



Development of low pH cement systems forming magnesium silicate hydrate (M-S-H)

Tingting Zhang^{a,b}, C.R. Cheeseman^{a,*}, L.J. Vandeperre^b

^a Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

^b Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

ARTICLE INFO

Article history:

Received 18 November 2010

Accepted 19 January 2011

Keywords:

Waste management (E)

MgO (D)

Silica fume (D)

pH (A)

Hydration (A)

ABSTRACT

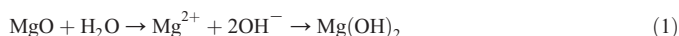
This work aimed to develop novel cement systems for waste encapsulation that would form with a pH of around 10. The approach taken was to investigate the formation of brucite by hydration of a light burned periclase (MgO). Commercially available MgO powders often contain some CaO, and therefore silica fume was added to form C-S-H gel. Identification of the hydrated phases in MgO/silica fume samples showed that brucite formed in substantial quantities as expected. However, brucite reacted with the silica fume to produce a magnesium silicate hydrate (M-S-H) gel phase. After 28 days, the pH of systems rich in MgO tended towards the pH controlled by residual brucite (~10.5), whereas when all brucite reacts with silica fume a cement with an equilibrium pH just below 10 was achieved.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Cements are widely used for waste encapsulation to limit contaminant mobility [1–8]. The cement forms a low permeability matrix and results in immobilisation of contaminants by incorporation into hydrated phases and by precipitation due to the prevailing pH in the pore solution [4]. The solubility of many heavy metals is low at around pH 10, and therefore cements with a pH in this range would be highly desirable for such applications. Such moderate pH cements are likely to be particularly desirable for nuclear waste management [9]. For example, in the UK there are significant quantities of mixed wastes containing both Mg and Al alloys. Whilst the high pH in Portland cement based binders passivates the corrosion of Mg alloys, Al alloys corrode under high pH conditions with evolution of H₂ gas. The pH range in which Al alloys show passive corrosion behaviour extends up to about pH 10 and therefore cements with equilibrium pore solutions in this pH range may balance the need for Mg alloy passivation whilst avoiding Al alloy corrosion.

The pH imposed by cement internally and on its environment is a function of the phases present. It follows that control of the pH is easier if the number of phases in the cement paste is limited. For example, the hydration of MgO is given by:



Magnesium hydroxide (Mg(OH)₂, brucite) is a useful starting point for the development of low pH cements because the pH of excess brucite in equilibrium with water is calculated readily from the solubility product of brucite to be around pH 10.5. Hence, in principle a cement based on the hydration of MgO powder, calcined at low temperature to ensure fast hydration, should yield a desirable pH.

However, most commercially available magnesium oxide powders contain some calcium oxide (lime, CaO) impurities. The presence of CaO has the potential to significantly increase the pH through dissolution of the oxide:



Only when a pH of 12.5 is reached, will precipitation of calcium hydroxide (Ca(OH)₂) mitigate further increases in pH.



A simple strategy to mitigate the pH increase due to the presence of CaO consists in adding a pozzolan capable of reaction with the Ca²⁺ ions or the calcium hydroxide (Ca(OH)₂, portlandite) formed during hydration of CaO, resulting in the formation of C-S-H gel. The aim of this paper was therefore to investigate whether mixtures of silica fume and commercial MgO could yield a pH close to 10.

2. Experimental methods

Blends of a commercially available MgO (MgO, MagChem 30, M.A.F. Magnesite B.V., The Netherlands) and silica fume (SF, Elkem Materials Ltd) were prepared. The chemical composition of the raw materials is reported in Table 1. Note that the MgO contains about 0.8 wt.% of CaO.

* Corresponding author. Tel.: +44 207 594 5971; fax: +44 207 823 9401.

E-mail address: c.cheeseman@imperial.ac.uk (C.R. Cheeseman).

Table 1
Characteristics of the raw materials determined by the manufacturers.

	MgO	Silica fume
<i>Composition</i>		
SiO ₂ (wt.%)	0.35	>97.5
Al ₂ O ₃ (wt.%)	0.1	<0.7
Fe ₂ O ₃ (wt.%)	0.15	<0.3
CaO (wt.%)	0.8	<0.3
P ₂ O ₅ (wt.%)	(n/a)	<0.1
MgO (wt.%)	98.2	<0.5
K ₂ O (wt.%)	(n/a)	<0.6
Na ₂ O (wt.%)	(n/a)	<0.3
SO ₃ (wt.%)	0.05	<0.4
Specific gravity (g cm ⁻³)	3.23	1.94
Mean particle size (μm) ^a	5	21.3
BET surface area (m ² g ⁻¹)	25	21.4

^a Mass median diameter (D₅₀).

Two methods were used to study the pH evolution with time. In the first method, a paste of 50 wt.% MgO and 50 wt.% SF with water to solids ratio of 1 was prepared by adding a mixture of the solids to water and mixing the paste for 15 min. 100 g of the paste was then moulded into a rectangular tile and allowed to set and cure in sealed polyethylene bags. The pH was determined by crushing and grinding 1 g of sample and dispersing the fragments in 5 g of water. Following 24 h mixing, the solids were allowed to settle and the pH was measured by placing a standard glass pH electrode in the supernatant. In a second method, 10 g of a range of blends of MgO and silica fume was added to a polyethylene cylindrical container containing 100 g of distilled water. The tubes were sealed and agitated by device rotation (10 rpm). For pH measurements, the solid particles in these suspensions were allowed to settle determining the pH of the supernatant. For both methods the samples were kept in a laboratory where the temperature was controlled to 23 ± 1 °C.

The hydration products of samples cured in polyethylene bags were investigated using X-ray diffraction (XRD, Philips PW1720 powder diffractometer with a Cu Kα source). This information was then used to guide predictions of the pH made using Visual MINTEQ 2.6 [10], a windows implementation of the MINTEQA2 algorithm [11] for calculation of geochemical aqueous equilibrium to interpret the results of the pH study. The equilibrium constants of the formation reactions for the species considered have been summarised in Table 2.

To clarify some of the XRD data obtained, pure M-S-H gel was synthesised according to the method described by Brew and Glasser [12]. Solutions of Na₂SiO₃·5H₂O and Mg(NO₃)₂·6H₂O were cooled at 0 °C and mixed by stirring in a three-necked flask at a 1:1 Mg/Si ratio with the flask kept immersed in an ice-water bath during the precipitation process. The Na₂SiO₃·5H₂O was initially added followed by the Mg(NO₃)₂·6H₂O. The precipitated composite was filtered and washed to remove all Na⁺ ions. The solid part was then dried in a desiccator at 20 °C for 7 days.

3. Experimental results

Fig. 1 shows that the pH evolution with time for both test methods is essentially the same. The agreement between the two methods was

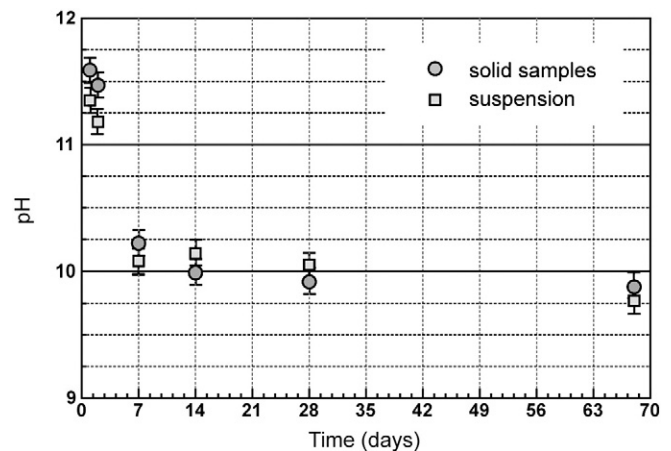


Fig. 1. Evolution with time of the pH for a blend of 50 wt.% MgO and 50 wt.% SF. Samples either remained in suspension throughout or the pH was measured by dispersing in water ground fragments of hydrated solid samples.

also observed for a much wider range of blends of MgO, Portland cement, metakaolin, blast furnace slag and silica fume [13], and confirms that the much easier method of using suspensions rather than pastes gives a good indication of the pH in this system. Fig. 2 shows the variation of pH with composition for blends of MgO and SF after 7 and 28 days. The following points can be observed:

- The pH of the suspensions containing only silica fume or only MgO hardly changes over 28 days. In fact, even when these measurements were extended to 63 days, the pH of the suspension containing only silica fume had decreased by only 0.08, and the pH of the suspensions containing only MgO had changed by only 0.02.
- After 7 days, mixtures with less than 50 wt.% SF have a higher pH than mixtures with more than 50 wt.% SF;
- and after 28 days the pH of most mixtures decreased relative to the 7 day value and mixtures with a higher SF content still show lower pH values than mixtures with a low SF content.

Fig. 3 shows XRD data after 7 and 28 days for two blends: one containing 50 wt.% SF and 50 wt.% MgO and one containing 80 wt.% SF and 20 wt.% MgO. For both types of blends little or no XRD signal for the original MgO remains after 7 days. Brucite is the main crystalline phase, and this is consistent with observations elsewhere when a MgO powder of similar reactivity is exposed to water [14]. After 28 days, brucite is present in samples with 50 wt.% MgO, but is not present in samples with 20 wt.% MgO in which only poorly crystalline phases remain. The amorphous phases give broad peaks at 18–25° 2θ, 32–37° 2θ and 58–62° 2θ. Comparison with the XRD data of fused silica and pure magnesium silicate hydrate gel (M-S-H), also shown in Fig. 3, shows that these broad peaks can only in part be explained by the presence of SF, and that the broad peaks in the 32–37° 2θ and the 58–62° 2θ regions are consistent with the characteristic XRD data of magnesium silicate hydrate (M-S-H) gel. Hence, brucite and SF have reacted to form M-S-H gel.

Table 2
Thermodynamic data used for pH predictions.

Species	Formation reaction	Log K	Ref.
Quartz	$H_4SiO_4 \rightarrow SiO_2 + 2H_2O$	4	[12]
Brucite	$Mg^{2+} + 2H_2O \rightarrow Mg(OH)_2 + 2H^+$	-17.1	[23]
Periclase	$Mg^{2+} + H_2O \rightarrow MgO + 2H^+$	-21.584	[12]
Chrysotile	$3Mg^{2+} + 2H_4SiO_4 + H_2O \rightarrow Mg_3(Si_2O_5)(OH)_4 + 6H^+$	-32.2	[12]
Sepiolite	$2Mg^{2+} + 3H_4SiO_4 \rightarrow \frac{1}{2}(Mg_4(Si_2O_5)_3(OH)_2 \cdot 6H_2O) + 4H^+ + \frac{1}{2}H_2O$	-15.76	[12]

Download English Version:

<https://daneshyari.com/en/article/1456924>

Download Persian Version:

<https://daneshyari.com/article/1456924>

[Daneshyari.com](https://daneshyari.com)