This is a repository copy of Phase Formation and Evolution in Mg(OH)(2)-Zeolite Cements.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/128663/

Version: Accepted Version

Article:
Walling, S.A., Bernal, S.A. orcid.org/0000-0002-9647-3106, Gardner, L.J. orcid.org/0000-0003-3126-2583 et al. (2 more authors) (2018) Phase Formation and Evolution in Mg(OH)(2)-Zeolite Cements. Industrial and Engineering Chemistry Research, 57 (6). pp. 2105-2113. ISSN 0888-5885

https://doi.org/10.1021/acs.iecr.7b04201

Reuse
Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.
Phase formation and evolution in Mg(OH)2 - zeolite cements

Sam A. Walling, Susan A. Bernal, Laura J. Gardner, Hajime Kinoshita, and John L. Provis

Ind. Eng. Chem. Res., Just Accepted Manuscript • DOI: 10.1021/acs.iecr.7b04201 • Publication Date (Web): 24 Jan 2018

Downloaded from http://pubs.acs.org on January 28, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Phase formation and evolution in Mg(OH)$_2$-

zeolite cements

Sam A. Walling, Susan A. Bernal, Laura J. Gardner, Hajime Kinoshita, John L. Provis*

Immobilisation Science Laboratory, Department of Materials Science & Engineering, The
University of Sheffield, S1 3JD, UK

* Corresponding author. Tel: +44 (0) 114 222 5490, email: j.provis@sheffield.ac.uk

Abstract

The mineralogy and structure of cements in the system Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O are investigated, with a view toward potential application in the immobilisation of Mg(OH)$_2$-rich Magnox sludges resulting from historic UK nuclear operations. The reaction process leading to the formation of these aluminosilicate binders is strongly exothermic, initially forming zeolite NaA (LTA structure), which is metastable in low SiO$_2$/Al$_2$O$_3$ binders, slowly evolving into the more stable sodalite and faujasite framework types. Notable chemical reaction of Mg(OH)$_2$ was only identified in the formulation with SiO$_2$/Al$_2$O$_3$ =1.3 (the lowest molar ratio among those tested), after extended curing times. In this case, some of the Mg(OH)$_2$ reacted to form an Mg-Al-OH layered double hydroxide. These results demonstrate that encapsulation of Magnox sludge waste streams could be carried out in these alternative binders, but that the binders would
encapsulate rather than chemically incorporate the Mg(OH)$_2$ into the wasteform unless low
SiO$_2$/Al$_2$O$_3$ ratios are used.

**Keywords:** Magnox sludge, cementation, brucite, zeolite

### 1. Introduction

During the past 60 years, the UK has relied on Magnox nuclear power plants for a significant
portion of its electricity supply. These are CO$_2$ cooled, graphite moderated reactors using natural
uranium fuel clad in a magnesium alloy (Magnox), of which 26 reactor units were constructed
and operated in the UK. Cooling and reprocessing of spent fuel from these reactors has, over half
a century, resulted in the accumulation of significant quantities of corrosion products and sludge
due to degradation of the magnesium alloy fuel cladding during storage in cooling ponds and
silos. This sludge consists primarily of Mg(OH)$_2$ with small quantities of hydrotalcite and artinite
$^1$-$^2$, along with an assortment of radioactive fission products and metallic residues. The
radioactivity of this sludge is such that it is classified as Intermediate Level Waste (ILW),
requiring conditioning by solidification in an appropriate matrix prior to disposal. Ongoing
decommissioning of legacy facilities containing this type of sludge has reinforced the need for
research into suitable encapsulation methods, to ensure that suitable potential immobilisation or
encapsulation matrices are available for deployment in the safe and cost-effective disposal of
these wastes.
Typically in the UK, ILW waste streams are conditioned within composite cements consisting of a blend of either blast furnace slag (BFS) or fly ash (FA), with Portland cement (PC). The chemistry of these blended cements is well understood, with decades of operational usage in waste cementation. These grouts have been assessed for immobilisation of Magnox sludges, and give solid monoliths with little reaction between the cementitious components and the sludge at early ages. Within the principal strength-giving phase in Portland cements, a calcium silicate hydrate (C-S-H) type gel, there is little uptake of magnesium. Under specific conditions both C-S-H and magnesium silicate hydrate (M-S-H) type gels can form, though at the higher pH levels achieved within undamaged PC systems, magnesium is likely to remain as Mg(OH)$_2$. This is in line with the known limited solubility of Mg(OH)$_2$ in alkaline media, although the longer term reactivity of Mg(OH)$_2$ within these systems has not yet been quantified. Although such grouts can safely encapsulate the wastes, this method is not optimal in reducing the overall volume of waste packages, as only moderate quantities of the sludges can be encapsulated without hindering the hardening of the wasteform.

In an earlier study by the authors, cementitious binders within the Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O system were studied up to 90 days of age, and the formation of a range of zeolites was identified, depending on the Si/Al ratio. Although the inclusion of NaAlO$_2$ significantly reduced the setting time of these binders, there was no evidence for M-S-H gel formation, with or without Al substitution. Instead, a layered double hydroxide with a hydrotalcite-like structure was observed in one of the formulations assessed, and it was noted that this may be potentially valuable in binding radionuclides, in particular $\Gamma$ and TcO$_4^-$ along with Cs$^+$ and Sr$^{2+}$, of which significant quantities exist within Magnox sludge.
The utilisation of Mg(OH)$_2$ as a raw material reacting to form a binding phase could potentially enable a reduction in wasteform volume compared to the current baseline grout formulations. Other alternative cements are able to perform in this way, however they also have certain disadvantages. Magnesium-oxysalt cements such as oxychloride or oxysulfate cements are deleteriously affected by water $^{13-14}$, severely reducing their scope for use as wasteforms. Magnesium phosphate cements (i.e. those based on struvite / struvite-K) typically require low-reactivity MgO as a raw material, suffering from flash setting when produced from Mg(OH)$_2$ $^{15}$. Recently, magnesium silicate based cements have been produced by blending Mg(OH)$_2$ with reactive silica (in contrast to more common synthesis routes based on MgO); with extended curing at 40 °C, these blends form a M-S-H type gel as the sole binding phase, totally consuming the Mg(OH)$_2$, although with significantly slower setting times than are observed for Portland based grouts $^{16}$.

This study further evaluates phase evolution in Mg(OH)$_2$-SiO$_2$-NaAlO$_2$-H$_2$O samples cured for up to 2 years, to identify whether this combination of mix components may be tailored to achieve desirable long-term characteristics. Fresh pastes were assessed through isothermal calorimetry, while fresh (up to 120 h cured) and aged (up to 2 years cured) hardened specimens were characterised via X-ray diffraction, thermogravimetry coupled with mass spectrometry, and solid state $^{27}$Al, $^{29}$Si and $^{25}$Mg magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy.
2. Experimental methodology

2.1. Materials and sample preparation

As the principal raw materials, silica fume (Microsilica 940-U, Elkem, >90% SiO$_2$), sodium aluminate (NaAlO$_2$, technical grade, Fisher Scientific), Mg(OH)$_2$ (>95% purity, Alfa Aesar) and distilled water were used. Surface area and particle size distribution were determined by laser diffraction: Mg(OH)$_2$ surface area 3565 m$^2$/kg ($D_{10} 0.7\mu$m, $D_{50} 4.2\mu$m, $D_{90} 29.0\mu$m), silica fume 718 m$^2$/kg ($D_{10} 4.4\mu$m, $D_{50} 20.0\mu$m, $D_{90} 118\mu$m), indicating some degree of agglomeration between the particles.

Samples were formulated with a fixed quantity of Mg(OH)$_2$, but varying quantities of SiO$_2$ and NaAlO$_2$ to progressively increase the SiO$_2$/Al$_2$O$_3$ molar ratio. Samples are labelled by their SiO$_2$/Al$_2$O$_3$ molar ratios ($R_x$, where $x$ is between 1.3 and 3.3). The water / solids mass ratio (w/s) was kept constant at 0.6. The binder compositions are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mg(OH)$_2$</th>
<th>SiO$_2$</th>
<th>NaAlO$_2$</th>
<th>SiO$_2$/Al$_2$O$_3$ molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1.3</td>
<td>3.0</td>
<td>1.0</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>R2.0</td>
<td>3.0</td>
<td>1.5</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>R3.0</td>
<td>3.0</td>
<td>1.5</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>R3.3</td>
<td>3.0</td>
<td>2.5</td>
<td>1.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>
To produce each cement sample, dry powders were mixed together by hand to produce a homogeneous blend, to which the required quantity of distilled water was added to achieve w/s = 0.6, and further mixed for 5 minutes to produce a workable paste. Samples were cast into 15 mL centrifuge tubes and cured at 40 °C and 95% relative humidity in a Sanyo Atmos Chamber MTH-2400, until analysis.

2.2. Tests conducted

Isothermal calorimetry was undertaken for fresh pastes using a TAM Air calorimeter (TA Instruments) at 40 °C. Raw materials and water were preheated to 40 °C using an oven, then mixed externally and weighed into a polymeric (HDPE) ampoule. This was placed into the calorimeter, and the heat output measured for 30 days (720 hours), with heat flow normalized to the total sample mass (unless otherwise noted) in each sample.

Hardened paste samples were removed from the curing chamber at specified ages, and dried in a vacuum desiccator (13.3 kPa) over silica gel and solid NaOH for 6 hours to ensure the cessation of reaction and the removal of adsorbed water. Samples were then ground in an agate mortar and sieved to -63 µm for analysis.

X-ray diffraction analysis of young (24, 65 and 120 h cured) and aged (2 years cured) specimens was undertaken using a STOE STADI P diffractometer (Cu Kα radiation, 1.5418Å) with an image plate detector (IP-PSD), collecting data between 3.5-60° 2θ. Data were angle corrected using an external silicon standard (NIST 640d).
Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA 4000 coupled with a Hiden Analytical mass spectrometer. The mass spectrometer signals for H$_2$O and CO$_2$ were continuously recorded. The samples were assessed at a heating rate of 5ºC/min up to 900 ºC, using alumina crucibles and nitrogen as a purge gas (20 mL/min).

$^{27}$Al and $^{29}$Si MAS NMR spectroscopy was performed on a Varian VNMRS 400 (9.4 T) spectrometer. $^{27}$Al MAS NMR spectra were collected at 104.198 MHz, spinning at 14 kHz (12 kHz for 720 day samples) using a 4 mm o.d. zirconia rotor with a pulse duration of 1.0 µs, acquisition time of 10 ms and a recycle delay of 0.2 s, for a minimum of 1900 scans. Chemical shifts were referenced to 1.0 M aqueous Al(NO$_3$)$_3$. $^{29}$Si MAS NMR spectra were collected at 79.435 MHz at a spinning speed of 6.8 kHz (6 kHz for 720 day samples) with a pulse duration of 6.2 µs (4.5 µs for 720 day samples), acquisition time of 20 ms (30 ms for 720 day samples) and a recycle delay of 60 s, for a minimum of 47 scans (912 for 720 day samples). Chemical shifts were externally referenced to tetramethylsilane (TMS) at 0 ppm. $^{25}$Mg MAS NMR spectra were collected on a Bruker Avance III 850 (19.96 T) spectrometer using 4 mm o.d zirconia rotors, collected at 52.042 MHz at a spinning speed of 10.0 kHz, pulse duration of 5.0 µs and recycle delay of 2.0 s, for 5800 scans. Simulations were performed using Bruker Topspin 3.2 software. Chemical shifts were externally referenced to MgO.

3. Results and discussion

3.1 Early-age reaction processes
Calorimetric measurements were undertaken for samples R1.3, 2.0, 3.0 and 3.3 to determine the kinetics of reaction of binders within the Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O system, and the processes which lead to solidification. All samples reacted in a strongly exothermic manner upon initial mixing, and formed viscous pastes. In the heat release curves (Figure 1) it is identified that each sample exhibits four distinct regions of interest, <1 h, 1-20 h, 20-70 h and 70-140 h. The region <1 h, corresponding to the induction period, shows the heat release associated with a combination of instrumentation effects due to emplacement of samples, and the initial dissolution of NaAlO$_2$ (followed by the heat of solution for NaOH formed$^{17-18}$) which produced pastes that were notably hot to touch within minutes of mixing.

![Figure 1. Normalised heat flow of fresh pastes within the systems Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O (peak heat flow marked in parentheses)](image-url)
Each of the samples exhibited an exothermic peak in the region 1-20 hours (with R3.0 and R3.3 exhibiting earlier, sharper heat output peaks than R2.0 and R1.3), which is assigned to dissolution of NaAlO$_2$, alkaline dissolution of SiO$_2$ and initial precipitation of Al(OH)$_3$, discussed in more detail below. This is followed by a dormant or induction period of low heat output, lasting 20-60 hours. After the dormant period, a high intensity peak corresponding to the acceleration-deceleration stage of the reaction was observed. During this stage a significant nucleation and growth of reaction products must be occurring in the samples assessed.

The time of onset of the acceleration period changes significantly upon lowering the SiO$_2$/Al$_2$O$_3$ ratio of these binders. The acceleration-deceleration period for samples with a higher silica content (R3.3 and R3.0) is observed between 30-60 hours. The formation of two overlapping but distinct heat release peaks indicates that different types of reaction products are precipitating at different times during the reaction process. Conversely, in samples containing less silica (R2.0 and R1.3), the second peak is less distinct, resulting in a single asymmetric peak observed after 75 to 150 hours of reaction, which appears latest in R1.3, the sample with the lowest silica content among the samples tested.

To identify the phases forming at the early stages of the reaction of these binders, X-ray diffraction (XRD) analysis was carried out on pastes cured under identical conditions to those used during the calorimetry test, at times where the higher rates of heat release were identified (24, 65 and 120 hours). After 24 h of reaction (Figure 2A), the only crystalline phases identified in these binders were unreacted brucite (Mg(OH)$_2$, powder diffraction file (PDF) # 01-074-2220) and traces of poorly crystalline bayerite (α-Al(OH)$_3$, PDF # 00-020-0011). No crystalline
NaAlO$_2$ is observed, indicating that this compound has fully dissolved, resulting in Al(OH)$_3$ precipitation, nor is any remnant SiO$_2$ observed (although as it is non-crystalline, identification of this phase amongst crystalline peaks is more challenging). This indicates that the first calorimetric peak at very early age is related, at least in part, to NaAlO$_2$ dissolution and the precipitation of this phase.

No differences in the diffraction patterns of R1.3 and R2.0 are identified (Figure 2B) after 65 hours compared to 24 hours, consistent with the identification of a dormant period in these pastes, spanning this period of time. Conversely, in samples R3.0 and R3.3 with higher silica content, the precipitation of zeolites of the structure type LTA (zeolite NaA: Na$_{12}$Si$_{12}$Al$_{12}$O$_{48}$·27H$_2$O, PDF# 00-039-0219) is observed, which can explain the exothermic event identified via isothermal calorimetry. XRD analysis after 120 hours of reaction (Figure 2C) shows the formation of the LTA zeolite in all of the samples assessed. Regardless of chemical composition, after the initial reaction takes place in these binders, the main crystalline reaction products identified are Al(OH)$_3$ and LTA.
Figure 2. X-ray diffraction patterns of samples R1.3, 2.0, 3.0 and 3.3 after (A) 24, (B) 65 and (C) 120 hours of curing.

Cumulative heat release curves normalised to the total mass of paste (Figure 3) show that the heat released is dominated by the reaction between SiO$_2$ and NaAlO$_2$ to form LTA, with some contribution from excess NaAlO$_2$. Given the composition of LTA (Na$_{12}$Si$_{12}$Al$_{12}$O$_{48}$·27H$_2$O), sample R2.0 results in the highest heat generation as this can produce the most LTA per gram: 15 mol SiO$_2$ + 15 mol NaAlO$_2$ yields 1.25 mol LTA. In both R1.3 and R3.0 less LTA is produced, as the reacting mix is off-stoichiometric (e.g. R1.3 has 10 mol SiO$_2$ to 15 mol NaAlO$_2$, yielding 0.83 mol LTA). The difference in heat output between R1.3 and R3.0 must be due to heat from processes involving excess reactants, suggesting that the dissolution and then reprecipitation (as Al(OH)$_3$) of excess NaAlO$_2$ produces additional heat. R3.3 can produce as much LTA as R2.0, but has an excess of SiO$_2$, reducing overall heat output per gram as this does not undergo a reaction process.
Figure 3. Cumulative heat of reaction of pastes within the system Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O, normalized to the total mass of paste in each case. Total heat of reaction (J/g) in parentheses.

3.2 X-ray diffractometry of aged samples

The diffractograms of samples R1.3-R3.3 after 28, 360 and 720 days of curing are shown in Figure 4. Each of the samples displays an array of crystalline zeolites that varies depending on the formulation. After 28 days of curing, the higher SiO$_2$/Al$_2$O$_3$ samples R3.0 and R3.3 exhibit only LTA and Mg(OH)$_2$ as crystalline features, along with an amorphous component presenting a broad feature around 20° 2θ. The samples, R1.3 and R2.0 also contain additional Na-X (low silica faujasite: Na$_{86}$Si$_{106}$Al$_{86}$O$_{384}$·175H$_2$O, PDF# 00-012-0246, IZA zeolite framework type FAU). In sample R1.3, the LTA observed after 120 h (Figure 2C) was not longer observed at 28 days, with only Na-X, Mg(OH)$_2$ and traces of a sodalite-type structure. This corresponds to basic
hydrosodalite according to the nomenclature of Engelhardt et al.\textsuperscript{19} (\(\text{Na}_8\text{Al}_6\text{Si}_{10}\text{O}_{24}(\text{OH})_2\cdot2\text{H}_2\text{O}\), PDF\# 04-009-2429, IZA zeolite framework type SOD).

After longer curing times, the trends in the zeolite assemblages within these samples diverge. Samples R3.0 and R3.3 (Figure 4) do not show any changes in crystalline composition up to 720 days of curing, displaying considerable stability. However, samples R1.3 and R2.0, with lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios, do show significant changes. Sample R2.0 shows a change in zeolite mineralogy, with basic hydrosodalite and Na-P1 appearing after 360 days of curing, coinciding with a decrease in the intensity of LTA peaks. After 720 days no LTA remained, and the system is dominated by basic hydrosodalite along with some Na-P1 (\(\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot12\text{H}_2\text{O}\), PDF\# 04-009-5257, IZA framework type GIS) and Na-X.

The transient nature of LTA in samples R1.3 and R2.0 can be explained by the fact that their lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios are achieved through a high NaAlO\textsubscript{2} content, which also results in more alkaline conditions within the pore fluid of these binders compared to the higher-silica R3.0 and R3.3. The LTA framework is also known to transform into sodalite type phases\textsuperscript{20-22} and/or Na-P1\textsuperscript{23-25} in caustic media, although the process is slower in these cements, possibly due to the limited ionic mobility under the relatively low water/solids ratios used here compared to a regular hydrothermal synthesis process.

Sample R1.3, with the lowest SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, undergoes a transformation whereby Na-X decreases in intensity, and basic hydrosodalite emerges as the dominant aluminosilicate phase. In addition to this, a hydrotalcite-like Mg-Al layered double hydroxide (LDH), potentially true
hydrotalcite (\(\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})\cdot4\text{H}_2\text{O}\), PDF# 00-054-1029) or a related structure differing in Mg/Al ratio or interlayer anions, forms by 360 days, increasing in intensity slightly at 720 days of curing. The identity of this phase will be further examined in Section 3.3, as hydrotalcite-group phases are challenging to distinguish from XRD data of moderate resolution as is the case here.
Figure 4. X-ray diffractograms of samples (A) R1.3, (B) R2.0, (C) R3.0 and (D) R3.3 as a function of the curing time in days (as marked). Some of the 28 day data are from 9.

Although sample R1.3 forms this additional magnesium-containing phase, all of the samples display strong reflections for Mg(OH)$_2$, suggesting that little reaction between the aluminosilicate components and Mg(OH)$_2$ has occurred up to 720 days of curing, except in R1.3. No evidence for the presence of an M-S-H phase can be detected (this would typically be identified from broad features at 20, 35 and 60° 2θ 7,16), even in the mixture R3.3 which was formulated to provide a large quantity of SiO$_2$ available for reaction.

3.3 Layered double hydroxide identification by thermal analysis

Although a layered double hydroxide (LDH) phase was identified during XRD analysis, the LDH family can encompass a wide range of compositions defined by the formula $[M^{2+} \cdot \chi M^{3+}(OH)_{2}]t^[A^{n-}n\alpha]-mH_2O$, in which $M^{2+}$ and $M^{3+}$ are di- and tri-valent metallic ions
respectively, and $A^{n-}$ can be one of many anions (e.g. $\text{CO}_3^{2-}$, $\text{OH}^-$, $\text{Cl}^-$) $^{26}$. For brevity this was labelled a ‘hydrotalcite-like’ phase in Figure 4, however as the samples were cured in a sealed container, this is likely to preclude much $\text{CO}_2$ ingress leading to formation of true (carbonate-containing) hydrotalcite. To determine the nature of this LDH, thermogravimetric analysis was undertaken with an attached mass spectrometer to distinguish between $\text{H}_2\text{O}$ and $\text{CO}_2$ evolution, as shown in Figure 5.

**Figure 5.** TG-MS data for sample R1.3 after 720 days curing, showing DTG (black), $\text{H}_2\text{O}$ signal (blue) and $\text{CO}_2$ signal (red)

The multiple phases observed by XRD analysis (Figure 5) within sample R1.3 result in a complex TG-MS response in Figure 5. The mass loss is dominated by the decomposition of $\text{Mg(OH)}_2$ at 383°C $^{27}$, and by an Mg-Al layered double hydroxide containing hydroxyl species in the interlayer (denoted OH-LDH) which accounts for much of the remaining mass change, with characteristic decomposition peaks at ~90 °C, ~200 °C, and as shoulders on the $\text{Mg(OH)}_2$
decomposition peak at ~300°C and 350°C, suggesting that this phase may have a composition similar to Mg₄Al₂(OH)₁₈·ₙH₂O, akin to a carbonate-free form of quintinite. It is likely that the Mg/Al ratio is at the lower end of the range associated with hydrotalcite-group phases (between 2 and 3) due to the limited reactivity of the Mg(OH)₂ and excess of Al(OH)₃ here. Some mass loss from bound water is also attributed to the release of zeolitic water from Na-X (~167°C) as well as dehydration of hydrosodalite, which decomposes slowly over a wide range, from ~80-750 °C. A small signal for CO₂ is, however, observed at ~400°C, pointing to some formation of CO₂-containing LDH as a minor constituent.

3.4 Solid-state NMR spectroscopy

Although various crystalline phases have formed within these cements, the presence of diffuse scattering in many of the XRD patterns (e.g. at ~20° in Figure 4C and D) suggests either that unreacted silica fume remains, or that non-crystalline reaction products are forming. To further elucidate this, ²⁷Al and ²⁹Si MAS NMR spectra were measured for all of the samples after 360 and 720 days of curing. The 360-day data are shown in Figure 6.
Figure 6. (A) $^{27}$Al and (B) $^{29}$Si MAS NMR spectra of pastes within the system Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O, after 360 days of curing

The $^{27}$Al MAS NMR spectra of the samples, Figure 6A, reveal the presence of two Al environments, identified as Al(IV) and Al(VI), at 58-61 and ~9 ppm respectively. The peaks close to 60 ppm are characteristic of tetrahedrally coordinated Al in zeolites, consistent with the
formation of aluminosilicate zeolites in these samples. The peaks at ~9 ppm correspond to octahedrally coordinated Al, typical of non-framework Al species. Sample R1.3 exhibits a stronger signal here, consistent with the identification of a hydrotalcite-like LDH as discussed above. In the remaining samples, although LDH phases have not been observed through XRD analysis, the presence of this octahedral Al might be evidence of some small, poorly crystalline LDH phase, or perhaps the presence of Al(VI) might be evidence of residual α-Al(OH)₃ as postulated through XRD analysis earlier.

The $^{29}$Si MAS NMR data in Figure 6B further support the identification of zeolites. The single peak at -89.1 ppm in samples R2.0-R3.3 is assigned to Q⁴(4Al) units in the LTA framework. Sample R2.0 exhibits a more complicated spectrum, with an additional signal at -86.6 ppm from Q⁴(4Al) units in the sodalite framework structure, and a small signal at -84.3 ppm associated with Q⁴(4Al) units in low silica Na-X. R1.3 exhibits a single peak at -86.5 ppm, consistent with the identification of the sodalite framework type as the primary zeolite at this age by XRD, Figure 4.

High field $^{25}$Mg MAS NMR spectra were also collected to clarify the role of Mg within this binding system. These data are shown in Figure 7 for sample R3.3 at 360 days of curing. The experimental data were fitted with simulations based on established literature values for magnesium minerals (Table 2), and found to represent predominantly Mg(OH)₂, with some MgO present as an impurity. M-S-H would present a diffuse resonance centred at ~0 ppm at this field strength. As the experimental data can be fitted well using a simulation describing Mg(OH)₂ and MgO alone, no M-S-H can be said to exist within this sample. Equally, as no other...
Mg sites are observable, the formation of an Al-bearing M-A-S-H phase can also be excluded. Unfortunately, restricted access to in-demand equipment precluded the collection of data for sample R1.3 which contains hydrotalcite-group phases.

![Figure 7. $^{25}$Mg MAS NMR spectra of sample R3.3 at 360 days of curing, with experimental data, simulation, and component peaks.](image)

**Table 2.** $^{25}$Mg MAS NMR simulation parameters for R3.3 at 360 days of curing

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>26.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>11.7</td>
<td>3.1</td>
<td>0</td>
</tr>
</tbody>
</table>

All of the samples were analysed again after curing for 720 days, to determine whether there were any further changes over time. The NMR spectra remained similar for samples R3.0 and
R3.3, with only minor shifts in peak positions in both $^{27}$Al and $^{29}$Si MAS NMR (Figure 8). These samples all exhibit broad signals in their $^{29}$Si spectra, and are deconvoluted in Figure 9. Samples R1.3 and R2.0, however, do show changes from 360 to 720 days, consistent with their changing zeolite assemblages identified by XRD (Figure 5). In sample R1.3, a second peak appeared at -84 ppm, consistent with an increase in the observed Na-X content, while in sample R2.0 the peak at -86.5 ppm (identified as sodalite) increased in intensity, while that assigned to LTA (-89.1 ppm) disappeared entirely; both of these trends are in full agreement with the XRD assignments.
Figure 8. (A) $^{27}$Al and (B) $^{29}$Si MAS NMR spectra of pastes within the system Mg(OH)$_2$-NaAlO$_2$-SiO$_2$-H$_2$O, after 720 days of curing.

Deconvolution was undertaken on the $^{29}$Si MAS NMR spectra for samples R3.0 and R3.3, which both display broad features. Alongside the prominent peak at -89.1 ppm, assigned to LTA (Q$^4$(4Al)), are four additional broad peaks centred -85.8, -92.7, -99.6 and -109.3 ppm. The peak at -109.3 ppm can be assigned to fully polymerised Q$^4$ species in unreacted silica fume. The next peak downfield, at -99.6 ppm, is assigned to Q$^3$ species formed through surface hydroxylation of the silica fume due to partial dissolution, forming Q$^3$ (>Si-OH single silanol) sites surrounding an unreacted Q$^4$ silica fume core.$^{38}$ The two remaining peaks at -92.7 and -85.8 ppm are assigned to Q$^3$(1Al) and Q$^2$(1Al) sites respectively. Both of these sites occur as the Al(OH)$_4^-$ released by sodium aluminate dissociation form either surface Q$^3$(1Al), or further depolymerised Q$^2$(1Al) units.
In general, there appears to be a larger contribution from the disordered phases within R3.3 than R3.0 (assuming no substantive change in the $^{29}$Si T$_1$ relaxation time between samples), suggesting that a higher SiO$_2$/Al$_2$O$_3$ ratio in the formulation favours an increased fraction of the Q$^4$, Q$^3$ and Q$^3$(1Al) sites, while a lower SiO$_2$/Al$_2$O$_3$ content results in a larger contribution from the Q$^4$(4Al) site of LTA. With a higher silica content, more unreacted silica is contributing to the spectrum, along with hydroxylated and aluminated silica surface sites. Overall there is no evidence of a M-S-H or M-A-S-H type phase forming, despite the presence of unreacted and partially aluminated silica. As this has not occurred within 2 years of curing, it is concluded that Mg incorporation into silicate phases is unlikely to occur in these samples within a meaningful engineering timeframe, and if this does eventually happen, the kinetics of the process are very slow compared to the zeolite formation.
4. Conclusions

The results of this study demonstrate the feasibility of producing an alternative cementitious system which can encapsulate and utilise very high mass fractions of Mg(OH)$_2$ as a constituent material. The addition of reactive NaAlO$_2$ into the Mg(OH)$_2$-SiO$_2$-H$_2$O system promotes the formation of mixed zeolites, the composition of which varies depending on the SiO$_2$/Al$_2$O$_3$ content of the samples.

Initially all samples precipitated Al(OH)$_3$, followed by zeolites after 20-60 hours. Higher SiO$_2$/Al$_2$O$_3$ ratios resulted in faster zeolite formation, although all samples initially exhibited strong heat output during mixing. All samples first formed LTA zeolite, before slowly showing
alterations in the zeolite assemblage over time. High SiO$_2$/Al$_2$O$_3$ ratios stabilized LTA, while lower ratios resulted in formation of a low silica faujasite (Na-X) zeolite, Na-P1, hydroxysodalite, and a hydrotalcite-type phase in the lowest SiO$_2$/Al$_2$O$_3$ ratio sample. This was determined through TG-MS analysis to be a hydroxide-containing layered double hydroxide with very limited carbonate incorporation, formed from some reaction of Mg(OH)$_2$ with the added NaAlO$_2$.

$^{27}$Al and $^{29}$Si solid state MAS NMR spectroscopy confirmed the zeolite assignments from the XRD analysis, and also revealed unreacted silica fume, a hydroxylated Q$^3$ site and aluminated Q$^2$(1Al) and Q$^3$(1Al) sites, which were not detectable by XRD due to lack of long-range ordering. Further analysis using $^{25}$Mg NMR was not able to detect any M-S-H or M-A-S-H formation, despite the presence of large quantities of both Mg(OH)$_2$ and SiO$_2$.

Although no M-S-H or M-A-S-H phases have been identified here, the addition of high quantities of NaAlO$_2$ promoted the formation of a magnesium-aluminium layered double hydroxide. Aside from this sample, none of the other formulations resulted in reacted Mg(OH)$_2$, which was encapsulated within the matrix rather than chemically bound. The potential for ion-exchange between the zeolites, the LDH and any radionuclides may be of benefit for the immobilisation of radionuclide bearing wastes, specifically Magnox sludges. U and Pu typically have very low solubility in high pH environment, often forming hydroxides. Trivalent actinides (such as Am), though also exhibiting low solubility at high pH could incorporate into hydrotalcite minerals. More problematic species such as Cs can be irreversible incorporated into sodalite and Na-P1 structures, while anions such as Cl$^-$ and TeO$_4^-$ could potentially...
exchange with anionic species in hydrotalcite \(^{42-44}\). This would point towards the lowest SiO\(_2\)/Al\(_2\)O\(_3\) ratio formulation, R1.3, potentially being preferable due to formation of a hydrotalcite-type mineral. However, ionic binding in hydrotalcites is often reversible, and dependent on existing anions \(^{43,45}\), and therefore deserves further study.

**Acknowledgements**

This study was sponsored by the Engineering and Physical Sciences Research Council (EPSRC) through the University of Sheffield/ University of Manchester Doctoral Training Centre ‘Nuclear FiRST’ (EP/G037140/1) and through a Nuclear Decommissioning Authority CASE award, under supervision by the National Nuclear Laboratory. The donation of microsilica by Elkem Silicon Materials is greatly appreciated. Solid-state NMR spectra for \(^{27}\)Al and \(^{29}\)Si were obtained at the EPSRC UK National Solid-state NMR Service at Durham. The UK 850 MHz solid-state NMR Facility used in this research to collect \(^{25}\)Mg spectra was funded by EPSRC and BBSRC, as well as the University of Warwick including via part funding through Birmingham Science City Advanced Materials Projects 1 and 2 supported by Advantage West Midlands (AWM) and the European Regional Development Fund (ERDF). The assistance of Dr. David Apperley and Dr Dinu Iuga in NMR data collection is greatly appreciated. This research was performed in part at the MIDAS Facility, at the University of Sheffield, which was established with support from the Department of Energy and Climate Change.

**References**


45. Miyata, S., The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties - I: The systems Mg$^{2+}$-Al$^{3+}$-NO$_3^-$, Mg$^{2+}$-Al$^{3+}$-Cl$, Mg^{2+}$-Al$^{3+}$-ClO$_4^-$, Ni$^{2+}$-Al$^{3+}$-Cl$^-$. *Clays Clay Miner.* 1975, 23 (5), 369-375.
For Table of Contents Only