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Formation and properties of cements prepared from zinc oxide and aqueous solutions of zinc nitrate

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Novel cements formed from zinc oxide powder and aqueous solutions of zinc nitrate are described. They belong to the class of material known as acid–base reaction cements. The zinc oxide/zinc nitrate cements have been found to show reasonable resistance to dissolution in dilute aqueous acid and in alkali, and to develop compressive strengths comparable with those of the related zinc oxychloride cements. Compressive strength was found to increase with increasing ratio of ZnO to $Zn(NO_3)_2$ solution, and with increasing concentration of $Zn(NO_3)_2$ in the aqueous solution. The cements appeared to be completely amorphous and exhibited no sign of crystallinity. The significance of these findings is discussed.

1. Introduction

Oxysalt cements were first prepared in 1855 by Sorel [1]. The original cements of this type were the zinc oxychlorides, made by reacting powdered zinc oxide with aqueous solutions of zinc chloride. Sorel later reported two further series of oxysalt cements which were based on magnesia, the magnesium oxychlorides and the magnesium oxysulphates [2].

Oxysalt cements belong to the class of materials known as acid–base reaction cements, as originally defined by Wygant [3]. The cements are typically non-uniform and have been found to contain a number of phases: for example, the zinc oxychloride has been shown to contain phases corresponding to $ZnO:ZnCl_2:H_2O$ in the ratio 4:1:6 [4], 2:2:3 [4] and 4:1:5 [5–7]. While the structures of some of these phases have been determined by X-ray crystallography [8, 9], the bulk of the material appears to be amorphous. This is certainly true of freshly prepared cements; Sorrell [9] has shown that crystalline phases are formed in zinc oxychloride some time after the initial setting reaction is over.

Similar results have been obtained for magnesium oxychloride and magnesium oxysulphate cements. In magnesium oxychloride, crystalline phases have been found corresponding to $Mg(OH)_2:MgCl_2:H_2O$ of 5:1:8 and 3:1:8, respectively [10]. Both forms have been shown to react slowly with atmospheric CO_2 so that, after a long period, a basic magnesium carbonate is formed [10]. More recently, Sorrell and Armstrong [11] have studied both the phase relationships and the kinetics of interconversion between the phases, mainly using the technique of X-ray diffraction (XRD).

In magnesium oxysulphates, phases corresponding to $Mg(OH)_2:MgSO_4:H_2O$ of 3:1:8, 5:1:3, 1:1:5 and 1:2:3, respectively, have been identified [12]. Their relationships to each other and to the starting materials, powdered MgO and aqueous magnesium sulphate, have also been established. Again, X-ray crystallography was the technique employed, which emphasized the crystalline phases and overlooked the amorphous nature of a significant amount of the cement.

The original application proposed for these oxysalt cements was as dental filling materials [1]. However, the zinc oxychloride cements proved to have insufficient resistance to hydrolysis to be effective for this purpose [1]. Of the other cements, the magnesium oxysulphates have found a number of uses in architecture, including uses as binders in light-weight panels and as insulating materials [13].

Apart from these cements, a number of other acid–base oxysalt cements have been described. These include calcium oxychloride reported in only one paper [14], and cobalt oxychloride, reported as part of a preliminary account of acid–base reaction cements for use as controlled-release devices [15]. Also included are the zinc phosphate cements used in dentistry, which are formed from zinc oxide and aqueous phosphoric acid. These latter cements have been shown to consist of complex oxysalts similar to those found in the other oxysalt cements of zinc [16].

Apart from the zinc oxychloride, magnesium oxychloride and magnesium oxysulphate cements, few oxysalt cements have been described in detail. Indeed there is some doubt about the validity of the observa-

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tion that calcium oxychloride is a stable cement (Nicholson, unpublished observations). In addition, no oxysalt cements containing nitrates have been reported to date. In the current paper, we report for the first time a series of oxysalt cements formed from aqueous solutions of zinc nitrate. We also report results of a study of the factors affecting their formation, stability and compressive strength.

2. Experimental procedure

The reagents used in this study were zinc oxide (general purpose reagent grade) and zinc nitrate (AnalaR reagent grade), both from BDH Ltd, Poole, Dorset, UK. Aqueous solutions of zinc nitrate were made up at concentrations of 25, 50 and 75 mass %.

Cements were prepared from these components at varying powder to liquid ratios by spatulating the zinc oxide powder into the zinc nitrate solution on a glass block. Setting times were determined using an oscillating rheometer, with specifications as described previously [17], consisting of a pair of grooved metal plates between which the cement is placed. The upper plate is oscillated with respect to the lower by applying a continuous reciprocating force to a spring. As the cement sets, so the degree of motion imparted to this upper plate via the spring decreases. The motion of the upper plate is plotted using a chart recorder, and changes from a large movement to little or no movement as the cement sets.

Samples were prepared for the measurement of compressive strength by placing newly mixed pastes in cylindrical moulds 12 mm high by 6 mm in diameter. These were stored for 24 h in an incubator at 37 °C before testing. Compressive strength was evaluated using a universal testing machine (Instron 1185) at a crosshead speed of 1 mm min^{-1}. The compressive strength values quoted are the average of six determinations; standard deviations were also recorded.

Similarly sized specimens were used to test stability in various media. These included aqueous acetic acid, sodium hydrogen carbonate and sodium chloride.

3. Results and discussion

Cements were prepared from powdered zinc oxide and aqueous zinc nitrate at ratios of 1:1 and 2:1. Attempts to prepare cements having greater powder:liquid ratios were not successful because the mixtures set too quickly and rapidly became too stiff to mix. Setting times and compressive strength were determined for each of the formulations prepared and these are given in Table I.

The rate of setting correlated with pH of the zinc nitrate solutions, which were 4.0, 2.5 and 2.2 for 25%, 50% and 75%, respectively, as assessed using indicator strips. Setting was accompanied by a noticeable exotherm in all cases.

The cements were all similar in appearance, being opaque, white materials. There was no sign of any crystalline phases visible to the naked eye, either at the specimen surface or at the fracture surfaces within the body of the specimen, following measurement of compressive strength. Specimens were tested when relatively young (24 h) so that it was not clear whether crystalline phases might have developed with time in these cements. Previous studies of zinc oxide/zinc chloride systems have also shown no evidence of crystallinity early in the life of the cements. However, after a few days small amounts of crystalline material did develop, corresponding to $ZnCl_2$:ZnO:H_2O in well-defined ratios [8, 9]. These crystalline phases were not implicated in the initial setting process, since this was complete well before crystallization was detectable. Indeed the amorphous phase continued to make up a proportion of the set cement even after ageing, despite the development of detectable crystallinity. The existence of such an amorphous phase is probably essential for cement formation. If the product formed was purely crystalline, the final material would lack strength and integrity, and would therefore not exist as a solid body.

Both the setting time and the compressive strength of the specimens were found to depend on the powder:liquid ratio and the concentration of zinc nitrate in the aqueous phase. Setting times ranged from 30.5 min for the 25% solution at a powder:liquid ratio of 1:1, to 1.25 min for the 75% solution at 2:1. Results for compressive strength varied along broadly similar lines, though the strongest cement prepared was actually that made from the 75% solution at 1:1. Values of compressive strength appeared to be more affected by an increase in the concentration of the zinc nitrate solution than by a change in the powder:liquid ratio.

The compressive strengths of the zinc oxide/zinc nitrate cements were fairly low, particularly by comparison with related oxysalt cements. The so-called zinc phosphate dental cement, which consists essentially of a complex amorphous zinc oxide/zinc phosphate mixture [16], can reach 100 MPa compressive strength at 24 h. Admittedly, because of the insolubility of zinc phosphate, this cement cannot be made by reaction of the acid salt with the metal oxide: instead it

TABLE I Properties of zinc oxide/zinc nitrate cements

Concentration of $Zn(NO_3)_2$ (%)	Powder:liquid ratio	Setting time (min)	Compressive strength (MPa) [standard deviation]
25	1:1	30.5	1.80 [0.40]
25	2:1	16.0	2.37 [0.61]
50	1:1	3.0	5.25 [1.15]
50	2:1	2.0	5.87 [1.52]
75	1:1	3.0	11.93 [3.54]
75	2:1	1.25	9.81 [1.77]

TABLE II Effect of aqueous media on zinc oxide/zinc nitrate cements

Concentration of $Zn(NO_3)_2$ (%)	Powder:liquid ratio	Resistance to		
		Acetic acid (5%)	$NaCO_3$ (5%)	NaCl (0.9%)
25	1:1	2	1	2
25	2:1	2	2	2
50	1:1	2	1	2
50	2:1	2	1	2
75	1:1	1	1	2
75	2:1	1	1	2

is prepared by reaction of phosphoric acid with zinc oxide. However, despite this difference there is evidence that some of these oxysalt cements can be prepared with compressive strengths very much higher than those achieved in the present study for the zinc oxide/zinc nitrate system.

The resistance of the zinc oxide/zinc nitrate cements to various aqueous media was determined by immersion of a pellet of the cement in the particular aqueous solution for up to 17 h. All cements survived this treatment in each of the solutions, although in certain cases some cloudiness developed in the solution by the end of the exposure period, indicating that the cement had shown slight signs of breaking up. The results are shown in Table II, where the number 1 indicates complete resistance to dissolution within 17 h, and 2 indicates that the cement had shown some signs of dissolution.

The cements were all reasonably resistant to these aqueous solutions, showing that despite the high initial water-solubility of zinc nitrate, the product of the cementition reaction was largely insoluble in water. In the main, the cements formed at a powder:liquid ratio of 2:1 were more resistant to dissolution than those formulated at 1:1. Cements prepared from more concentrated $Zn(NO_3)_2$ solutions were also more resistant to attack. These results would both have been predicted in advance and are typical of results from a wide range of acid–base reaction cements [18].

In general, these cements were slightly more resistant to attack in dilute alkali, which indicates that the final cements consisted of an essentially neutral salt matrix with unreacted zinc oxide embedded in them. Such a structure is typical of acid–base reaction cements, and would be expected to be slightly more susceptible to attack by mildly acidic solutions.

Overall, these cements showed good but not complete resistance to hydrolysis in the different aqueous media. They are similar in this respect to the zinc oxychloride cements of Sorel [1].

4. Conclusions

This study has shown for the first time that cements can be made from zinc oxide and aqueous zinc nitrate, the setting reaction being rapid and exothermic. There was no evidence of crystallinity in the final materials within 24 h of formation, which is similar to the findings for related cements. This confirms the view that, for successful cement formation, a largely amorphous matrix is required.

The compressive strengths of the resulting cements have been found to increase both with an increased powder-to-liquid ratio, and with an increased concentration of zinc nitrate in the initial solution. By comparison with other oxysalt cements, particularly those used in dentistry, the zinc oxide/zinc nitrate cements reported in this paper were fairly weak, the maximum value of compressive strength obtained in the present study being about 12 MPa.

The zinc oxide/zinc nitrate cements were found to be reasonably stable on exposure to aqueous solutions; in this regard they are similar to the well-known zinc oxychloride cements.

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