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The chemistry of cements formed between zinc oxide and aqueous zinc chloride

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A series of cements has been prepared from zinc oxide powder and aqueous zinc chloride, using solutions corresponding to concentrations of 20%, 30%, 40%, 50% and 60% and a ratio of ZnO powder to zinc chloride solution of 1 : 1. As with cements of the zinc oxide/zinc nitrate system, these ZnO/$ZnCl_2$ cements were found to be weak in compression (not exceeding 10 MPa) with strength rising with increasing concentration of $ZnCl_2$. The pH change as the reaction proceeded was monitored and generally showed a rapid increase, followed by a slight decrease, and a subsequent slower increase. This is assumed to arise because the doubly charged aquo-zinc cation, $Zn(H_2O)_n^{2+}$ ($n = 4$ or 6) behaves as a weak acid, due to so-called salt hydrolysis: $Zn(H_2O)_n^{2+} + H_2O \rightleftharpoons ZnOH(H_2O)_{(n-1)}^{+} + H_3O^{+}$ and reacts to form a salt, thus setting up a classic weak acid/salt buffer system. Finally, cements were stored in water for 1 month, and were generally found to increase in mass during the first week, with the greatest increase occurring in the cement made from 20% $ZnCl_2$ solution. All cements lost mass between 1 week and 1 month, showing them to be sparingly soluble at room temperature. © *1998 Chapman & Hall*

1. Introduction

The original report that a cementitious salt can be made from zinc oxide and aqueous zinc chloride appeared in 1855 [1]. The material was proposed as a dental restorative, but did not prove suitable for this purpose. Subsequently, a number of other cements of this type have become available and are widely used in clinical dentistry. They include the so-called zinc phosphate cement [2], prepared from zinc oxide and modified phosphoric acid, the zinc polycarboxylate cement, prepared from aqueous poly(acrylic acid) [3], and the zinc oxide–eugenol cement [4]. All belong to the class known as acid–base cements [5].

Typically, acid–base cements are formed from aqueous solutions of acids and powdered insoluble bases. The acids are at sufficient concentration that salt formation does not result in loss of water. Instead, the viscous aqueous paste simply sets without phase separation, the water becoming bound into the cement at a variety of locations, including in the co-ordination sphere of the metal ions and in hydration sites around the counterion [5].

Cements of this type consist of a composite structure, in which the salt acts as the matrix and unreacted base acts as filler. In the case of the zinc oxide/zinc chloride system, the salt itself has a complex structure, and has been shown to contain a number of phases. All contain ZnO, $ZnCl_2$ and water, and well-defined phases corresponding to these components in the ratios 4 : 1 : 6 [6], 2 : 2 : 3 [5] and 4 : 1 : 5 [7–9] have been identified. The structures of some of these phases have been determined by X-ray crystallography [10, 11]. However, the bulk of the material appears to be amorphous; freshly prepared cements which have set hard do not immediately contain any detectable crystalline material but instead this forms gradually as the hardened cements are allowed to age [11].

Other cements of this type have been reported, including magnesium oxide/magnesium sulphate [12], magnesium oxide/magnesium chloride [13] and zinc oxide/zinc nitrate [14]. All have been described in reasonable detail in the literature, and one group of these materials, the magnesium sulphate-based cements, find practical application in architecture as binders in lightweight panels and as insulating materials [15].

In the present paper, we report studies aimed at elucidating in more detail the chemistry of the zinc oxide/zinc chloride cement system. We have examined the setting chemistry, using both pH measurements and oscillating rheometry to monitor changes as the reaction takes place. We have also studied the water uptake when these cements are stored in aqueous conditions. In all cases, the aim has been to monitor

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the effect of varying the proportions of the zinc chloride to zinc oxide on the properties, both physical and chemical, of the resulting cements.

2. Materials and methods

The reagents used in this study were zinc oxide (General Purpose Reagent grade) and zinc chloride (AnalaR grade), both supplied by BDH Ltd, Poole, Dorset, UK. Aqueous solutions of zinc chloride were made up corresponding to 20%, 30%, 40%, 50% and 60% by adding the appropriate mass of zinc chloride to water and making up to volume in Grade A volumetric flasks (e.g. for 20% $ZnCl_2$, 20.00 g was made up to 100 ml).

Cements were prepared by spatulating the zinc oxide powder into the zinc chloride solution on a glass block. The powder : liquid ratio was 1.0 g to 1.0 ml. Changes in pH with setting were determined using a hand-held pH meter ("Checker" ex Hanna Instruments).

Setting times were evaluated using a custom built oscillating rheometer designed for studying setting characteristics of dental cements and described previously [16]. It consists of a pair of grooved plates between which the cement is placed. The upper plate receives a continuous reciprocating force from a spring, and oscillates with respect to the lower plate. As the cement sets, so the freedom of this upper plate to move decreases. The motion of the upper plate is plotted using a chart recorder. Conventionally in this field, setting time is taken to be the point at which the oscillation reaches 5% of its initial amplitude. In the current work, however, the cements set so sharply that this point could not be determined, and the point at which the cement had become too rigid to allow any motion at all was taken as the setting time.

Water uptake was determined in duplicate by placing specimens of cement of approximate dimensions 2.5 mm high by 6 mm diameter in deionized water at room temperature and determining weight change after time intervals of 1 week and 1 month. Weight was measured using an analytical balance (Mettler).

Compressive strength was determined using sets of five cylindrical specimens (6 mm high by 4 mm diameter) for each sample. They were made by placing freshly mixed cements in moulds and storing them for 24 h at room temperature prior to testing. Measurements were made using a Universal Testing Machine (Type EU2, ex. R. D. P. Howden, Leamington Spa, Warwick, UK). Strengths were quoted as the means of the five individual strengths, and standard deviations were recorded.

Differences in compressive strength data were analysed by Student's *t*-test to determine statistical significance.

3. Results

The initial pH values for the individual solutions of zinc chloride are shown in Table I. From this it can be seen that there was, as expected, a decrease in pH with increasing concentration. The change in pH as cements underwent setting is shown in Fig. 1.

TABLE I Variation in pH with concentration of $ZnCl_2$

Concentration of $ZnCl_2$ (%)	pH
20	5.3
30	5.1
40	5.0
50	4.8
60	4.7

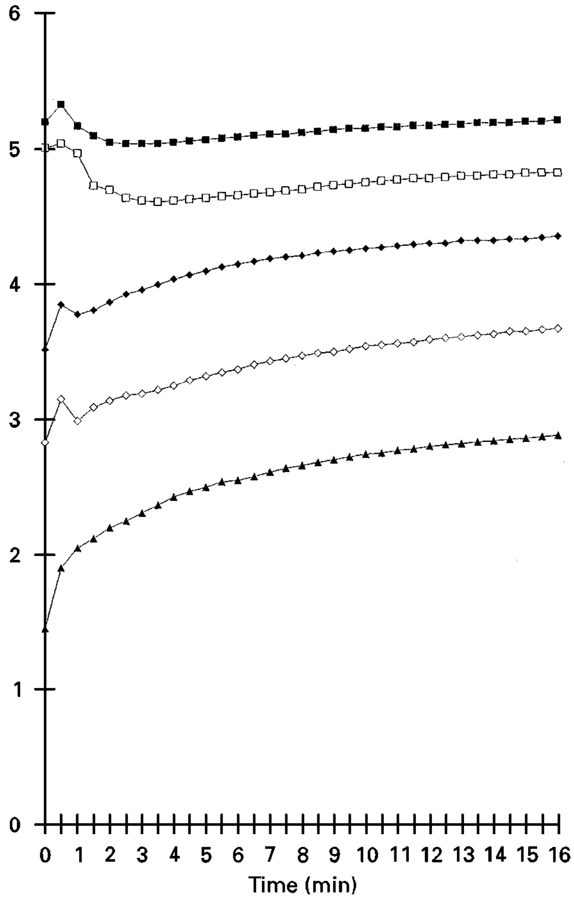

Figure 1 Changes in pH on setting for ZnO/$ZnCl_2$ cements with varying concentrations of $ZnCl_2$. (■) 20%, (□) 30%, (◆) 40%, (◇) 50%, (▲) 60%.

TABLE II Setting times for ZnO/$ZnCl_2$ cements at 18.5 °C determined by oscillating rheometry

Concentration of $ZnCl_2$ (%)	Setting time (min)
20	7.0
30	5.8
40	3.6
50	2.1
60	1.6

Variations in setting times with concentration of $ZnCl_2$ are shown in Table II and variations in compressive strength with concentration of $ZnCl_2$ are shown in Table III. The differences between successive

TABLE III Variation of compressive strength with concentration of $ZnCl_2$ (standard deviations in parentheses)

Concentration of $ZnCl_2$ (%)	Compressive strength (MPa)
20	0.9 (0.4)
30	2.0 (0.6)
40	4.9 (1.2)
50	6.8 (1.3)
60	9.1 (0.9)

compressive strength values were significant to at least $p < 0.05$ in all cases.

Finally, results for mass change on storage in water for 1 week and 1 month, respectively, are shown in Table IV.

4. Discussion

As can be seen in Table I, all of the solutions of $ZnCl_2$ were found to be acidic, with pH decreasing with increasing concentration of $ZnCl_2$. In aqueous solution, zinc chloride is known to dissociate into Zn^{2+} and Cl^- ions, with the former ion becoming hydrated with either four or six water molecules, depending on concentration [17]. The acidic nature of these solutions may be attributed to partial salt hydrolysis of the aquated zinc ion

$$Zn(H_2O)_n^{2+} + H_2O \rightleftharpoons ZnOH(H_2O)_{(n-1)}^{+} + H_3O^{+} \tag{1}$$
$$(n = 4 \text{ or } 6)$$

This dissociation occurs to such an extent that it has been shown that solutions approaching the composition $ZnCl \cdot 4H_2O$ are powerful acids in the Lowry–Brønsted sense [18]. It was originally argued [18] that their proton-donating capability rivalled that of known strong mineral acids, such as phosphoric acid. This was subsequently shown to be incorrect [19], but the fact remains that aqueous zinc chloride is a reasonably effective Lowry–Brønsted acid, as the results in Table I testify, and this acidity arises from the so-called salt hydrolysis mechanism.

As the cements prepared from 20%, 30%, 40% and 50% $ZnCl_2$ underwent setting, they showed similar trends in change of pH. Initially, there was an increase in pH, as would be expected from a rapid reaction of an acid with a base. However, this was followed by a slight shift towards lower values (increased acidity), after which the pH again rose, and continued to rise quite slowly. Thus the early change in pH is reversed as the reaction proceeds, suggesting that the initial product is acting as a buffer.

These observations can be readily interpreted by considering the details of the chemical species present. The initial reaction would be between the base, ZnO, and hydrated protons from the aquated $Zn(H_2O)_n^{2+}$ species ($n = 6$ or 4; the latter being more likely under the present reaction conditions). This reaction would consume H_3O^+ ions and remove them from solution, leading to a rise in pH. This would then cause a shift in the equilibrium towards the right-hand side of the above equation according to the principle of Le Chatelier. This shift would lead, in turn, to an approximate restoration of the pH in the aqueous phase. The additional acidic hydroxonium ion generated by this equilibrium shift would react with the base. This process would continue and eventually consume the system's buffering capacity, leading to the observed slow move towards neutral pH.

At the highest concentration of $ZnCl_2$, 60%, early shifts in pH were not detected. This might be because they occur very rapidly in the presence of relatively large amounts of acid. In general, though, these pH changes on setting are consistent with reaction of a weak acid to form its salt, and the behaviour of the resulting acid–salt pair as a buffer.

Setting times were determined using the oscillating rheometer, and these are shown in Table II. The oscillating rheometer is a crude instrument, and a detailed analysis has shown that what it measures is actually a complex mixture of the dynamic viscosity and the storage modulus of the material, plus the spring constant of the rheometer [20]. Despite this, setting times obtained using this apparatus can be usefully compared for similar materials. The property of setting time was found to vary in the expected way with concentration of $ZnCl_2$, i.e. becoming shorter as concentration rose. This is a well-established relationship for acid–base cements [5], and is what would be expected from increasing the concentration of the reacting species. As the results in Table III show, the set cements were all fairly weak, though there was a clear trend of strength increasing with increasing concentration of $ZnCl_2$. Again, this behaviour is typical of acid–base cements [5].

The compressive strengths of cements of the $ZnO/ZnCl_2$ system were comparable with those of cements made by reaction of ZnO with aqueous zinc nitrate [14], but much lower than the related oxysalt cements formed by reaction of zinc oxide with modified phosphoric acid. The zinc oxyphosphate cements typically reach a compressive strength at 24 h of 85 MPa, and can reach 100 MPa [2], but due to the lack of solubility of zinc phosphate in water, they cannot be made by the analogous reaction of the acid salt with zinc oxide powder. However, the great difference in compressive strength between the zinc oxyphosphate cements and the zinc oxide/zinc chloride or zinc oxide/zinc nitrate cements suggests there is a major structural difference between the two groups of materials. Such a major difference is surprising because, in principle, similar types of cements would be expected from either route. It is known, for example, that mixtures of aqueous HCl and ZnO can be used to determine all points on the H_2O–ZnO–$ZnCl_2$ phase diagram [11], because they will generate the appropriate quantities of $ZnCl_2$. On the other hand, the behaviour of the zinc oxyphosphate system is complicated by the presence of aluminium and zinc phosphates in the phosphoric acid solution, and it may be that these compounds, in addition to modifying the rate of the setting reaction, act in some way to reinforce the set cements. Certainly, these differences require further investigation.

TABLE IV Change in mass of $ZnO/ZnCl_2$ cements on storage in water

Concentration of $ZnCl_2$ (%)	Change after 1 week (%)	Change after 1 month (%)
20	+ 56.4	+ 55.3
30	+ 41.3	+ 40.9
40	+ 36.2	+ 33.8
50	+ 1.0	+ 0.9
60	− 1.3	− 1.5

On storage in water, cements formulated from low concentrations of $ZnCl_2$ took up very large amounts of water (Table IV). Cements formulated from higher concentrations of $ZnCl_2$ took up much less water than those made from lower concentrations, and in the case of the 60% chloride solution, actually lost small amounts of mass. Zinc chloride is well known to be very hygroscopic. For example, it takes up water readily from the atmosphere, even in apparently well-closed containers, and dissolves in this water to form syrupy solutions [21]. The fact that cements made from high concentrations of $ZnCl_2$ actually lose water is evidence that they do not contain the free chloride, but that whatever the structural detail of the product(s), they are sufficiently well hydrated to be relatively stable in water.

By contrast, cements formulated from low concentrations of $ZnCl_2$ took up large quantities of water. This indicates that the reaction products in this case were not sufficiently hydrated as formed; however, they, too, must contain little or no free chloride, because so little was used to prepare them.

Regardless of initial gain or loss of water, all cements lost a small mass between 1 week and 1 month. Thus, all of the zinc oxide/zinc chloride cements were shown to be sparingly soluble in water at room temperature.

5. Conclusions

This study of zinc oxide/zinc chloride cements has given detailed consideration to their setting chemistry, water balance and compressive strength. The setting behaviour of these cements has been shown to be consistent with their being formed by the Lowry–Brønsted acid ($Zn(H_2O)_n^{2+}$; $n = 4$ or 6), whose salt, based on the counterion ($ZnOH(H_2O)_{(n-1)}^{+}$), is sparingly soluble in water. Resulting cements have been shown to be weak, not exceeding 10 MPa in compressive strength. They take up water in amounts that vary inversely with the original concentration of zinc chloride. Cements containing higher proportions of $ZnCl_2$ had low water uptake, despite the well-known hygroscopic nature of $ZnCl_2$; the cement made from the 60% solution actually showed a modest reduction in mass. This suggests that the set cements do not contain free $ZnCl_2$ as such, but rather consist of zinc compounds formed from the chloride, possibly with varying degrees of hydration.

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