14 (0.47)
0.5 M $CaCl_2$	1.83 (0.25)
0.1 M $CaCl_2$	0.95 (0.27)

TABLE VIII pH of 1:1 mixtures of 1 mol dm^{-3} metal chloride solutions and 25% poly(acrylic acid) at 25 °C

Salt solution	pH
None	1.5
$MgCl_2$	0.6
$CaCl_2$	0.8
$SrCl_2$	0.7
$ZnCl_2$	1.0
NaCl	1.1

Results were more complicated for the glass polyalkenoate than for the zinc polycarboxylate. The 1 mol dm^{-3} did not give an identical set of compressive strengths. The $ZnCl_2$ cement was stronger than all the others made from chloride solutions, to at least $P < 0.002$, though it was significantly weaker than the additive-free cement ($P < 0.001$). The $CaCl_2$ solutions of increasing concentration followed similar trends to those seen for the zinc polycarboxylate, with a significant decrease in strength from 1–2 mol dm^{-3} ($P < 0.001$), and the 0.1 mol dm^{-3} solution giving a result that did not differ significantly from that of pure water.

The values of nett weight gain for the various cements are shown in Tables VI and VII.

Nett weight change (assumed to be predominantly due to water movement) varied with metal chloride, though trends were far from clear. The zinc polycarboxylate activated with pure water showed a negligible weight change over 24 h, but this increased to approximately 1% when $MgCl_2$, $SrCl_2$ or $ZnCl_2$ were present. The result for 1 mol dm^{-3} $CaCl_2$ was surprising, since there was a negligible weight change (− 0.01%), yet in the presence of only 0.01 mol dm^{-3} $CaCl_2$, there was an increase of 0.69%.

The glass polyalkenoate increased in weight when prepared from pure water, but all of the metal chlorides reduced this. In the case of $MgCl_2$, there was a nett loss.

Results for pH measurement are shown in Table VIII. In all cases, the presence of the metal chloride enhanced the acidity of the polyacid, with the Group II metals being more effective than either zinc or sodium. Some indication of the mechanism of this enhancement was obtained from the infrared spectra, important details of which are given in Table IX. They showed some sort of interaction of the carboxylic acid of the polymer with the metal halide, as evinced by the band in the region 1525–1640 cm^{-1}, characteristic of metal–carbonyl chelation [9].

4. Discussion

4.1. Working and setting times

For the zinc polycarboxylate, results were similar to those previously obtained with monovalent halides, in that the presence of the salts increased the speed of setting. This effect was shown to depend on concentration, cements containing $CaCl_2$ setting increasingly rapidly as concentration was increased from 0.1 mol dm^{-3} to 2.0 mol dm^{-3}. This may be explained readily, as before, in that the metal halides stabilize charge-separated configurations of the poly(acrylic acid [10–12] which in turn allows greater dissociation of the carboxylic acid functional groups, enhancing their acidity. This enhanced acidity was demonstrated in that the pH of all of the solutions containing metal

TABLE IX Infrared bands of 1:1 mixtures of 1 mol dm^{-3} metal chloride solutions and 25% poly(acrylic acid)

Salt solution	νCO_2 asym. (cm^{-1})	νCO_2 sym. (cm^{-1})	$\Delta\nu$ (cm^{-1})
None	–	1450	–
$MgCl_2$	1637 (strong); 1527 (medium)	1450	187/77
$CaCl_2$	1639 (strong); 1556 (medium)	1450	189/106
$SrCl_2$	1630 (strong); 1547 (medium)	1451	179/96
$ZnCl_2$	1617 (strong)	1451	168
NaCl	1527 (strong)	1449	76

chlorides was lower than that of aqueous poly(acrylic acid) alone.

Working and setting time results were more complicated for the glass polyalkenoate than for the zinc polycarboxylate. The salts $MgCl_2$, $CaCl_2$ and $ZnCl_2$ shortened the working time, whereas $SrCl_2$ increased it. On the other hand, all of the salts except $ZnCl_2$ increased the setting time. These salts can thus be seen to have different effects on the various setting reactions of the glass polyalkenoate. This cement is now considered to set by two essentially distinct mechanisms, namely neutralization of the poly(acrylic acid) and reaction of the ion-depleted glass species to form a silicate/phosphate network [13]. Increasing the rate of neutralization by adding metal halides may inhibit the latter reaction, with the result that the cement forms more slowly, particularly in the later stages of reaction. The difference in balance between these two possible setting reactions also tends to yield a weaker cement. The fact that the results for zinc polycarboxylate are less complicated that those for the glass polyalkenoate is further evidence that this cement sets by a simpler mechanism.

4.2. Compressive strength and mass changes

For the zinc polycarboxylate, the 1 mol dm^{-3} solutions of metal chloride all led to weaker cements than with pure water. There was no distinction between the results for $MgCl_2$, $CaCl_2$, $SrCl_2$ or $ZnCl_2$. These results contrast with those for various mono-halides (NaCl, KCl, KBr and KI), where no differences in strength were found [5, 7]. However, the divalent ions have been shown to bind more strongly to the polyelectrolyte molecules than do the monovalent ones, and they are known to disrupt the layer of water that hydrates the polyelectrolyte and to become site bound [14]. If this occurs in the setting of zinc polycarboxylate, it would mean the divalent metal ions were less mobile than Na^+ or K^+, and hence likely to disrupt cross-linking and interfere with strength development.

With the exception of $CaCl_2$, the divalent chlorides caused an increase in mass after 24 h, which is assumed to be mainly due to water uptake. All four salts are extremely hygroscopic as solids, taking up large amounts of water to form syrupy solutions [15]. In view of this, the result for calcium is somewhat surprising.

For the glass polyalkenoate, previous results have shown a weakening in the presence of added salts [5, 7], and similar results are found in the present study. The current results are striking in that the metal salts form two sets, one based on Group II chlorides, with strengths in the region of 45 MPa, and the other consisting of only $ZnCl_2$, but with a strength of 63.8 MPa (S.D. 3.4 MPa). The Group II chlorides all formed solutions with poly(acrylic acid) of comparable pH, i.e. approximately 0.7, whereas the zinc chloride formed a solution of pH 1.0. It is notable that NaCl gave a very similar result for pH (1.1), and has previously been shown to give a comparable compressive strength (59.8 MPa, S.D.4.4 MPa). Compressive strength of glass polyalkenoate cements thus seems to correlate with the initial pH of the polyacid solution, a result that contrasts with those for zinc polycarboxylates and which merits further investigation.

4.3. Infrared spectroscopy and pH measurements

The infrared spectra suggest there are differences in the binding to poly(acrylic acid) of the Group II metal chlorides compared with $ZnCl_2$, and that there is a further difference with NaCl. Table IX makes tentative assignments of the bands, based on extensive previous studies of such spectra [9, 16]. However, whether the band at about 1450 cm^{-1} can be unambiguously assigned is doubtful [17], because it also appears in the spectrum of pure poly(acrylic acid). The bands assigned to the CO_2 asymmetric stretch seem more certain, as there are no corresponding bands in the spectrum of pure poly(acrylic acid).

The precise position of the band due to the asymmetric carbonyl stretch is well known to depend on the precise details of the co-ordination between the metal ion and the $-CO_2$ group. This band generally appears between 1550 and 1620 cm^{-1} for metal carboxylate and polycarboxylate salts [18, 19], though for the fairly unusual case of the unidentate structure, it moves as far as about 1634 cm^{-1} [20]. It is significant that all of the Group II metal halides give a band in this region, the mean value being 1635 cm^{-1}. There thus seem to be interactions of this type between these chlorides and poly(acrylic acid).

The second band for these salts varies in position. For $MgCl_2$ it comes at 1527 cm^{-1}, whereas for $CaCl_2$ and $SrCl_2$ it is closer to 1550 cm^{-1}. Nonetheless, all of these bands are in the region usually associated with a chelating bidentate structure (see Fig. 1). There thus appear to be two interactions for each of the Group II chlorides, both of which seem to possess some degree of covalent character, this being necessary for site-binding. These interactions are different from those for salts of these ions with poly(acrylic acid).

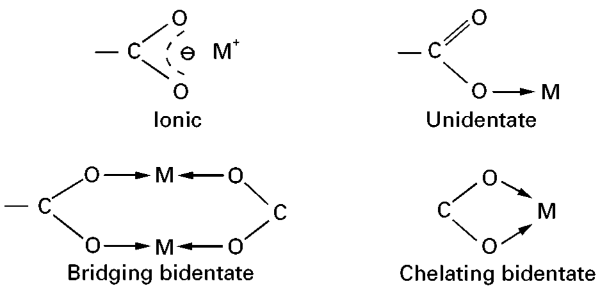

Figure 1 Possible structures resulting from metal ion-carboxylic acid interactions.

Magnesium polyacrylate, for example, gives a single asymmetric stretch, either at $1535\,cm^{-1}$ for the well-hydrated state [21] or at $1580\,cm^{-1}$ for the dehydrated state [22]. Calcium polyacrylate gives a single band at $1572\,cm^{-1}$, a position characteristic of purely ionic carboxylates; this does not appear to vary with hydration state [22].

For $ZnCl_2$, there is a single band at $1617\,cm^{-1}$. This is generally characteristic of a bridging bidentate structure, though such an assignment here is very tentative. There is no band in this position in a zinc polycarboxylate cement [23], despite the large number of distinct bands, all attributable to zinc–carboxylate interactions, exhibited by this cement, nor is there a band in this position in pure zinc polyacrylate [24]. The position of the band suggests a bidentate structure, which is also partially covalent, as would be necessary to cause site-binding.

Finally, the NaCl–poly(acrylic acid) spectrum also showed evidence of an interaction that might be a chelating one. The band in this spectrum at $1527\,cm^{-1}$ is well away from the ionic band at about $1575\,cm^{-1}$ found in the spectrum of sodium polyacrylate [19, 25], but close to one of the bands found in the spectrum of the $MgCl_2$–poly(acrylic acid) complex. However, sodium does not usually form co-ordination compounds [15], and this result is therefore somewhat surprising. Whatever its significance, though, the fact is that there is only one band in the spectrum of the NaCl–poly(acrylic acid) complex, and this suggests that the interaction is considerably different from that shown by the Group II metal chlorides. This result is consistent with previous studies on binding of these ions to poly(acrylic acid) and with results reported in this paper for setting rate and compressive strength.

5. Conclusion

Divalent metal chlorides have been found to give different results from univalent metal halides when used as additives in both zinc polycarboxylate and glass polyalkenoate cements. In both cements, they generally reduced the working time, though in the glass polyalkenoate this was usually accompanied by an increase in the setting time. Both types of cement were weaker at 24 h when these salts were present, and in both cements, water uptake characteristics were altered. Studies employing pH and infrared spectroscopy revealed that the salts all increased the acidity of the poly(acrylic acid) and showed clear chemical interactions with the polymer. In all of these, $ZnCl_2$ was distinct from $MgCl_2$, $CaCl_2$ and $SrCl_2$, which formed a clear set; NaCl was found to differ from both $ZnCl_2$ and the Group II set. The interactions of these salts leading to reduced pH were shown to be an important factor in determining the compressive strength of the glass polyalkenoate. However, such a straightforward conclusion could not be drawn for the zinc polycarboxylate cement.

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