

# THE INFLUENCE OF GROUP I METAL CHLORIDES ON WATER LOSS AND CHLORIDE RELEASE FROM MAGNESIUM OXYCHLORIDE CEMENTS

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*The water loss and chloride release from four different formulations of magnesium oxychloride cement have been studied. The formulations were all based on 25% m/m aqueous MgCl<sub>2</sub> and the solutions employed to prepare cements consisted of either MgCl<sub>2</sub>:water or MgCl<sub>2</sub>:aqueous MCl (M = Li, Na or K, all MCl salts at 1 mol dm<sup>-3</sup>). Solutions were mixed with solid MgO at a ratio of 1:1 (m/v) and allowed to harden at room temperature for 1 hour. Five disc-shaped specimens (6 mm diameter × 2 mm thickness) of each were prepared, stored in a desiccating atmosphere and weighed at regular intervals. All were found to lose water rapidly, equilibrating within three hours. Water loss was Fickian to values of  $M_t/M_\infty$  of around 0.7 in all cases. Diffusion coefficients were slightly smaller than for the additive-free cement ( $1.52 \times 10^{-6}$  cm<sup>2</sup>/s) and fell in the range  $1.27$ - $1.39 \times 10^{-6}$  cm<sup>2</sup>/s. Equilibrium water losses varied from 23.1% (with NaCl) to 20.0% (with KCl), but only with NaCl did the value differ significantly from that for the additive-free cement (20.7%). Chloride release was increased by the presence of the additives. It followed a consistent pattern, with a maximum generally at about 5 hours, followed by a reduction up to 2 weeks (336 hours). This shows that a proportion of the released chloride was taken back up as the cement matured.*

## INTRODUCTION

Solid cements may be formed from magnesium oxide (magnesia) with aqueous magnesium chloride [1]. They have useful properties, with compressive strengths that exceed those of Portland cement [2], and they find application in the construction industry as, inter alia, flooring, materials, stuccos and renders for wall insulation panels [3, 4].

Magnesium oxychloride cements have been shown to set rapidly [5] with early formation of Mg<sub>3</sub>(OH)<sub>2</sub>Cl·4H<sub>2</sub>O in the form of needle-like crystals [6]. The setting reactions are complex [7-10] and involve the neutralization and partial dissolution of solid MgO. This is followed by the formation of various polynuclear complexes of the type [Mg<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub>]<sup>(2x-y)+</sup>, whose composition is uncertain [9]. The concentrated solutions of MgCl<sub>2</sub> from which these cements are made are known to contain amorphous assemblies of [Mg<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub>]<sup>(2x-y)</sup> (x, y = 1-5) together with Cl<sup>-</sup> and OH<sup>-</sup> ions, all dissolved in water. On setting, these may form essentially amorphous phases, or may generate crystalline phases of well-established composition [9].

Studies have been reported recently on the subject of water transport in the magnesium oxide-aqueous magnesium chloride cement system [10]. Cements were

stored in desiccating conditions at room temperature and water loss monitored. Mass stabilised in about 3 hours and water loss was shown to occur by diffusion, with diffusion coefficients in the range of  $1.23$ - $1.84 \times 10^{-6}$  cm<sup>2</sup>/s [10]. At equilibrium, the water content ranged from 6.9 to 27%, depending on composition, with lower values being associated with high MgCl<sub>2</sub> concentrations.

The present study has been undertaken to determine the influence of Group 1 metal chlorides on the kinetics of water loss. As before, water loss from has been modelled using Fick's Second Law of Diffusion. For disc-shaped specimens edge effects can be neglected and uptake can be shown to take the form of the Stefan approximation, *ie*

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

where  $M_t$  is the mass uptake at time  $t$  (s),  $M$  is equilibrium mass loss,  $2l$  is the thickness of the specimen and  $D$  is the diffusion coefficient [11]. The diffusion coefficient,  $D$ , can be determined by measuring water uptake at convenient time intervals, then plotting  $M_t/M_\infty$  against  $t^{1/2}$ . Where Fick's law is followed, this gives a straight line of slope  $s$ , where:

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

from which

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

In addition, chloride release from these cements has been determined, and the variation in chloride release with time determined.

There have been no previous studies on the effect of ionic additives in magnesium oxychloride cements. However, there have been equivalent studies for the glass-ionomer dental cement [12], a material which has some resemblance to magnesium oxychlorides in that they are acid-base cements that contain reasonable amounts of water when set [1]. When the ionic additives LiCl, NaCl and KCl were present, glass-ionomers were found to lose water faster than when they were absent, though the equilibrium water loss did vary significantly [12]. The present study was undertaken to determine whether magnesium oxychloride behaves similarly.

## EXPERIMENTAL

Magnesium chloride (General Purpose Reagent grade, ex BDH, Poole, UK) was used to prepare a solution of 25% mass/mass from which cements were prepared. The other component of the solutions was either deionised water, or a 1 mol dm<sup>-3</sup> solution of LiCl, NaCl or KCl (all General Purpose Reagents, ex BDH, Poole, UK). Details of the compositions are shown in Table 1.

Cements were prepared from these liquids by mixing 1.0 cm<sup>3</sup> with 1.0 g of magnesium oxide (General Purpose reagent grade, ex BDH, Poole, UK) on a ceramic tile with a metal spatula. Having mixed the pastes to a homogeneous consistency in about 10 seconds, they were placed in silicone rubber moulds and held between

microscope slides and allowed to set at room temperature (ca. 22°C). The geometry of the specimens was disc-shaped, with a diameter of 6 mm and depth of 2 mm. Five specimens were prepared for each cement formulation, and mass changes were averaged and standard deviations determined.

Specimens were allowed to mature for 1 hour sealed in the moulds, then removed and weighed. There were then transferred to a desiccating environment in a sealed desiccator over concentrated sulphuric acid (Spectrosol<sup>®</sup>, ex BDH, Poole, UK), a system designed to give a relative humidity of 5% or lower [13]. Specimens were weighed at time intervals of 15, 30, 45, 60, 90, 120, 150 and 180 minutes. By this time, weights had equilibrated.

Mass losses were plotted as  $M_t/M_\infty$  against  $t^{1/2}$ , and the slopes determined using least squares regression. Using the slope of this graph,  $s$ , diffusion coefficients were determined from  $D = s^2\pi^2/4$ .

Chloride release from cements was determined from additional cement discs that were prepared and placed in deionised water after the curing process was complete. Chloride levels released into water were determined using an ion-selective electrode (Orion 4 Star ISE, ex Thermo Scientific, UK) that had previously been calibrated using NaCl solutions of known concentration. Determinations were made at time intervals of 1, 2, 3, 4, 5 and 24 hours, then after 1 and 2 weeks. Specimens were stored at room temperature throughout these experiments.

Where appropriate, differences in values were tested for statistical significance using Student's t-test.

## RESULTS

The cements were found to lose mass in all cases when stored in desiccating conditions (Table 1). This loss followed Fick's law in each case, with a short induction period (Table 2). The latter value was determined by extrapolation of the Fick's Law plot to the intercept with the  $t^{1/2}$  axis, as previously used in studies of water loss from magnesia-based cements [10], and then calculating the value of time at this point.

Diffusion was found to occur up to high proportions of loss, generally to  $M_t/M_\infty$  of at least 0.7. This was apparent from inspection of the full graphs, and after these limits, lines curved towards the asymptotic value of  $M_\infty$ . Lines of best fit were determined for  $M_t/M_\infty$  against  $t^{1/2}$  (Table 3) and these are shown plotted in Figure 1.

Table 1. Mean masses for cements stored in desiccating conditions at varying time intervals (Standard deviations in parentheses).

time (min)	mean mass (g)			
	MgCl <sub>2</sub> (water)	MgCl <sub>2</sub> (1M LiCl)	MgCl <sub>2</sub> (1M NaCl)	MgCl <sub>2</sub> (1M KCl)
0	0.0767 (0.0029)	0.0863 (0.0031)	0.0877 (0.0032)	0.0833 (0.0033)
15	0.0790 (0.0020)	0.0832 (0.0029)	0.0840 (0.0039)	0.0838 (0.0031)
30	0.0779 (0.0009)	0.0811 (0.0016)	0.0812 (0.0024)	0.0832 (0.0024)
45	0.0771 (0.0013)	0.0785 (0.0022)	0.0790 (0.0015)	0.0824 (0.0019)
60	0.0769 (0.0027)	0.0763 (0.0019)	0.0770 (0.0027)	0.0823 (0.0022)
90	0.0772 (0.0020)	0.0736 (0.0024)	0.0740 (0.0015)	0.0824 (0.0019)
120	0.0763 (0.0017)	0.0707 (0.0022)	0.0724 (0.0013)	0.0821 (0.0010)
180	0.0763 (0.0011)	0.0685 (0.0011)	0.0702 (0.0012)	0.0702 (0.0013)

Table 2. Induction periods for water loss from cements.

Liquid composition	Induction period (min)
25% MgCl <sub>2</sub>	3.5
25% MgCl <sub>2</sub> + LiCl	5.3
25% MgCl <sub>2</sub> + NaCl	3.9
25% MgCl <sub>2</sub> + KCl	2.9

re 1. In all cases, masses equilibrated within 3 hours. Values of equilibrium mass loss and diffusion coefficient for all cements are shown in Table 4.

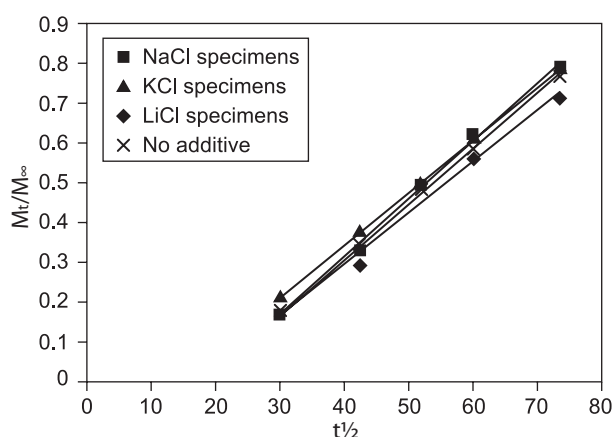


Figure 1. Plot of  $M_t/M_\infty$  against  $t^{1/2}$  for water loss from the cements containing additives.

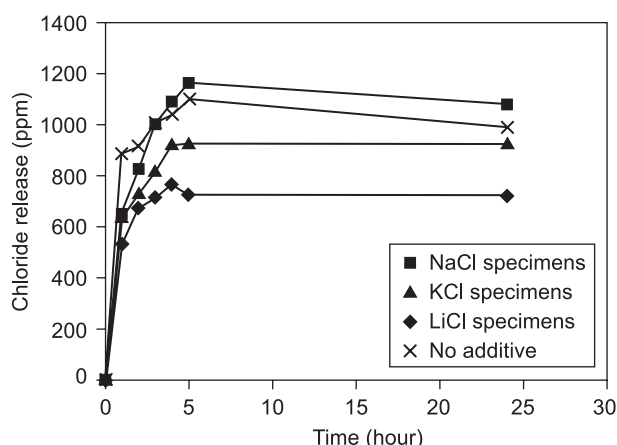


Figure 2. Plots of chloride release vs time for the first 24 hours for all cements.

Table 3. Lines of best fit for  $M_t/M_\infty$  ( $y$ ) against  $t^{1/2}$  ( $x$ ).

Liquid composition	Equation	Limit of linearity	Correlation coefficient, $r$
25% $MgCl_2$	$y = 0.0139x - 0.240$	0.8	0.999
25% $MgCl_2 + LiCl$	$y = 0.0130x - 0.232$	0.7	0.998
25% $MgCl_2 + NaCl$	$y = 0.0133x - 0.203$	0.7	0.997
25% $MgCl_2 + KCl$	$y = 0.0127x - 0.168$	0.7	0.996

Table 4. Equilibrium mass loss and diffusion coefficients for cements.

Liquid composition	Equilibrium mass loss (%) (Standard deviation)	Diffusion coefficient ( $cm^2 s^{-1}$ )
25% $MgCl_2$	20.7 (0.5)	$1.52 \times 10^{-6}$
25% $MgCl_2 + LiCl$	20.6 (0.3)	$1.33 \times 10^{-6}$
25% $MgCl_2 + NaCl$	23.1 (0.3)	$1.39 \times 10^{-6}$
25% $MgCl_2 + KCl$	20.0 (0.4)	$1.27 \times 10^{-6}$

Differences between % water loss at equilibrium for cements with additive and the parent cement were significant only for those cements fabricated with NaCl ( $p > 0.001$ ). For both LiCl and KCl, equilibrium water loss was not significantly different from that of the parent.

All cements were found to release chloride ions into solution (Table 5), with the cements that contained additives releasing greater amounts. At most time intervals (up to 3 hours and at 1 and 2 weeks), chloride levels followed the order  $K > Li > Na > no\ additive$ . At 4 and 5 hours onwards, the order was  $Li > K > Na > no\ additive$ . All cements showed the same pattern of release, with a gradual increase up to 5 hours, but with clear reductions at one week and a further decrease at week 2.

## DISCUSSION

The results obtained show clearly that the presence of Group I metal chlorides in magnesium oxychloride cements affects some of their key chemical properties. Unlike the case for glass-ionomer cements [12], water diffusion occurred more slowly, as determined from the diffusion coefficients. However, equilibrium water content was hardly affected in the case of LiCl and KCl, whereas with NaCl it increased by a statistically significant amount. These latter results are similar to the findings for glass-ionomers, where no significant difference was found in equilibrium water loss for any of the Group I metal chlorides studied [12].

The reduction in diffusion coefficients, indicating a slowing in the rate of water diffusion, is consistent for all three additives (LiCl, NaCl and KCl). The diffusion coefficients associated with these additives are all very similar, and do not follow any clear pattern, possibly because they are so close in value. However, all three are lower than the value for the additive-free cement, demonstrating that the alkali metal chlorides slow down

the rate of water movement through these cements. They can be presumed to do so on account of their strongly hydrophilic nature, which inhibits water movement.

At equilibrium, very similar amounts of water were lost for the cements containing LiCl and KCl, and these did not differ significantly from that for the parent (additive-free) cement. By contrast water loss for NaCl cements proved to be significantly higher than for all the others ( $p > 0.001$ ), though the reason for this is not clear. The hydrophilic properties of sodium chloride are not notably different from those of the other alkali metal chlorides, and the hydration enthalpies are similar to those of LiCl and KCl [14], so similar values for water loss might have been anticipated.

Chloride release by cements has been shown to give variable results. All cements, including the additive-free one, released chloride over time. The cements containing the alkali metal chlorides released more, as expected, but not in a consistent pattern. First, during the initial 3 hours, release followed the order KCl > LiCl > NaCl > no additive. Then, in the middle time range (4-24 hours), this order changed to LiCl > KCl > NaCl > no additive. Finally, for the longer two time periods (1 week and 2 weeks), it reverted to KCl > LiCl > NaCl > no additive. The reason for these changes is not clear.

The other notable feature is that, in all cases, there was a reduction in measured chloride release between weeks 1 and 2, and for LiCl and NaCl, there was also a reduction between 24 hours and 1 week. This suggests that the cements change their affinity for chloride ion as they mature, and that they take up some of the ions previously released into their structure.

Maturation processes have not been much studied in these cements, though there is some evidence that crystallinity increases with time [4]. This would occur by a process analogous to Ostwald ripening in glasses, as notionally amorphous regions gradually crystallise. In fact, the amorphous regions cannot be completely amorphous, as the energetics of ionic interactions would cause the constituent ions ( $Mg^{2+}$ ,  $Na^+$ ,  $Li^+$ ,  $K^+$ ,  $Cl^-$ ,  $O^{2-}$ , etc) to be reasonably close together in the solid state. The distinction between "amorphous" and "crystalline" domains in such cements is therefore one of size only,

and the energy required to form visible crystalline phases is likely to be small. It may be that this growth of crystallinity is aided by resorption of  $Cl^-$  ions from the surrounding storage solution. Whatever the explanation, it remains apparent that chloride is taken up by these cements, and that the amount in solution falls by between 7.8% (for the additive-free cement) and 26.7% (for the LiCl cement) as a result of this uptake.

## CONCLUSIONS

The water loss behaviours of magnesium oxide-25% aqueous magnesium chloride cement with LiCl, NaCl or KCl additives have been studied. In desiccating conditions, all cements lost water by a process followed Fick's Second Law of diffusion. There was an initial induction period for water loss, which varied slightly with composition. Diffusion coefficients where additives were present were lower than for the parent cement and fell in the range  $1.27$  to  $1.39 \times 10^{-6} \text{ cm}^2/\text{s}$ . Equilibration took no more than 3 hours in all cases, and equilibrium water losses varied slightly with additive, from 23.1% (NaCl) to 20.0% (KCl).

All cements released chloride ions, and this was increased by the presence of the additives. In all cases, it followed the pattern of a maximum at about 5 hours, followed by a reduction up to 2 weeks (336 hours). Cements were thus shown to take back up a portion of the released chloride as they matured. The mechanism of this uptake is unclear, though it may be associated with increasing crystallinity.

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Table 5. Chloride release (ppm) with time for  $MgCl_2$ -based cements (Standard deviations in parentheses).

Storage time (hr)	$MgCl_2$ only	$MgCl_2 + LiCl$	$MgCl_2 + NaCl$	$MgCl_2 + KCl$
1	538 (23)	653 (21)	643 (22)	889 (21)
2	676 (18)	828 (40)	734 (23)	918 (23)
3	718 (27)	1003 (41)	820 (30)	1006 (16)
4	771 (33)	1094 (32)	925 (27)	1042 (28)
5	729 (927)	1168 (46)	926 (18)	1104 (51)
24	726 (18)	1080 (33)	927 (42)	989 (27)
168	808 (29)	944 (26)	872 (31)	1018 (29)
336	745 (23)	860 (27)	844 (21)	980 (26)

References

1. Wilson A.D., Nicholson J.W.: *Acid-Base Cements*, University Press, Cambridge 1993.
2. Beaudoin J.J., Ramachandran V.S.: *Cement Concrete Res.* 5, 617 (1975).
3. Shand M.A.: *The Chemistry and Technology of Magnesia*, Wiley-Interscience, New Jersey, 2006.
4. Liska M., Al-Tabbaa A.: *Constr. & Build. Mater.* 22, 1789 (2008).
5. Beaudoin J.J., Ramachandran V.S.: *Cement Concrete Res.* 8, 103 (1978).
6. Tooper B., Cartz L.: *Nature* 211, 64 (1966).
7. Chau C.K., Li Z.: *Mater. & Struct.* 41, 853 (2008).
8. Bilinski H., Matkovic B., Mazuravic C., Zunic T.A.: *J. Am. Ceram. Soc.* 67, 266 (1984).
9. Deng D., Zhang C.: *Cement Concrete Res.* 29, 1365 (1999).
10. Cannesson E., Manier S., Nicholson J.W.: *Ceramics-Silikaty* 54, 341 (2010).
11. Crank J., Park G.S.: *Diffusion in Polymers*, Academic Press, London 1968.
12. Nicholson J.W.: *Ceramics-Silikaty* 53, 1 (2009).
13. Lange N.A.: *Handbook of Chemistry*, McGraw Hill, New York 1961.
14. Greenwood N.N., Earnshaw A.: *Chemistry of the Elements*, 2<sup>nd</sup> ed., Butterworth-Heinemann, Oxford 1997.