

WATER LOSS FROM MAGNESIA-BASED CEMENTS

ELODIE CANNESON, SULIANE MANIER, JOHN W. NICHOLSON*[#]

*Department of Chemistry, IUT Bethune,
University of Artois, France*

**Department of Pharmaceutical, Chemical and Environmental Sciences,
University of Greenwich, Medway Campus, Chatham, Kent, ME4 4TB, United Kingdom*

[#]Corresponding author, e-mail: J.W.Nicholson@gre.ac.uk

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The water loss from four different formulations of magnesium oxychloride cement and two of magnesium oxysulphate cement has been studied. Five specimens of each were stored in a desiccating atmosphere and all lost water rapidly, equilibrating within three hours. For all the magnesium chloride cements, and for one of the magnesium oxysulphate cements (25 % m/m MgSO₄) water loss was Fickian to values of M_t/M_∞ around 0.8 for the oxychloride cements and 0.6 for the oxysulphate cement. However, plots did not go through the origin, as there was an induction time of between 3.1 and 6.3 minutes before true diffusion began. Diffusion coefficients were in the range $1.23\text{--}1.84 \times 10^{-6} \text{ cm}^2/\text{s}$. Equilibrium water losses varied from 27.4% (10 % MgCl₂) to 6.9% (75 % MgCl₂), and from 28.1 % (10 % MgSO₄) to 11.9% (25 % MgSO₄). Water transport properties were shown to be strongly influenced by the chloride or sulphate content of the cement formulation.

INTRODUCTION

Cements formed from magnesia (magnesium oxide) with either aqueous magnesium chloride or magnesium sulphate belong to the category of acid-base cements [1]. The magnesium chloride cements were first reported by Sorel in 1867 [2] and have compressive strengths and microhardness that exceed those of Portland cement [3]. They are used in a variety of construction applications, and find applications in industrial and residential flooring, fire protection coatings, stuccos and as renders for wall insulation panels [4, 5].

Magnesium oxysulphates were first reported somewhat later, in 1934 [6]. They are less widely used than the oxychloride, though have similar strengths and setting characteristics [4].

The cements prepared from aqueous magnesium chloride have been the more widely studied. They have been shown to set rapidly in a highly exothermic reaction [7] by the formation of needle-like crystals of $\text{Mg}_3(\text{OH})_2\text{Cl}\cdot 4\text{H}_2\text{O}$ [8]. Detailed studies of the setting chemistry show that these cements set by the formation of the hydrated phases within the cement pastes [9–12]. Reaction involves the neutralization and partial dissolution of MgO powder followed by the formation of various polynuclear complexes of the type $[\text{Mg}_x(\text{OH})_y(\text{H}_2\text{O})_z]^{(2x-y)+}$ of uncertain composition [11].

Within the concentrated MgCl_2 solutions, these form an amorphous hydrogel consisting of assemblies of $[\text{Mg}_x(\text{OH})_y(\text{H}_2\text{O})_z]^{(2x-y)}$ complexes, Cl^- and OH^- ions and H_2O , which may remain amorphous or form hydrated crystalline phases. The values of x and y have not been specified in the literature [11], but are low (1–5), with the value of y generally exceeding that of x . Leaching these cements with water at 85°C leaves residual material that comprises mainly $\text{Mg}(\text{OH})_2$ and this material seems to have considerable structural integrity [8].

Phase relations in the $\text{MgO}\text{--}\text{MgSO}_4\text{--}\text{H}_2\text{O}$ cements have been shown to be more complex than for the equi-valent magnesium chloride cements [13]. Five stable phases have been identified at 23°C, namely MgO , $\text{Mg}_3(\text{OH})_2$, and $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$, plus $\text{MgSO}_4\cdot n\text{H}_2\text{O}$ ($n = 1, 6$ and 7). In addition, hydrated magnesium sulphate with $n = 4$ and 5 have been observed but these are thought to be metastable [13]. In addition, in the range 30–120°C, the phase $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$ has been found to be stable [14].

Studies have been reported recently on the subject of water transport in the related zinc oxide–aqueous zinc chloride system [15]. Water in these cements had previously been shown to be labile, as a consequence of the layer structure containing interspersed water molecules [16]. Cements were stored in desiccating conditions at room temperature and water loss monitored.

Mass stabilised in 4 hours or less and water loss was shown to occur by diffusion. Diffusion coefficients varied from $1.56 \times 10^{-5} \text{ cm}^2/\text{s}$ for the cement made from 75 % mass/mass aqueous zinc chloride to $2.75 \times 10^{-5} \text{ cm}^2/\text{s}$ for the cement made from 50 % ZnCl_2 [15]. At equilibrium, substantial amounts of water were retained in the cement, varying between 12.4 % and 28.8 %, depending on the formulation.

The present study has been undertaken to determine the kinetics of water loss from various formulations of magnesia cements prepared from aqueous magnesium chloride and magnesium sulphate. Water loss from a variety of cements 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*

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

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 [17]. 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 followed, this gives a straight line of slope s , where:

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

from which

$$D = s^2 \pi l^2 / 4 \quad (3)$$

MATERIALS AND METHODS

Magnesium chloride and magnesium sulphate (both General Purpose reagent grade, ex BDH, Poole, UK) were used to prepare solutions from which cements were prepared. These were at 10, 25, 50 and 75 % mass/mass for MgCl_2 and 10 and 25 % for MgSO_4 . The other component of the solutions was deionised water. Prior to use the densities of these solutions were determined by weighing a 1.0 cm^3 volume on a 4-figure analytical balance in a pre-weighed plastic syringe (total volume 2 ml, ref 300185, ex Plastipak, Madrid, Spain).

Cements were prepared from these solutions by mixing 1.0 cm^3 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[®], ex BDH, Poole, UK), a system designed to give a relative humidity of 5 % or lower [18]. Specimens were weighed at time intervals of 15, 30, 45, 60, 90, 120, 150 and 180 minutes. Preliminary experiments confirmed that, by this time, weights had equilibrated.

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

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

RESULTS

The densities of the solutions used, together with the resulting cement compositions, are shown in Table 1. Preliminary experiments showed that it was not possible to prepare solutions of MgSO_4 corresponding to 50 % by mass or higher, so such formulations could not be studied.

Storing the cements in desiccating conditions led to water loss in all cases. Mass loss was found to follow Fick's law for each cement except the one made from 10% MgSO_4 , though typically with a short induction period. For the 10% MgSO_4 cement, the correlation coefficient for the plot of M_t/M_∞ against $t^{1/2}$ was only 0.951, which is why this was considered not to conform to Fick's Law. Diffusion was found to occur up to unusually high proportions of loss, generally to M_t/M_∞ of circa 0.8. Lines of best fit were determined for M_t/M_∞ against $t^{1/2}$ where possible (Table 2). A typical plot is shown (Figure 1), the specimen being the one formulated from the 75 % mass/mass MgCl_2 solution. In all cases,

Table 1. Cement compositions.

Nominal liquid composition	Density of liquid (g/cm^3)	Mass ratio of powder : liquid	MgO : MgX : H_2O by mass (%)	MgO : MgX : H_2O calculated mole ratio
10 % MgCl_2	1.05	1.0 : 1.05	48.8 : 5.1 : 46.1	22.3 : 1.0 : 48.3
25 % MgCl_2	1.09	1.0 : 1.09	47.8 : 13.0 : 39.2	8.6 : 1.0 : 16.1
50 % MgCl_2	1.25	1.0 : 1.25	44.4 : 27.8 : 27.8	3.7 : 1.0 : 5.4
75 % MgCl_2	1.37	1.0 : 1.37	42.2 : 43.4 : 14.4	2.3 : 1.0 : 1.8
10 % MgSO_4	1.05	1.0 : 1.05	48.8 : 5.1 : 46.1	28.1 : 1.0 : 61.0
25 % MgSO_4	1.31	1.0 : 1.31	43.3 : 14.2 : 42.5	8.9 : 1.0 : 9.4

masses were found to reach equilibrium at or within 3 hours. Values of equilibrium mass loss and diffusion coefficient for all cements are given in Table 3.

In all cases, there was an induction time before the period of diffusion as determined by extrapolation of the Fick's Law plot (Table 3). This induction period was shorter for the magnesium sulphate cements, 3.1 and 3.5 minutes for 10 % and 25 % solutions respectively, than for the magnesium chloride cements. For the latter, induction times ranged from 4.3 to 6.3 minutes, with lower water contents corresponding to shorter induction times.

Differences between % water loss at equilibrium were significant ($p > 0.01$) except in the case of the cements prepared from 10 % MgCl_2 and MgSO_4 , where there was no significant difference between water loss values.

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

Nominal liquid composition	Equation	Limit of linearity	Correlation coefficient, r
10 % MgCl_2	$y = 0.0153x - 0.297$	0.8	0.999
25 % MgCl_2	$y = 0.0139x - 0.240$	0.8	0.999
50 % MgCl_2	$y = 0.0125x - 0.201$	0.8	0.998
75 % MgCl_2	$y = 0.0125x - 0.212$	0.8	0.990
10 % MgSO_4	$y = 0.0137x - 0.294$	0.6	0.951
25 % MgSO_4	$y = 0.0136x - 0.197$	0.6	1.000

Table 3. Equilibrium mass loss and diffusion coefficients for magnesia-based cements.

Nominal liquid composition	Equilibrium mass loss (%)	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
10 % MgCl_2	27.4 (0.9)*	1.84×10^{-6}
25 % MgCl_2	20.6 (0.5)*	1.52×10^{-6}
50 % MgCl_2	14.1 (0.4)*	1.23×10^{-6}
75 % MgCl_2	6.9 (0.5)*	1.23×10^{-6}
10 % MgSO_4	28.1 (1.7)*	–
25 % MgSO_4	11.9 (0.7)*	1.45×10^{-6}

* Standard deviation

Table 4. Induction times for water loss from cements.

Nominal liquid composition	Induction time (min)
10 % MgCl_2	3.1
25 % MgCl_2	3.5
50 % MgCl_2	6.3
75 % MgCl_2	5.0
10 % MgSO_4	4.3
25 % MgSO_4	4.8

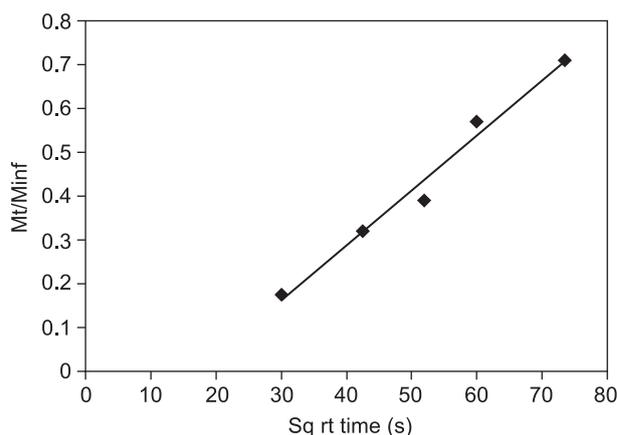


Figure 1. Plot of M_t/M_∞ against $t^{1/2}$ for water loss from the cement 75 % aqueous MgCl_2 + MgO (1 cm^3 : 1.0 g).

DISCUSSION

Magnesia cements of varying composition have been prepared in this study, and their water loss examined. Formulations based on up to 75 % mass/mass could be prepared for magnesium chloride but not for magnesium sulphate. For the latter substance, it did not prove possible to prepare m/m solutions above 25 %.

All cements except that based on 10 % MgSO_4 lost water by diffusion. Diffusion has previously been found for water loss from various cements, including zinc oxychloride [15] and Portland cements [19]. In the cements, diffusion coefficients were high, and of similar magnitude (1.03 – $2.75 \times 10^{-5} \text{ cm}^2/\text{s}$ for zinc oxychloride; 0.6 – $2 \times 10^{-5} \text{ cm}^2/\text{s}$ for Portland cement). For the magnesia-based cements, diffusion was slower and diffusion coefficients an order of magnitude lower, *ie* 1.23 – $1.84 \times 10^{-6} \text{ cm}^2/\text{s}$. For the magnesium chloride cements, for which a greater range of solution concentrations was available than for magnesium sulphate, diffusion coefficients went down slightly as water content was reduced, and reached a limiting value of 1.23×10^{-6} for 50 % MgCl_2 . This was the same as for 75 % MgCl_2 . This suggests that the lower water content cements form less penetrable materials than those with high water contents. Details of the composition are not known for these materials. Even though specific crystalline phases have been identified in them, the region of concentrations used for cement preparation is such that setting occurs rapidly, and there is probably mainly amorphous material in the final set cement [1]. This is characteristic of acid-base cements.

Water loss behaviour has similarities to and differences from that in zinc oxychloride cements. In both systems, it occurs by diffusion and has distinctive induction times [16]. However, in magnesium oxychloride cements it continued for longer, *ie* up to M_t/M_∞ of about 0.8, rather than 0.6–0.75; and diffusion

coefficients were much lower. In both systems, the concentration of the aqueous component influenced the water loss behaviour. For magnesium oxychloride, the diffusion coefficient was lower with higher levels of chloride, as was found to be the case in zinc oxychloride cements. For the magnesium oxysulphate cements, the cement made from the lower concentration solution did not show diffusion behaviour for the loss of water, and for the one which did, diffusion continued only to M_t/M_∞ of about 0.6.

Equilibrium water losses also followed the order of water concentration in the initial cement formulation. More water led to greater losses at equilibrium. This suggests that phases are formed containing strongly bound water but calculations of the mole ratios involved after this water loss were not very revealing. Mole ratios of water to MgX (X = Cl₂ or SO₄) varied from 61.0 to 1.8 (Table 5), and no structural conclusions can be reached from these figures. However, the retention of very high mole ratios of water in some of these formulations suggests that water is physically trapped within the materials, rather than chemically bound at discrete co-ordination sites. Also, the fact that most of these cements were able to retain their structural integrity when desiccated shows one of the reasons for their success in technical applications in the construction industry.

Table 5. Calculated Water : MgX mole ratios at equilibrium.

Nominal liquid composition	Mole ratio H ₂ O : MgX
10 % MgCl ₂	26.2 : 1
25 % MgCl ₂	12.5 : 1
50 % MgCl ₂	4.6 : 1
75 % MgCl ₂	1.6 : 1
10 % MgSO ₄	41.6 : 1
25 % MgSO ₄	17.4 : 1

CONCLUSIONS

The water loss behaviours of magnesium oxide-magnesium chloride and of magnesium oxide-magnesium sulphate cements have been shown to be influenced by the initial composition of the cement. In desiccating conditions, all cements lost water and, with the exception of the 10 % m/m MgSO₄ cement, the process followed Fick's Second Law of diffusion. There was an initial induction period for water loss, which varied with composition. The magnesium oxysulphate cements showed shorter induction periods than the magnesium

oxychloride cements and diffusion coefficients for both series of cements varied from 1.23 to 1.84 × 10⁻⁶ cm²/s. These values are an order of magnitude lower than the diffusion coefficients previously reported for zinc oxychloride cements. Equilibration took about 3 hours in all cases, and equilibrium water losses varied with initial water content, from 27.4 % (10 % MgCl₂) to 6.9 % (75 % MgCl₂), and from 28.1 % (10 % MgSO₄) to 11.9 % (25 % MgSO₄). Like the zinc oxychloride cements, the magnesium chloride or magnesium sulphate content of the cements was found to have a strong influence on the final water retention by the cements and also on the water loss kinetics.

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