WATER TRANSPORT IN ZINC OXY-CHLORIDE CEMENTS

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The water uptake and water loss behaviour in three different formulations of zinc oxy-chloride cement have been studied in detail. Specimens of each material were subjected to a high humidity atmosphere (93% RH) over saturated aqueous sodium sulfate, and a low humidity desiccating atmosphere over concentrated sulfuric acid. In high humidity, the cement formulated from the nominal 75% $ZnCl_2$ solutions gained mass, eventually becoming too sticky to weigh further. The specimens at 25% and 50% $ZnCl_2$ by contrast lost mass by a diffusion process, though by 1 week the 50% cement had stated to gain mass and was also too sticky to weigh. In low humidity, all three cements lost mass, again by a diffusion process. Both water gain and water loss followed Fick's law for a considerable time. In the case of water loss under desiccating conditions, this corresponded to values of M_t/M_∞ well above 0.5. However, plots did not go through the origin, showing that there was an induction period before true diffusion began. Diffusion coefficients varied from 1.56×10^{-5} (75% $ZnCl_2$) to 2.75×10^{-5} cm²/s (50% $ZnCl_2$), and appeared to be influenced not simply by composition. The drying of the 25% and 50% $ZnCl_2$ cements in high humidity conditions occurred at a much lower rate, with a value of D of 2.5×10^{-8} cm²/s for the 25% $ZnCl_2$ cement. This cement was found to equilibrate slowly, but total water loss did not differ significantly from that of the cements stored under desiccating conditions. Equilibration times for water loss in desiccating conditions were of the order of 2-4 hours, depending on $ZnCl_2$ content; equilibrium water losses were respectively 28.8 [25% $ZnCl_2$], 16.2 [50%] and 12.4 [75%] which followed the order of $ZnCl_2$ content. It is concluded that the water transport processes are strongly influenced by the $ZnCl_2$ content of the cement.

INTRODUCTION

Zinc oxy-chloride cements belong to the category of oxysalt bonded cements [1] and were first described by Sorel in 1855 [2]. Since then, their chemistry has been subject to several investigations. Although they are predominantly amorphous, some 17 crystalline compounds have been claimed to occur within them [3].

Phases corresponding to $ZnO:ZnCl_2:H_2O$ of 4:1:6 and 1:1:1.5 have been known since 1910 [4], when Droit identified them in a detailed study of the solubility of zinc oxide in zinc chloride solutions at 18°C. The first of these was decribed as amorphous [4], and lost five of the six water molecules on heating at 200°C to yield a 1:1:1 phase. The final water molecule was not lost until a much higher temperature, and was associated with loss of both HCl and $ZnCl_2$ as well, suggesting that the phase was undergoing substantial decomposition [4]. The existence of this 1:1:1 phase has been confirmed by X-ray diffraction [5, 6], and it has been shown to have a rhombohedral layer structure.

Independent evidence for a 1:1:1 phase was given by Holland in 1930 [7], though this claim was not supported by any unequivocal data, such as X-ray characterization [8]. A 4:1:5 phase has been suggested [9-11], which may or may not be associated with the 1:1:1 phase. A 4:1:4 phase was studied in detail using X-ray diffraction by Feitknecht in the 1930s [12], and shown to have a layer structure with interspersed water molecules. Such a structure would allow ready addition and removal of water molecules without altering the distance between the layers, and it has been suggested that all phases based on a $ZnO:ZnCl_2$ ratio of 4:1 may be closely related and readily interconverted [1].

The role of water in these systems has been considered in some studies. Sorrell in 1977 [8] reported on the overall phase relationships in the $ZnO:ZnCl_2:H_2O$ system. He reported preparing the 1:1:2 phase and showed that it reacted with water extremely rapidly to generate the 4:1:5 phase. These changes were consistent with predictions from the $ZnO:ZnCl_2:H_2O$ phase diagram, and no departures from this, such as the formation of $Zn(OH)_2$ were observed [8].

Most of these studies, particularly those of Sorrell [8] have been concerend with phase relationships, and hence with cements at thermodynamic equilibrium. To date, there have been no studies of the kinetics of water gain or loss in these cements. The present study seeks to rectify this, and has involved exposure of freshly prepared zinc oxy-chloride cements of various compositions either to very high or very low humidities. Rates of water gain or loss have been determined, and related to composition.

Water gain and loss can be described by Fick's law of diffusion. For disc-shaped specimens, edge effects can be neglected, and water uptake or loss follows the form of the so-called Stefan approximation, i.e.:

$$M_t/M_\infty = 2(D\mathrm{t}/\pi l^2)^{1/2}$$

where M_t is the mass uptake/loss at time t (s), M_∞ is the equilibrium uptake/loss, $2l$ is the thickness of the specimen and D is the diffusion coefficient [13]. The later stages up to equilibrium are given by:

$$M_t/M_\infty = 1 - (8/\pi^2)\Sigma 1(2\mathrm{n} + 1) \times \exp[-\pi^2 D/4\mathrm{l}^2(2\mathrm{n} + 1)\mathrm{t}]$$

The diffusion coefficient, D, can be determined by measuring water uptake at convenient time intervals, then plotting M_t/M_∞ against $t^{1/2}$. Where Fick's law is obeyed, this gives a straight line of slope s, where:

$$s = 2(D/\pi l^2)^{1/2}$$

from which

$$D = s^2\,\pi l^2/4.$$

EXPERIMENTAL

Zinc chloride (General Purpose Reagent grade, ex. BDH, Poole, UK) was used to prepare three concentrated solutions. These were designated 75%, 50% and 25% and comprised 7.5 g, 5.0 g and 2.5 g respectively dissolved in 10.0 cm^3 deionised water (ie corresponded to 43%, 33% and 20% by mass respectively). Prior to use, the density of each of these solutions was determined by weighing on a 4-figure balance a 1.00 cm^3 volume in a pre-weighed plastic syringe (2 ml, ref 300185, ex. Platipak, Madrid, Spain).

Cements were prepared from these solutions by spatulating them with the appropriate mass of powdered zinc oxide (General Purpose Reagent grade, ex. BDH, Poole, UK) on a glass block at a powder:liquid ratio of 1.0 g: 1 cm^3. A typical mixture consisted of 0.5g ZnO and 0.5 cm^3 $ZnCl_2$ solution. Having mixed the pastes to a homogeneous consistency in 5-10 seconds, they were transferred to silicone rubber moulds held between microscope slides and allowed to harden. The moulds gave circular specimens of diameter 6 mm and depth of 2 mm. Four specimens were prepared per cement, results for mass changes were averaged and standard deviations calculated.

Specimens were allowed to mature for approximately 15 minutes in the moulds, then weighed and transferred to a controlled atmosphere environment, either high or low humidity. The high humidity atmosphere was created in a sealed chamber over saturated $Na_2SO_4\cdot 10H_2O$ (General Purpose reagent, ex. BDH, Poole, UK), which creates an atmosphere of 93% relative humidity at 20°C [14]. Specimens were then weighed at 1 hour intervals for the first 6 hours, then daily until equilibrium was achieved (a situation that was considered to be indicated by two successive weighings within 0.0002 g) or until the specimens had become too sticky to weigh.

The low humidity atmosphere was created in a desiccator containing concentrated sulfuric acid as desiccant (Spectrosol®, ex BDH, Poole, approximately 98% H_2SO_4). Specimens placed under these conditions were weighed at 10 minute intervals for the first hour, then at hourly intervals until equilibrium was achieved.

Equilibrium mass changes were determined as appropriate, and where water was lost from specimens, plots were made of M_t/M_∞ against $t^{1/2}$. Using the slope of this graph, s, diffusion coefficients were determined from the equation $D = s^2\,\pi l^2/4$.

Differences in values were examined for statistical significance using the Student's t-test as appropriate.

RESULTS

The densities of the three solutions employed to prepare cements are shown in Table 1, together with the corresponding overall composition of the cements. Mass change data for the cement based on 75% $ZnCl_2$ in high humidity are given in Table 2. The cements based on 25% and 50% $ZnCl_2$ lost mass, and details are shown in Table 3. The 25% cement eventually equilibrated, with values as shown in Table 3. The cement based on 50% $ZnCl_2$, by contrast, lost water over a period of 24 hours, but after 1 week had begun to absorb water and became too sticky to weigh. This suggests that the water loss process reversed at some stage between 1 day and 7 days, and the cement began taking up water under these conditions. The diffusion coefficient shown in

Table 1. Details of cement compositions.

Nominal liquid composition (% $ZnCl_2$)	Density of liquid (g/cm^3)	Mass ratio of powder:liquid	$ZnO:ZnCl_2:H_2O$ by mass (%)	$ZnO:ZnCl_2:H_2O$ mole ratio
25	0.96	1.00:0.96	51.0 : 9.8 : 39.2	8.8 : 1 : 30.7
50	1.13	1.00:1.13	47.0 : 17.5: 35.5	4.5: 1 : 15.6
75	1.22	1.00:1.22	45.0 : 23.4: 31.6	3.2: 1 : 10.2

Table 3 is an estimate and was obtained using the value for equilibrium water loss determined under desiccating conditions to calculate the M_t/M_∞ values.

Mass loss in desiccating conditions was more staightforward and found to be Fickian in all three cases. Figure 1 shows a typical plot of M_t/M_∞ against $t^{1/2}$ for 75% $ZnCl_2$. This gives a straight line for all experimental values, but does not pass through the origin, which indicates that there was an induction period before true diffusion commenced. Data for all three cements (equilibrium mass loss and diffusion coefficients) are shown in Table 4. Mole ratios of $ZnCl_2$ to water at equilibrium in the cements are given in Table 5.

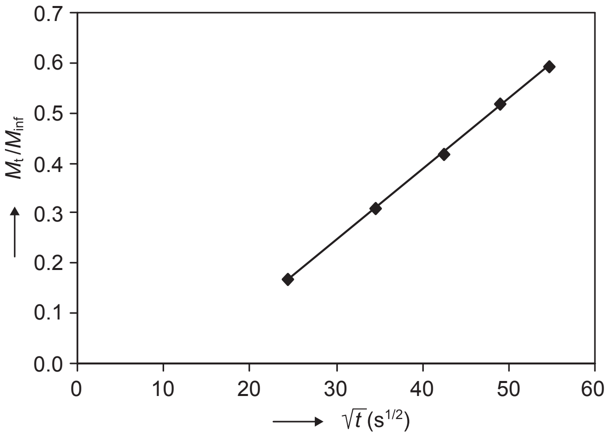

Figure 1. Graph of M_t/M_∞ against $t^{1/2}$ for the 75% $ZnCl_2$ cement.

Table 2. Mass change data for 75% $ZnCl_2$ cements stored at 93% relative humidity (Standard deviations in parentheses).

Time (h)	Mass loss (%)
0	0.0 (0.0)
1	1.6 (0.6)
2	3.2 (0.9)
3	4.2 (1.2)
4	4.9 (1.3)
5	5.6 (1.4)
24	24.6 (2.2)

Differences in equilibrium mass losses were statistically significant for the three different cements under desiccating conditions ($p > 0.01$). On the other hand, the difference between the equilibrium water losses for the 25% $ZnCl_2$ cement under high humidity and desiccating conditions was not significant.

DISCUSSION

Zinc oxy-chloride cements are complicated substances at the molecular level. They are prepared from highly concentrated aqueous solutions of $ZnCl_2$ which are themselves complex. Calculations using an *ab initio* molecular orbital approach have predicted the occurrence of the species $Zn(H_2O)_6^{2+}$, $ZnCl_2(H_2O)_2$, $ZnCl_3(H_2O)^-$ and $ZnCl_4^{2-}$ in these solutions [15] and this is consistent with the limited structural and energetic data that are available. At high concentrations, the undissociated species *trans*-$ZnCl_2(H_2O)_4$ is known to occur [16]. Aqueous solutions of zinc chloride behave as protonic acids [17], though are weaker than mineral acids such as nitric, sulfuric or phosphoric acid [18]. This behaviour has been attributed to so-called *salt hydrolysis* [19], ie the occurrence of the following process:

$$Zn(H_2O)_6^{2+} + H_2O \rightarrow ZnOH(H_2O)_5^+ + H_3O^+$$

Table 5. Water : $ZnCl_2$ mole ratios at equilibrium.

Composition	Equilibrium mole ratio of H_2O to $ZnCl_2$
25% $ZnCl_2$	13 : 1
50% $ZnCl_2$	8 : 1
75% $ZnCl_2$	6 : 1

Table 3. Data for the 25% and 50% $ZnCl_2$ cements stored at 93% relative humidity.

Composition	Equilibrium mass loss (%) [Standard deviations]	Time to equilibrate (days)	Diffusion coefficient (cm^2/s)
25% $ZnCl_2$	25.7 [1.9]	14	2.5×10^{-8}
50% $ZnCl_2$	Could not be determined	Not determined	9.1×10^{-7} (estimated)

Table 4. Equilibrium mass loss, equilibration times and diffusion coefficients for cements in desiccating conditions.

Composition	Equilibrium mass loss (%) [Standard deviations]	Equilibration time (h)	Diffusion coefficient (cm^2/s)
25% $ZnCl_2$	28.8 [0.9]	2	2.03×10^{-5}
50% $ZnCl_2$	16.2 [0.7]	2	2.75×10^{-5}
75% $ZnCl_2$	12.4 [1.0]	4	1.56×10^{-5}

Despite the relatively weak acidity that results from this, aqueous solutions of zinc chloride are sufficiently acidic to react with the base zinc oxide and form cements [1]. The resulting cements are, however, very weak, with compressive strengths typically not exceeding 10 MPa [19].

Previous studies have suggested that water within these cements is labile, and that this is a consequence of a layer structure with interspersed water molecules [5, 6, 12]. In the present study, all cements contained an excess of water, and even after they had been equilibrated under desiccating conditions, they retained an excess of water by comparison with the amount required to form the previously reported 4:1:4 or 4:1:5 phases.

The results for water loss suggest that water is very lightly held within the cements, at least in the nominal 50% and 75% $ZnCl_2$ cements, since they lost water even at 93% relative humidity. The behaviour of the 75% $ZnCl_2$ cement was different, in that it absorbed water, and showed hygroscopic behaviour similar to zinc chloride itself. This suggests that there may be similar zinc-chlorine species within the cement to those that occur in $ZnCl_2$ itself, and that it is these which cause the observed water uptake. The 50% $ZnCl_2$ cement showed surprising behaviour, in that it lost water over the first few hours, but after 1 week had apparently gained mass and become too sticky to weigh properly. This suggests that there are post-hardening reactions within the cement, and that they shift the hydrolytic properties from water-losing to hygroscopic over a period of a few days.

Water loss under desiccating conditions was very rapid in all cases, and led to equilibration in only 2 hours for the 25% and 50% $ZnCl_2$ cements and 4 hours for the 75% $ZnCl_2$ cement. Diffusion coefficients were high ($1.03\text{-}2.75 \times 10^{-5}$ cm²/s), and were comparable with recently reported diffusion coefficients for water in Portland cement ($0.6\text{-}2 \times 10^{-5}$ cm²/s) [20]. Under desiccating conditions, diffusion coefficients were two orders of magnitude greater than diffusion coefficients in high humidity conditions, which is not surprising, given the resistance to drying that the latter impose. For each cement under desiccating conditions, there was a lag before diffusion established itself as Fickian but, in all three cases, this lasted less than 10 minutes. Once water loss had begun, it continued as a purely diffusion process until M_t/M_∞ reached between 0.6 and 0.75.

Overall, the properties were clearly strongly influenced by the initial $ZnCl_2$ content of the cements. High levels of $ZnCl_2$ were associated with hygroscopic behaviour in high humidity conditions, and with both the lowest diffusion coefficient and lowest % water loss in desiccating conditions. Though the reasons for these observations are not clear, in terms of the underlying chemistry, water has been found to be very readily gained or lost by these cements, and this is likely to limit their potential technological applications.

CONCLUSIONS

The water uptake and water loss behaviour of zinc oxy-chloride cements have been shown to be strongly influenced by the zinc chloride content. In high humidity atmosphere (93% RH) over saturated aqueous sodium sulphate, the cements containing 25% and 50% $ZnCl_2$ lost water, though with a very low diffusion coefficients (2.5×10^{-8} and 9.1×10^{-7} cm²/s respectively). Cements with the highest zinc chloride content studied (75%) gained water and eventually became too sticky to weigh further. The 50% cement also became sticky after a week at high humidity, and could not be weighed further.

In desiccating conditions, all cements lost water, and the process followed Fick's law for a considerable time, after an initial induction period. Diffusion coefficients varied from 1.56×10^{-5} (75% $ZnCl_2$) to 2.75×10^{-5} cm²/s (50% $ZnCl_2$), which does not relate simply to the differences in zinc chloride content. Drying of the 25% and 50% $ZnCl_2$ cements in high humidity conditions was much slower than in desiccating conditions but for the 25% $ZnCl_2$ cement, which reached equilibrium, the final water content did not differ from that of specimens stored under desiccating conditions.

Equilibration in desiccating conditions took between 2 and 4 hours, depending on $ZnCl_2$ content. Equilibrium water contents were respectively 28.8 (25% $ZnCl_2$),16.2 (50%) and 12.4 (75%) which followed the order of $ZnCl_2$ content. The $ZnCl_2$ content of the cement thus has a strong influence on the final composition of the cements, though has a less well defined effect on the kinetics of the process of water loss.

References

1. Wilson A.D., Nicholson J.W.: *Acid-base cements*, University Press, Cambridge 1993.
2. Sorel S.: Comptes rendus hebdomadaires des seances de l'Acadamie des sciences *41*, 784 (1855).
3. Mellor J.W.: *A comprehensive treatise on inorganic and theoretical chemistry*, Vol IV, pp 535-546, Longmans Green, London 1925.
4. Droit A.: Comptes rendus hebdomadaires des seances de l'Acadamie des sciences *150*, 1426 (1910).

5. Nowacki W., Silverman J.N.: Zeitschrift fur Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie *115*, 21 (1961).
6. Nowacki W., Silverman J.N. Zeitschrift fur Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie *117*, 238 (1962).
7. Holland H.C.: J.Chem.Soc. 643 (1930).
8. Sorrell C.A.: J. Am. Ceram. Soc. *60*, 217 (1977).
9. Feitknecht W.: Helv.Chim.Acta *13*, 22 (1930).
10. Hayek E.: Z.Anorg.&All.Chem. *207*, 41 (1932).
11. Aspelund H.: Acta Acad. Aboensis *7*, 1 (1933).
12. Feitknecht W.: Helv. Chim. Acta *16*, 427 (1933).
13. Crank J., Park G.S.: *Diffusion in Polymers*, Academic Press, London 1968.
14. Lange N.A.: *Handbook of Chemistry*, 10th ed., McGraw-Hill, New York 1961.
15. Parchment O.G., Vincent M.A., Hillier I.H.: J.Phys. Chem. *100*, 9686 (1996).
16. Yongyai Y., Kokpol S., Rode B.M.: J.Chem.Soc.Faraday Trans. *88*, 1537 (1992).
17. Duffy J.A., Ingram M.D.: Inorg.Chem. *17*, 2798 (1978).
18. McDaniel D.H.: Inorg.Chem. *18*, 1412 (1979).
19. Nicholson J.W., Parker L.: J.Mater.Sci. *33*, 2251 (1998).
20. Bordallo H.N., Aldridge L.P., Desmedt A.: J.Phys. Chem. B *110*, 17966 (2006).

PŘENOS VODY V CEMENTECH S OXYCHLORIDEM ZINEČNATÝM

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Podrobně byly zkoumány procesy příjmu a ztráty vody ve třech různých složeních cementu s oxychloridem zinečnatým. Každý vzorek materiálu byl vystaven atmosféře s vysokou vlhkostí (93 % rel. vlhkosti) a nasyceným vodným sulfátem sodným a sušení v podmínkách s nízkou vlhkostí s koncentrovanou kyselinou sírovou. Ve vyšší vlhkosti se cement vytvořený z 75% roztoků $ZnCl_2$ zhutnil, případně se příliš slepil a ztěžkl. Vzorky s 25% a 50% $ZnCl_2$ naopak zaznamenaly úbytek hmoty a difuzní proces, ačkoliv do týdne se 50% cement také zhutnil, slepil se a ztěžkl. Při nízké vlhkosti zaznamenaly všechny tři cementy úbytek hmoty znovu následkem difuzního procesu. Příjem i ztráta vody po dlouhou dobu sledovaly Fickův zákon. V případě ztráty vody v sušárně byl proces podle zákona až do M_t/M_∞ nad hodnotu 0,5. Děje však nepostupovaly podle zákona a před počátkem skutečné difuze vykazovaly indukční periodu. Difuzní koeficient byl v rozmezí od $1{,}56 \times 10^{-5}$ (75% $ZnCl_2$) do $2{,}75 \times 10^{-5}$ cm^2/s (50% $ZnCl_2$) a patrně byl ovlivněn nejen složením. Sušení 25% a 50% $ZnCl_2$ cementů při vysoké vlhkosti probíhalo při daleko nižší rychlosti s hodnotou D $2{,}5 \times 10^{-8}$ cm^2/s pro 25% cement $ZnCl_2$. Bylo zjištěno, že tento cement dosahoval rovnováhy pomalu, ale celková ztráta vody se významně nelišila od cementů uložených v sušárně. Vyrovnávací časy pro ztrátu vody v sušárně byly mezi 2-4 hodinami v závislosti na obsahu $ZnCl_2$; rovnovážné ztráty vody byly 28,8 [25% $ZnCl_2$],16,2 [50%] a 12,4 [75%], což bylo ovlivněno obsahem $ZnCl_2$. Závěrem lze konstatovat, že procesy přenosu vody jsou silně závislé na obsahu $ZnCl_2$ v cementu.