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Phase formation and evolution in $\text{Mg}(\text{OH})_2$ - zeolite cements

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Abstract

The mineralogy and structure of cements in the system $\text{Mg}(\text{OH})_2$ - NaAlO_2 - SiO_2 - H_2O are investigated, with a view toward potential application in the immobilisation of $\text{Mg}(\text{OH})_2$ -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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ binders, slowly evolving into the more stable sodalite and faujasite framework types. Notable chemical reaction of $\text{Mg}(\text{OH})_2$ was only identified in the formulation with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.3$ (the lowest molar ratio among those tested), after extended curing times. In this case, some of the $\text{Mg}(\text{OH})_2$ 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

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3 encapsulate rather than chemically incorporate the $\text{Mg}(\text{OH})_2$ into the wasteform unless low
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5 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are used.
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10 **Keywords:** Magnox sludge, cementation, brucite, zeolite
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14 **1. Introduction**

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19 During the past 60 years, the UK has relied on Magnox nuclear power plants for a significant
20 portion of its electricity supply. These are CO_2 cooled, graphite moderated reactors using natural
21 uranium fuel clad in a magnesium alloy (Magnox), of which 26 reactor units were constructed
22 and operated in the UK. Cooling and reprocessing of spent fuel from these reactors has, over half
23 a century, resulted in the accumulation of significant quantities of corrosion products and sludge
24 due to degradation of the magnesium alloy fuel cladding during storage in cooling ponds and
25 silos. This sludge consists primarily of $\text{Mg}(\text{OH})_2$ with small quantities of hydrotalcite and artinite
26 ¹⁻², along with an assortment of radioactive fission products and metallic residues. The
27 radioactivity of this sludge is such that it is classified as Intermediate Level Waste (ILW),
28 requiring conditioning by solidification in an appropriate matrix prior to disposal. Ongoing
29 decommissioning of legacy facilities containing this type of sludge has reinforced the need for
30 research into suitable encapsulation methods, to ensure that suitable potential immobilisation or
31 encapsulation matrices are available for deployment in the safe and cost-effective disposal of
32 these wastes.
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3 Typically in the UK, ILW waste streams are conditioned within composite cements consisting of
4 a blend of either blast furnace slag (BFS) or fly ash (FA), with Portland cement (PC) ³⁻⁴. The
5 chemistry of these blended cements is well understood, with decades of operational usage in
6 waste cementation. These grouts have been assessed for immobilisation of Magnox sludges, and
7 give solid monoliths with little reaction between the cementitious components and the sludge at
8 early ages ⁵⁻⁶. Within the principal strength-giving phase in Portland cements, a calcium silicate
9 hydrate (C-S-H) type gel, there is little uptake of magnesium. Under specific conditions both C-
10 -S-H and magnesium silicate hydrate (M-S-H) type gels can form, though at the higher pH levels
11 achieved within undamaged PC systems, magnesium is likely to remain as Mg(OH)₂ ⁷⁻⁸. This is
12 in line with the known limited solubility of Mg(OH)₂ in alkaline media, although the longer term
13 reactivity of Mg(OH)₂ within these systems has not yet been quantified. Although such grouts
14 can safely encapsulate the wastes, this method is not optimal in reducing the overall volume of
15 waste packages, as only moderate quantities of the sludges can be encapsulated without
16 hindering the hardening of the wasteform ⁶.

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19 In an earlier study by the authors ⁹, cementitious binders within the Mg(OH)₂-NaAlO₂-SiO₂-H₂O
20 system were studied up to 90 days of age, and the formation of a range of zeolites was identified,
21 depending on the Si/Al ratio. Although the inclusion of NaAlO₂ significantly reduced the setting
22 time of these binders, there was no evidence for M-S-H gel formation, with or without Al
23 substitution. Instead, a layered double hydroxide with a hydrotalcite-like structure was observed
24 in one of the formulations assessed, and it was noted that this may be potentially valuable in
25 binding radionuclides, in particular I⁻ and TcO₄⁻ along with Cs⁺ and Sr²⁺ ¹⁰⁻¹¹, of which
26 significant quantities exist within Magnox sludge ¹².

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5 The utilisation of $\text{Mg}(\text{OH})_2$ as a raw material reacting to form a binding phase could potentially
6 enable a reduction in wasteform volume compared to the current baseline grout formulations.
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8 Other alternative cements are able to perform in this way, however they also have certain
9
10 disadvantages. Magnesium-oxysalt cements such as oxychloride or oxysulfate cements are
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12 deleteriously affected by water¹³⁻¹⁴, severely reducing their scope for use as wasteforms.
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14 Magnesium phosphate cements (i.e. those based on struvite / struvite-K) typically require low-
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16 reactivity MgO as a raw material, suffering from flash setting when produced from $\text{Mg}(\text{OH})_2$ ¹⁵.
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18 Recently, magnesium silicate based cements have been produced by blending $\text{Mg}(\text{OH})_2$ with
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20 reactive silica (in contrast to more common synthesis routes based on MgO); with extended
21
22 curing at 40 °C, these blends form a M-S-H type gel as the sole binding phase, totally consuming
23
24 the $\text{Mg}(\text{OH})_2$, although with significantly slower setting times than are observed for Portland
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26 based grouts¹⁶.
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35 This study further evaluates phase evolution in $\text{Mg}(\text{OH})_2\text{-SiO}_2\text{-NaAlO}_2\text{-H}_2\text{O}$ samples cured for
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37 up to 2 years, to identify whether this combination of mix components may be tailored to achieve
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39 desirable long-term characteristics. Fresh pastes were assessed through isothermal calorimetry,
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41 while fresh (up to 120 h cured) and aged (up to 2 years cured) hardened specimens were
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43 characterised via X-ray diffraction, thermogravimetry coupled with mass spectrometry, and solid
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45 state ²⁷Al, ²⁹Si and ²⁵Mg magic angle spinning nuclear magnetic resonance (MAS NMR)
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47 spectroscopy.
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2. Experimental methodology

2.1. Materials and sample preparation

As the principal raw materials, silica fume (Microsilica 940-U, Elkem, >90% SiO₂), sodium aluminate (NaAlO₂, 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 m²/kg (D₁₀ 0.7μm, D₅₀ 4.2μm, D₉₀ 29.0μm), silica fume 718 m²/kg (D₁₀ 4.4μm, D₅₀ 20.0μm, D₉₀ 118μm), indicating some degree of agglomeration between the particles.

Samples were formulated with a fixed quantity of Mg(OH)₂, but varying quantities of SiO₂ and NaAlO₂ to progressively increase the SiO₂/Al₂O₃ molar ratio. Samples are labelled by their SiO₂/Al₂O₃ molar ratios (Rx, 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 1. Formulations of samples studied within the Mg(OH)₂-NaAlO₂-SiO₂-H₂O system. Values are reported on a molar basis.

Sample ID	Mg(OH) ₂	SiO ₂	NaAlO ₂	SiO ₂ /Al ₂ O ₃ molar ratio
R1.3	3.0	1.0	1.5	1.3
R2.0	3.0	1.5	1.5	2.0
R3.0	3.0	1.5	1.0	3.0
R3.3	3.0	2.5	1.5	3.3

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3 To produce each cement sample, dry powders were mixed together by hand to produce a
4 homogeneous blend, to which the required quantity of distilled water was added to achieve w/s =
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6 0.6, and further mixed for 5 minutes to produce a workable paste. Samples were cast into 15 mL
7
8 centrifuge tubes and cured at 40 °C and 95% relative humidity in a Sanyo Atmos Chamber
9
10 MTH-2400, until analysis.
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14 15 16 17 **2.2. Tests conducted** 18

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21 Isothermal calorimetry was undertaken for fresh pastes using a TAM Air calorimeter (TA
22 Instruments) at 40 °C. Raw materials and water were preheated to 40 °C using an oven, then
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24 mixed externally and weighed into a polymeric (HDPE) ampoule. This was placed into the
25
26 calorimeter, and the heat output measured for 30 days (720 hours), with heat flow normalized to
27
28 the total sample mass (unless otherwise noted) in each sample.
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35 Hardened paste samples were removed from the curing chamber at specified ages, and dried in a
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37 vacuum desiccator (13.3 kPa) over silica gel and solid NaOH for 6 hours to ensure the cessation
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39 of reaction and the removal of adsorbed water. Samples were then ground in an agate mortar and
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41 sieved to -63 µm for analysis.
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47 X-ray diffraction analysis of young (24, 65 and 120 h cured) and aged (2 years cured) specimens
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49 was undertaken using a STOE STADI P diffractometer (Cu K α radiation, 1.5418Å) with an
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51 image plate detector (IP-PSD), collecting data between 3.5-60° 2 θ . Data were angle corrected
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53 using an external silicon standard (NIST 640d).
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5 Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA 4000 coupled
6 with a Hiden Analytical mass spectrometer. The mass spectrometer signals for H₂O and CO₂
7 were continuously recorded. The samples were assessed at a heating rate of 5°C/min up to 900
8 °C, using alumina crucibles and nitrogen as a purge gas (20 mL/min).
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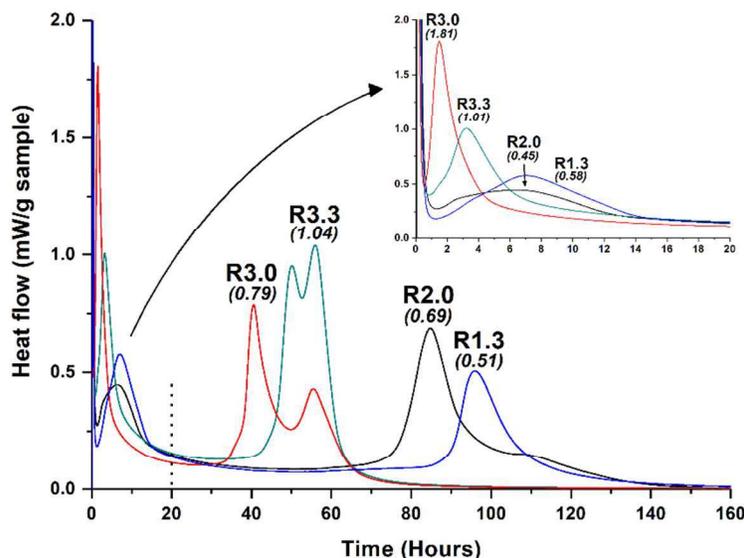
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17 ²⁷Al and ²⁹Si MAS NMR spectroscopy was performed on a Varian VNMRS 400 (9.4 T)
18 spectrometer. ²⁷Al MAS NMR spectra were collected at 104.198 MHz, spinning at 14 kHz (12
19 kHz for 720 day samples) using a 4 mm o.d. zirconia rotor with a pulse duration of 1.0 μs,
20 acquisition time of 10 ms and a recycle delay of 0.2 s, for a minimum of 1900 scans. Chemical
21 shifts were referenced to 1.0 M aqueous Al(NO₃)₃. ²⁹Si MAS NMR spectra were collected at
22 79.435 MHz at a spinning speed of 6.8 kHz (6 kHz for 720 day samples) with a pulse duration of
23 6.2 μs (4.5 μs for 720 day samples), acquisition time of 20 ms (30 ms for 720 day samples) and a
24 recycle delay of 60 s, for a minimum of 47 scans (912 for 720 day samples). Chemical shifts
25 were externally referenced to tetramethylsilane (TMS) at 0 ppm. ²⁵Mg MAS NMR spectra were
26 collected on a Bruker Avance III 850 (19.96 T) spectrometer using 4 mm o.d zirconia rotors,
27 collected at 52.042 MHz at a spinning speed of 10.0 kHz, pulse duration of 5.0 μs and recycle
28 delay of 2.0 s, for 5800 scans. Simulations were performed using Bruker Topspin 3.2 software.
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Chemical shifts were externally referenced to MgO.

3. Results and discussion

3.1 Early-age reaction processes

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3 Calorimetric measurements were undertaken for samples R1.3, 2.0, 3.0 and 3.3 to determine the
4 kinetics of reaction of binders within the $\text{Mg}(\text{OH})_2\text{-NaAlO}_2\text{-SiO}_2\text{-H}_2\text{O}$ system, and the processes
5 which lead to solidification. All samples reacted in a strongly exothermic manner upon initial
6 mixing, and formed viscous pastes. In the heat release curves (Figure 1) it is identified that each
7 sample exhibits four distinct regions of interest, <1 h, 1-20 h, 20-70 h and 70-140 h. The region
8 <1 h, corresponding to the induction period, shows the heat release associated with a
9 combination of instrumentation effects due to emplacement of samples, and the initial
10 dissolution of NaAlO_2 (followed by the heat of solution for NaOH formed¹⁷⁻¹⁸) which produced
11 pastes that were notably hot to touch within minutes of mixing.
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47 **Figure 1.** Normalised heat flow of fresh pastes within the systems $\text{Mg}(\text{OH})_2\text{-NaAlO}_2\text{-SiO}_2\text{-H}_2\text{O}$
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50 (peak heat flow marked in parentheses)
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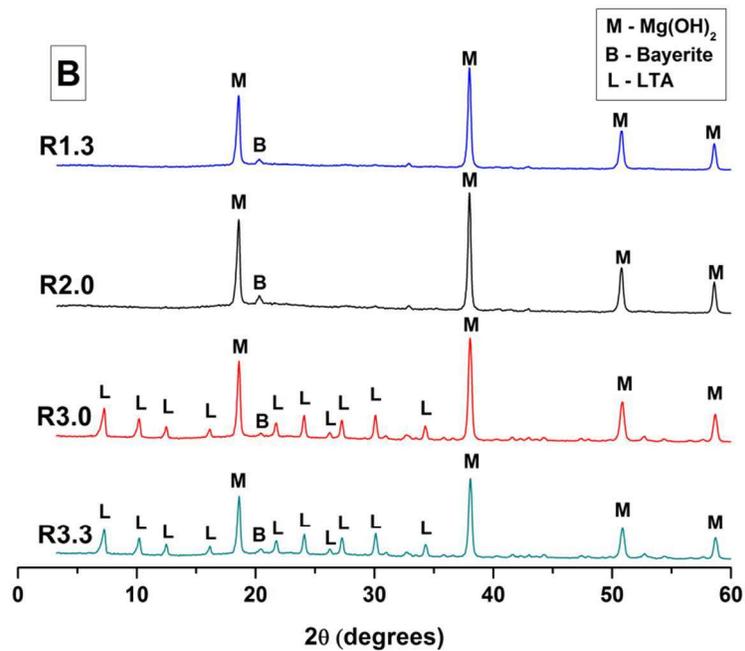
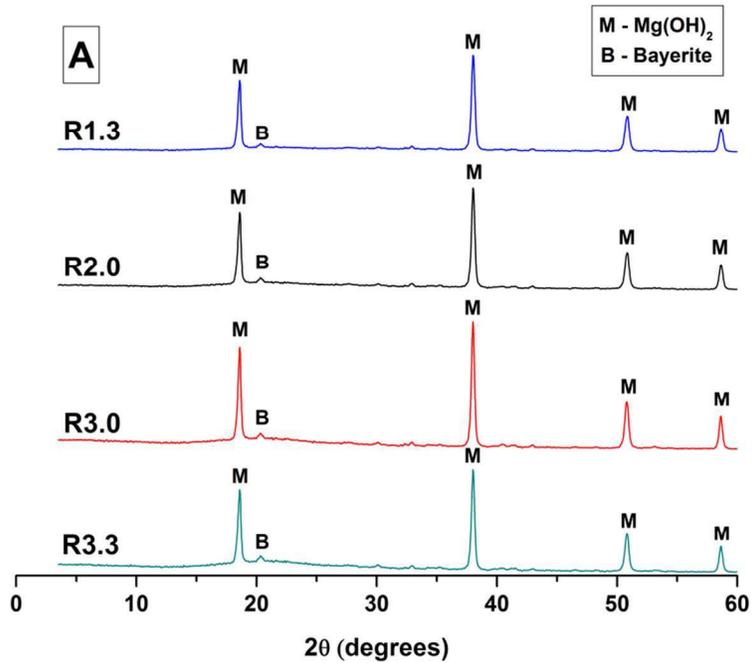
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3 Each of the samples exhibited an exothermic peak in the region 1-20 hours (with R3.0 and R3.3
4 exhibiting earlier, sharper heat output peaks than R2.0 and R1.3), which is assigned to
5 dissolution of NaAlO_2 , alkaline dissolution of SiO_2 and initial precipitation of $\text{Al}(\text{OH})_3$,
6 discussed in more detail below. This is followed by a dormant or induction period of low heat
7 output, lasting 20-60 hours. After the dormant period, a high intensity peak corresponding to the
8 acceleration-deceleration stage of the reaction was observed. During this stage a significant
9 nucleation and growth of reaction products must be occurring in the samples assessed.
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21 The time of onset of the acceleration period changes significantly upon lowering the $\text{SiO}_2/\text{Al}_2\text{O}_3$
22 ratio of these binders. The acceleration-deceleration period for samples with a higher silica
23 content (R3.3 and R3.0) is observed between 30-60 hours. The formation of two overlapping but
24 distinct heat release peaks indicates that different types of reaction products are precipitating at
25 different times during the reaction process. Conversely, in samples containing less silica (R2.0
26 and R1.3), the second peak is less distinct, resulting in a single asymmetric peak observed after
27 75 to 150 hours of reaction, which appears latest in R1.3, the sample with the lowest silica
28 content among the samples tested.
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42 To identify the phases forming at the early stages of the reaction of these binders, X-ray
43 diffraction (XRD) analysis was carried out on pastes cured under identical conditions to those
44 used during the calorimetry test, at times where the higher rates of heat release were identified
45 (24, 65 and 120 hours). After 24 h of reaction (Figure 2A), the only crystalline phases identified
46 in these binders were unreacted brucite ($\text{Mg}(\text{OH})_2$, powder diffraction file (PDF) # 01-074-2220)
47 and traces of poorly crystalline bayerite ($\alpha\text{-Al}(\text{OH})_3$, PDF # 00-020-0011). No crystalline
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3 NaAlO₂ is observed, indicating that this compound has fully dissolved, resulting in Al(OH)₃
4 precipitation, nor is any remnant SiO₂ observed (although as it is non-crystalline, identification
5 of this phase amongst crystalline peaks is more challenging). This indicates that the first
6 calorimetric peak at very early age is related, at least in part, to NaAlO₂ dissolution and the
7 precipitation of this phase.
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17 No differences in the diffraction patterns of R1.3 and R2.0 are identified (Figure 2B) after 65
18 hours compared to 24 hours, consistent with the identification of a dormant period in these
19 pastes, spanning this period of time. Conversely, in samples R3.0 and R3.3 with higher silica
20 content, the precipitation of zeolites of the structure type LTA (zeolite NaA:
21 Na₁₂Si₁₂Al₁₂O₄₈·27H₂O, PDF# 00-039-0219) is observed, which can explain the exothermic
22 event identified via isothermal calorimetry. XRD analysis after 120 hours of reaction (Figure 2C)
23 shows the formation of the LTA zeolite in all of the samples assessed. Regardless of chemical
24 composition, after the initial reaction takes place in these binders, the main crystalline reaction
25 products identified are Al(OH)₃ and LTA.
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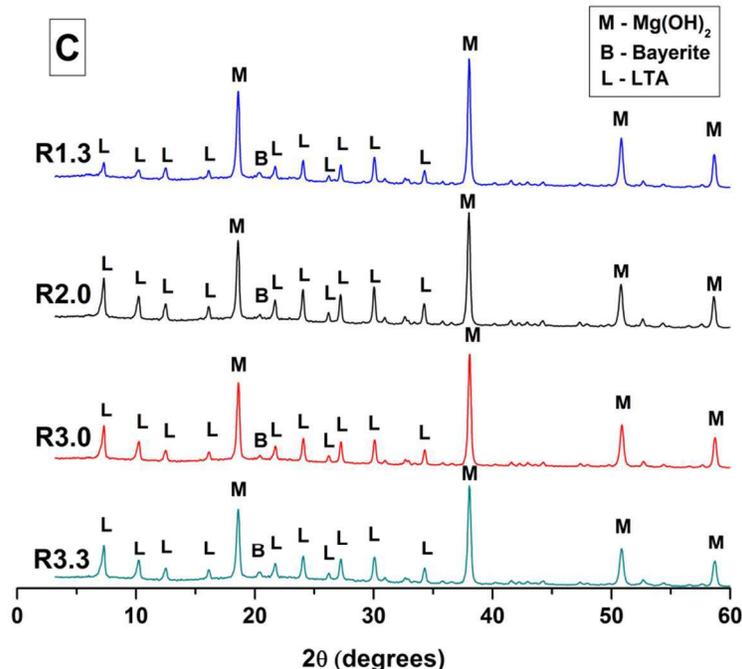


Figure 2. X-ray diffraction patterns of samples R1.3, 2.0, 3.0 and 3.3 after (A) 24, (B) 65 and (C) 120 hours of curing.

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 ($\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$), 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 $\text{Al}(\text{OH})_3$) 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.

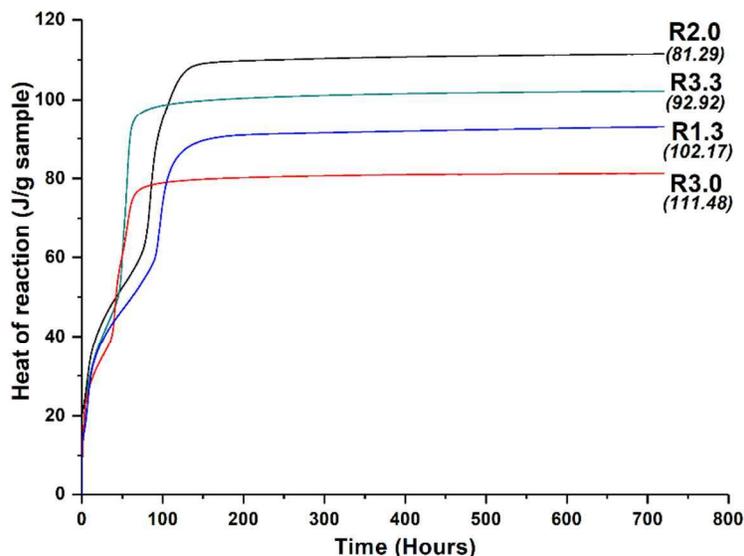


Figure 3. Cumulative heat of reaction of pastes within the system $\text{Mg}(\text{OH})_2\text{-NaAlO}_2\text{-SiO}_2\text{-H}_2\text{O}$, normalized to the total mass of paste in each case. Total heat of reaction (J/g) in parentheses.

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ samples R3.0 and R3.3 exhibit only LTA and $\text{Mg}(\text{OH})_2$ as crystalline features, along with an amorphous component presenting a broad feature around $20^\circ 2\theta$. The samples, R1.3 and R2.0 also contain additional Na-X (low silica faujasite: $\text{Na}_{86}\text{Si}_{106}\text{Al}_{86}\text{O}_{384}\cdot 175\text{H}_2\text{O}$, 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, $\text{Mg}(\text{OH})_2$ and traces of a sodalite-type structure. This corresponds to basic

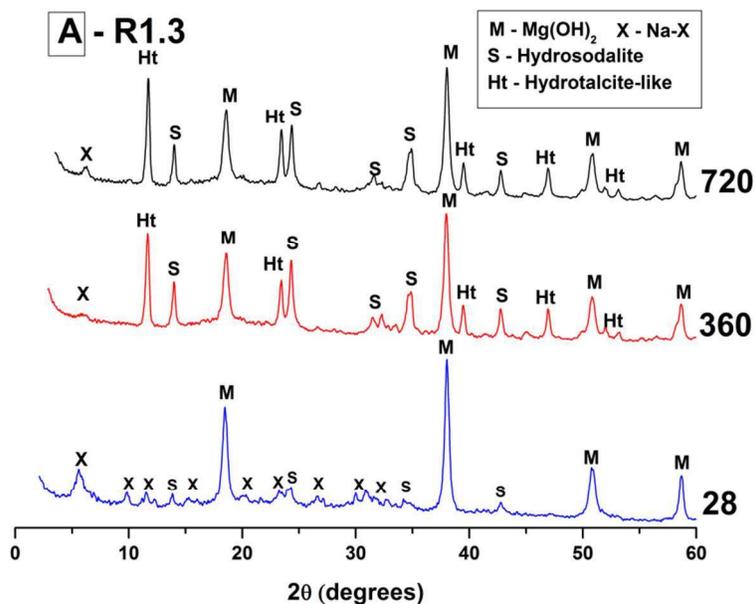
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3 hydrosodalite according to the nomenclature of Engelhardt et al.¹⁹ ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$,
4 PDF# 04-009-2429, IZA zeolite framework type SOD).
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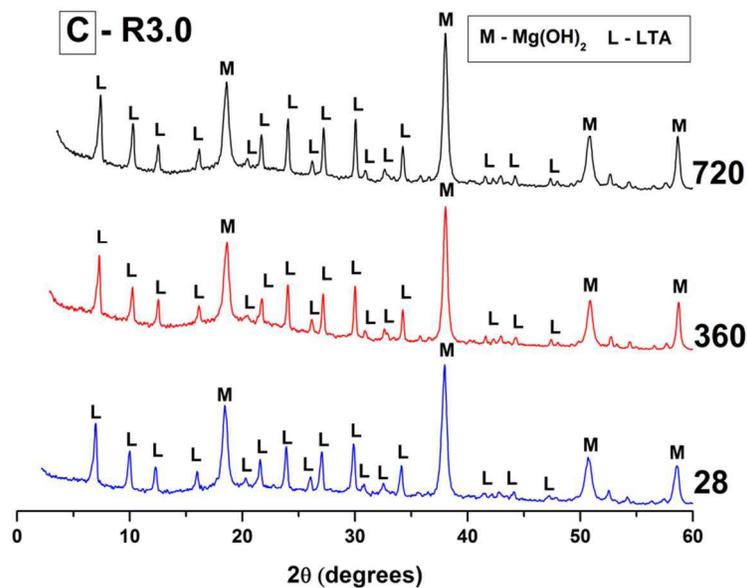
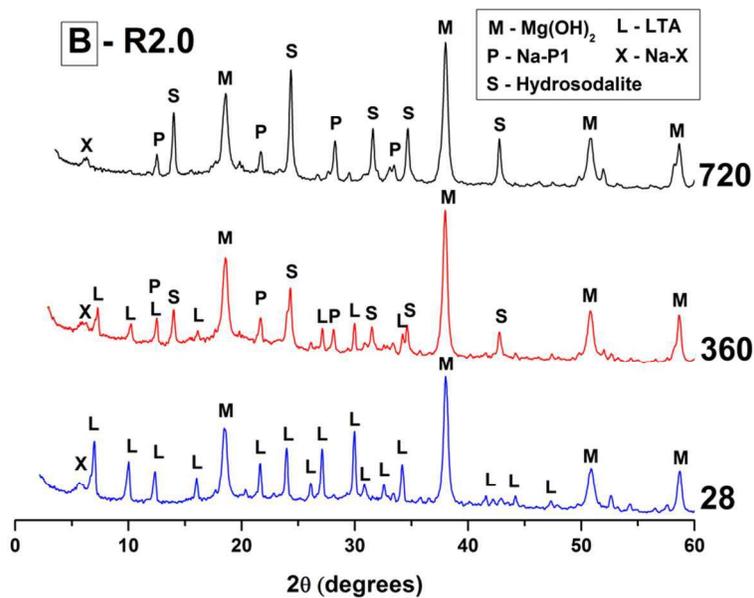
10 After longer curing times, the trends in the zeolite assemblages within these samples diverge.
11 Samples R3.0 and R3.3 (Figure 4) do not show any changes in crystalline composition up to 720
12 days of curing, displaying considerable stability. However, samples R1.3 and R2.0, with lower
13 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, do show significant changes. Sample R2.0 shows a change in zeolite
14 mineralogy, with basic hydrosodalite and Na-P1 appearing after 360 days of curing, coinciding
15 with a decrease in the intensity of LTA peaks. After 720 days no LTA remained, and the system is
16 dominated by basic hydrosodalite along with some Na-P1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$, PDF# 04-009-
17 5257, IZA framework type GIS) and Na-X.
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30 The transient nature of LTA in samples R1.3 and R2.0 can be explained by the fact that their
31 lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are achieved through a high NaAlO_2 content, which also results in more
32 alkaline conditions within the pore fluid of these binders compared to the higher-silica R3.0 and
33 R3.3. The LTA framework is also known to transform into sodalite type phases²⁰⁻²² and/or Na-P1
34 ²³⁻²⁵ in caustic media, although the process is slower in these cements, possibly due to the limited
35 ionic mobility under the relatively low water/solids ratios used here compared to a regular
36 hydrothermal synthesis process.
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49 Sample R1.3, with the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, undergoes a transformation whereby Na-X
50 decreases in intensity, and basic hydrosodalite emerges as the dominant aluminosilicate phase. In
51 addition to this, a hydrotalcite-like Mg-Al layered double hydroxide (LDH), potentially true
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3 hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})\cdot 4\text{H}_2\text{O}$, PDF# 00-054-1029) or a related structure differing in
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5 Mg/Al ratio or interlayer anions, forms by 360 days, increasing in intensity slightly at 720 days
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7 of curing. The identity of this phase will be further examined in Section 3.3, as hydrotalcite-
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9 group phases are challenging to distinguish from XRD data of moderate resolution as is the case
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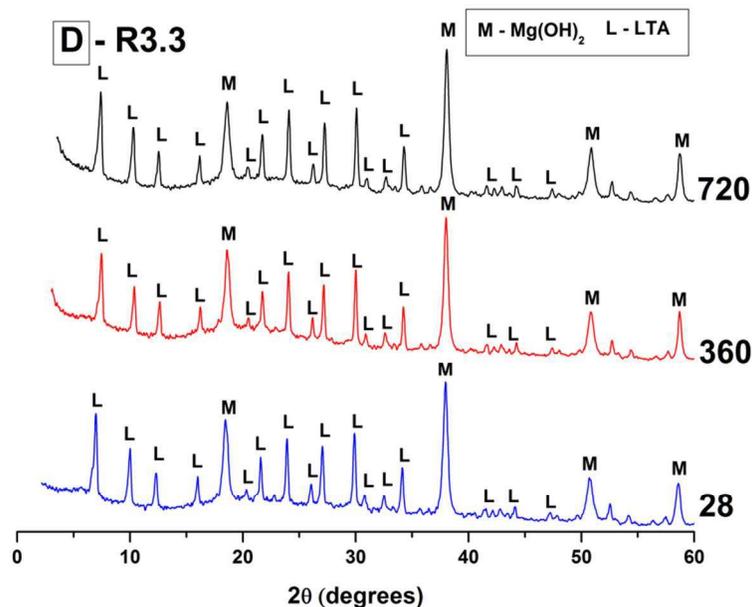


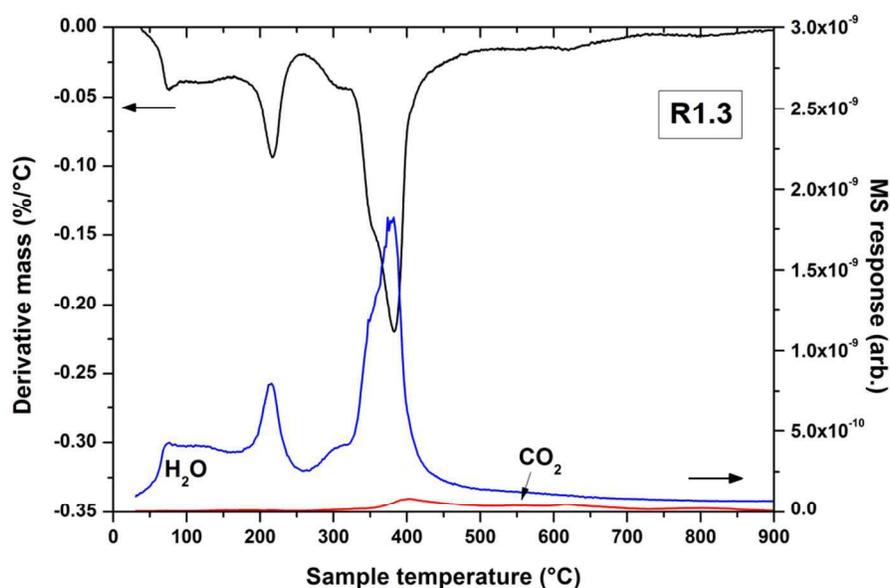
Figure 4. X-ray diffractograms of samples (A) R1.3, (B) R2.0, (C) R3.0 and (D) R3.3 as a function of the curing time in days (as marked). Some of the 28 day data are from ⁹.

Although sample R1.3 forms this additional magnesium-containing phase, all of the samples display strong reflections for $\text{Mg}(\text{OH})_2$, suggesting that little reaction between the aluminosilicate components and $\text{Mg}(\text{OH})_2$ 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 $60^\circ 2\theta$ ^{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 $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}] \cdot m\text{H}_2\text{O}$, in which M^{2+} and M^{3+} are di- and tri-valent metallic ions

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3 respectively, and A^{n-} can be one of many anions (e.g. CO_3^{2-} , OH^- , Cl^-)²⁶. For brevity this was
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5 labelled a ‘hydrotalcite-like’ phase in Figure 4, however as the samples were cured in a sealed
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7 container, this is likely to preclude much CO_2 ingress leading to formation of true (carbonate-
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9 containing) hydrotalcite. To determine the nature of this LDH, thermogravimetric analysis was
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11 undertaken with an attached mass spectrometer to distinguish between H_2O and CO_2 evolution,
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13 as shown in Figure 5.
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39 **Figure 5.** TG-MS data for sample R1.3 after 720 days curing, showing DTG (black), H_2O signal
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41 (blue) and CO_2 signal (red)
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46 The multiple phases observed by XRD analysis (Figure 5) within sample R1.3 result in a
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48 complex TG-MS response in Figure 5. The mass loss is dominated by the decomposition of
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50 $\text{Mg}(\text{OH})_2$ at 383°C ²⁷, and by an Mg-Al layered double hydroxide containing hydroxyl species in
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52 the interlayer (denoted OH-LDH) which accounts for much of the remaining mass change, with
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54 characteristic decomposition peaks at $\sim 90^\circ\text{C}$, $\sim 200^\circ\text{C}$, and as shoulders on the $\text{Mg}(\text{OH})_2$
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3 decomposition peak at $\sim 300^\circ\text{C}$ and 350°C ²⁸, suggesting that this phase may have a composition
4 similar to $\text{Mg}_4\text{Al}_2(\text{OH})_{18}\cdot m\text{H}_2\text{O}$, akin to a carbonate-free form of quintinite. It is likely that the
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decomposition peak at $\sim 300^\circ\text{C}$ and 350°C ²⁸, suggesting that this phase may have a composition similar to $\text{Mg}_4\text{Al}_2(\text{OH})_{18}\cdot m\text{H}_2\text{O}$, 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 $\text{Mg}(\text{OH})_2$ and excess of $\text{Al}(\text{OH})_3$ here. Some mass loss from bound water is also attributed to the release of zeolitic water from Na-X ($\sim 167^\circ\text{C}$) as well as dehydration of hydrosodalite, which decomposes slowly over a wide range, from ~ 80 - 750°C ²⁹⁻³⁰. A small signal for CO_2 is, however, observed at $\sim 400^\circ\text{C}$, pointing to some formation of CO_2 -containing LDH³¹⁻³² 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 $\sim 20^\circ 2\theta$ in Figure 4C and D) suggests either that unreacted silica fume remains, or that non-crystalline reaction products are forming. To further elucidate this, ^{27}Al and ^{29}Si 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.

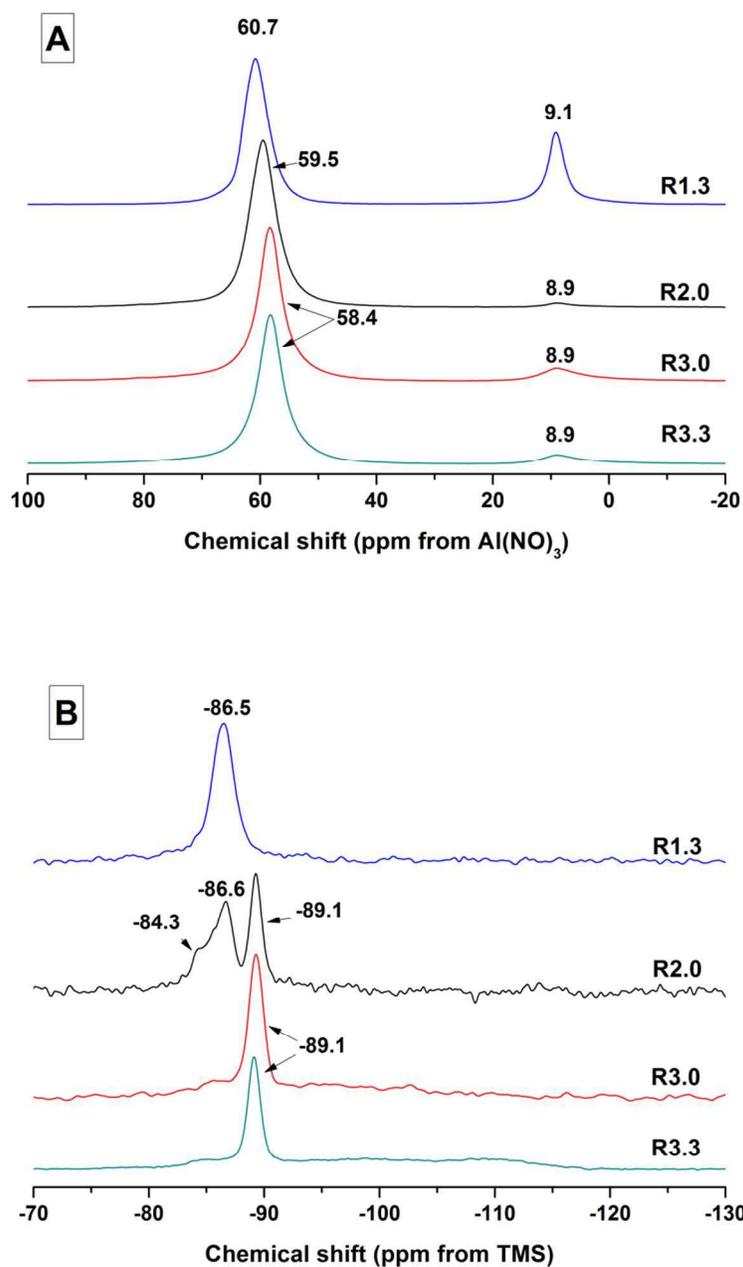


Figure 6. (A) ^{27}Al and (B) ^{29}Si MAS NMR spectra of pastes within the system $\text{Mg}(\text{OH})_2\text{-NaAlO}_2\text{-SiO}_2\text{-H}_2\text{O}$, after 360 days of curing

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

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3 formation of aluminosilicate zeolites in these samples ³³. The peaks at ~9 ppm correspond to
4 octahedrally coordinated Al, typical of non-framework Al species. Sample R1.3 exhibits a
5 stronger signal here, consistent with the identification of a hydrotalcite-like LDH as discussed
6 above ³⁴. In the remaining samples, although LDH phases have not been observed through XRD
7 analysis, the presence of this octahedral Al might be evidence of some small, poorly crystalline
8 LDH phase, or perhaps the presence of Al(VI) might be evidence of residual α -Al(OH)₃ as
9 postulated through XRD analysis earlier.
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21 The ²⁹Si MAS NMR data in Figure 6B further support the identification of zeolites. The single
22 peak at -89.1 ppm in samples R2.0-R3.3 is assigned to Q⁴(4Al) units in the LTA framework ^{33,35-}
23 ³⁶. Sample R2.0 exhibits a more complicated spectrum, with an additional signal at -86.6 ppm
24 from Q⁴(4Al) units in the sodalite framework structure ^{19, 36}, and a small signal at -84.3 ppm
25 associated with Q⁴(4Al) units in low silica Na-X ³⁵. R1.3 exhibits a single peak at -86.5 ppm,
26 consistent with the identification of the sodalite framework type as the primary zeolite at this age
27 by XRD, Figure 4.
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40 High field ²⁵Mg MAS NMR spectra were also collected to clarify the role of Mg within this
41 binding system. These data are shown in Figure 7 for sample R3.3 at 360 days of curing. The
42 experimental data were fitted with simulations based on established literature values for
43 magnesium minerals ^{16, 37} (Table 2), and found to represent predominantly Mg(OH)₂, with some
44 MgO present as an impurity. M-S-H would present a diffuse resonance centred at ~0 ppm at this
45 field strength ¹⁶. As the experimental data can be fitted well using a simulation describing
46 Mg(OH)₂ and MgO alone, no M-S-H can be said to exist within this sample. Equally, as no other
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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

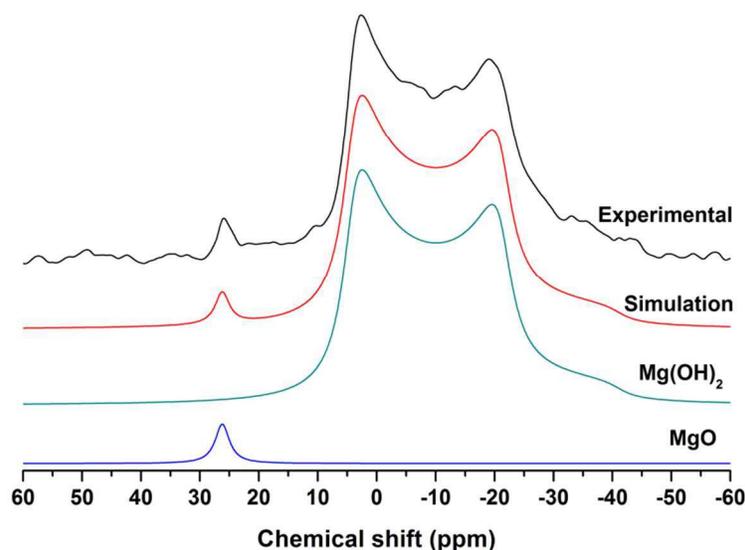


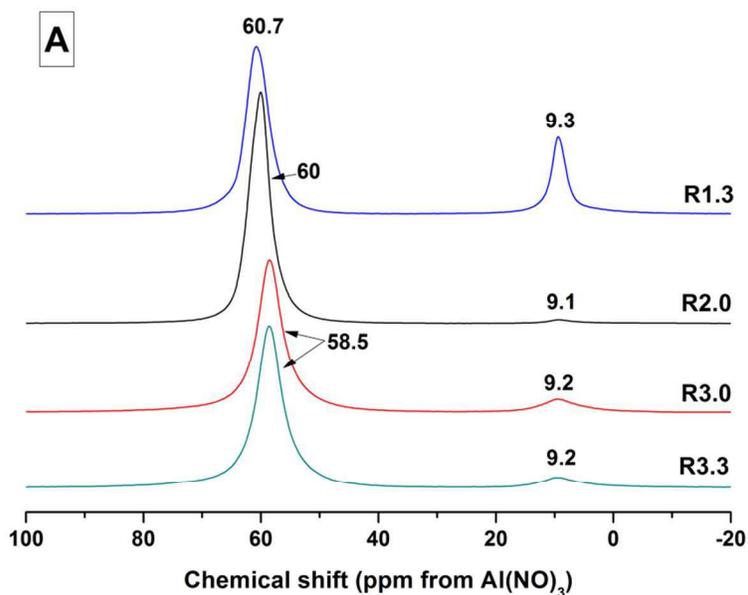
Figure 7. ^{25}Mg MAS NMR spectra of sample R3.3 at 360 days of curing, with experimental data, simulation, and component peaks

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

	δ_{iso} (ppm)	C_Q (MHz)	η_Q
MgO	26.2	0	0
Mg(OH)₂	11.7	3.1	0

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

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3 R3.3, with only minor shifts in peak positions in both ^{27}Al and ^{29}Si MAS NMR (Figure 8). These
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5 samples all exhibit broad signals in their ^{29}Si spectra, and are deconvoluted in Figure 9. Samples
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7 R1.3 and R2.0, however, do show changes from 360 to 720 days, consistent with their changing
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9 zeolite assemblages identified by XRD (Figure 5). In sample R1.3, a second peak appeared at -84
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11 ppm, consistent with an increase in the observed Na-X content, while in sample R2.0 the peak at
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13 -86.5 ppm (identified as sodalite) increased in intensity, while that assigned to LTA (-89.1 ppm)
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15 -86.5 ppm (identified as sodalite) increased in intensity, while that assigned to LTA (-89.1 ppm)
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17 disappeared entirely; both of these trends are in full agreement with the XRD assignments.
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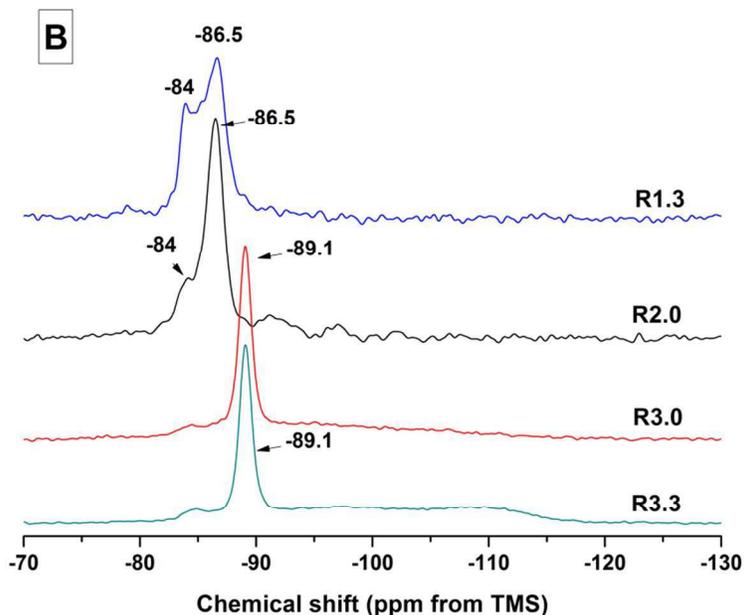
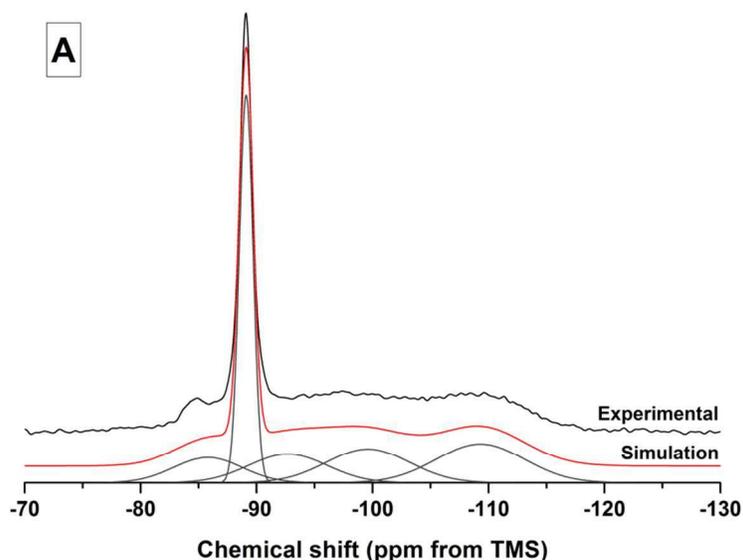


Figure 8. (A) ^{27}Al and (B) ^{29}Si MAS NMR spectra of pastes within the system $\text{Mg}(\text{OH})_2$ -
 NaAlO_2 - SiO_2 - H_2O , after 720 days of curing

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 ($\text{Q}^4(4\text{Al})$), 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 ($>\text{Si}-\text{OH}$ single silanol) sites surrounding an unreacted Q^4 silica fume core³⁸. The two remaining peaks at -92.7 and -85.8 ppm are assigned to $\text{Q}^3(1\text{Al})$ and $\text{Q}^2(1\text{Al})$ sites respectively. Both of these sites occur as the $\text{Al}(\text{OH})_4^-$ released by sodium aluminate dissociation form either surface $\text{Q}^3(1\text{Al})$, or further depolymerised $\text{Q}^2(1\text{Al})$ units.

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3 In general, there appears to be a larger contribution from the disordered phases within R3.3 than
4 R3.0 (assuming no substantive change in the ^{29}Si T_1 relaxation time between samples),
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6 suggesting that a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the formulation favours an increased fraction of the
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8 Q^4 , Q^3 and $Q^3(1\text{Al})$ sites, while a lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ content results in a larger contribution from
9
10 the $Q^4(4\text{Al})$ site of LTA. With a higher silica content, more unreacted silica is contributing to the
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12 spectrum, along with hydroxylated and aluminated silica surface sites. Overall there is no
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14 evidence of a M-S-H or M-A-S-H type phase forming, despite the presence of unreacted and
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16 partially aluminated silica. As this has not occurred within 2 years of curing, it is concluded that
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18 Mg incorporation into silicate phases is unlikely to occur in these samples within a meaningful
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20 engineering timeframe, and if this does eventually happen, the kinetics of the process are very
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22 slow compared to the zeolite formation.
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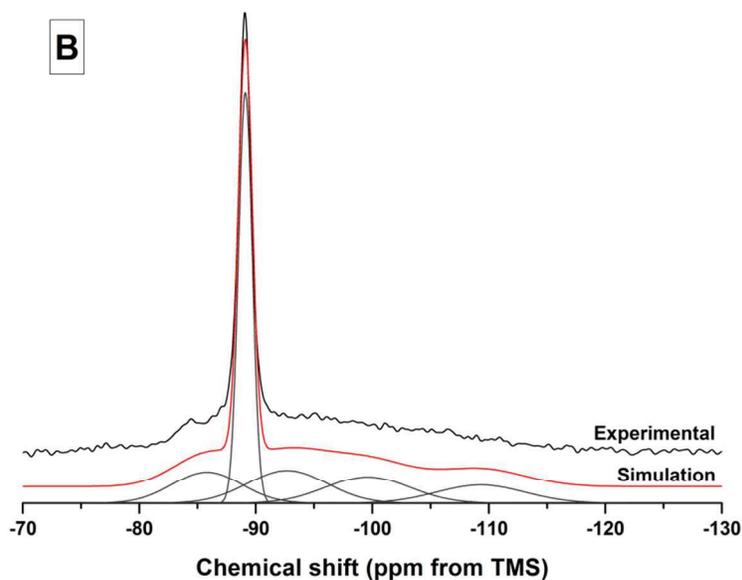


Figure 9. ^{29}Si MAS NMR spectra of samples (A) R3.3 and (B) R3.0 at 720 days of curing, featuring both experimental and simulated spectra, and decomposition into component peaks

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 $\text{Mg}(\text{OH})_2$ as a constituent material. The addition of reactive NaAlO_2 into the $\text{Mg}(\text{OH})_2$ - SiO_2 - H_2O system promotes the formation of mixed zeolites, the composition of which varies depending on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ content of the samples.

Initially all samples precipitated $\text{Al}(\text{OH})_3$, followed by zeolites after 20-60 hours. Higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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

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3 alterations in the zeolite assemblage over time. High $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios stabilized LTA, while
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5 lower ratios resulted in formation of a low silica faujasite (Na-X) zeolite, Na-P1,
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7 hydroxysodalite, and a hydrotalcite-type phase in the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio sample. This was
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9 determined through TG-MS analysis to be a hydroxide-containing layered double hydroxide with
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11 very limited carbonate incorporation, formed from some reaction of $\text{Mg}(\text{OH})_2$ with the added
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13 NaAlO_2 .
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19 ^{27}Al and ^{29}Si solid state MAS NMR spectroscopy confirmed the zeolite assignments from the
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21 XRD analysis, and also revealed unreacted silica fume, a hydroxylated Q^3 site and aluminated
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23 $\text{Q}^2(1\text{Al})$ and $\text{Q}^3(1\text{Al})$ sites, which were not detectable by XRD due to lack of long-range
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25 ordering. Further analysis using ^{25}Mg NMR was not able to detect any M-S-H or M-A-S-H
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27 formation, despite the presence of large quantities of both $\text{Mg}(\text{OH})_2$ and SiO_2 .
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33 Although no M-S-H or M-A-S-H phases have been identified here, the addition of high
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35 quantities of NaAlO_2 promoted the formation of a magnesium-aluminium layered double
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37 hydroxide. Aside from this sample, none of the other formulations resulted in reacted $\text{Mg}(\text{OH})_2$,
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39 which was encapsulated within the matrix rather than chemically bound. The potential for ion-
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41 exchange between the zeolites, the LDH and any radionuclides may be of benefit for the
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43 immobilisation of radionuclide bearing wastes, specifically Magnox sludges. U and Pu typically
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45 have very low solubility in high pH environment, often forming hydroxides³⁹. Trivalent
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47 actinides (such as Am), though also exhibiting low solubility at high pH could incorporate into
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49 hydrotalcite minerals³⁹. More problematic species such as Cs can be irreversible incorporated
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51 into sodalite and Na-P1 structures⁴⁰⁻⁴¹, while anions such as Cl^- and TcO_4^- could potentially
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3 exchange with anionic species in hydrotalcite ⁴²⁻⁴⁴. This would point towards the lowest
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5 SiO₂/Al₂O₃ ratio formulation, R1.3, potentially being preferable due to formation of a
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7 hydrotalcite-type mineral. However, ionic binding in hydrotalcites is often reversible, and
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9 dependent on existing anions ^{43, 45}, and therefore deserves further study.
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54 **References**

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58
59
60

1. Gregson, C. R.; Goddard, D. T.; Sarsfield, M. J.; Taylor, R. J., Combined electron microscopy and vibrational spectroscopy study of corroded Magnox sludge from a legacy spent nuclear fuel storage pond. *J. Nucl. Mater.* **2011**, *412* (1), 145-156.
2. Parry, S.; Livens, F.; O'Brien, L., Corroded Magnox sludge and plutonium waste cementation. *Geochim. Cosmochim. Acta* **2007**, *71* (15, Supplement), A747-A815.
3. Atkins, M.; Glasser, F. P., Application of portland cement-based materials to radioactive waste immobilization. *Waste Manag.* **1992**, *12* (2-3), 105-131.
4. Ojovan, M. I.; Lee, W. E., *An Introduction to Nuclear Waste Immobilisation*. Elsevier: Oxford, 2005.
5. Collier, N. C.; Milestone, N. B., The encapsulation of Mg(OH)₂ sludge in composite cement. *Cem. Concr. Res.* **2010**, *40* (3), 452-459.
6. Hough, T.; Palethorpe, S., Development of a direct encapsulation technique for the treatment of a mixed sludge / solid waste. In *WM'07 Conference*, Tucson, AZ, 2007.
7. Lothenbach, B.; Nied, D.; L'Hôpital, E.; Achiedo, G.; Dauzères, A., Magnesium and calcium silicate hydrates. *Cem. Concr. Res.* **2015**, *77*, 60-68.
8. Dauzères, A.; Achiedo, G.; Nied, D.; Bernard, E.; Alahrache, S.; Lothenbach, B., Magnesium perturbation in low-pH concretes placed in clayey environment—solid characterizations and modeling. *Cem. Concr. Res.* **2016**, *79*, 137-150.
9. Walling, S. A.; Bernal, S. A.; Kinoshita, H.; Collier, N. C.; Provis, J. L., Cementitious binders in the system Mg(OH)₂-NaAlO₂-SiO₂-H₂O. *Adv. Appl. Ceram.* **2014**, *113* (8), 496-501.
10. Kulyukhin, S. A.; Krasavina, E. P.; Gredina, I. V.; Rumer, I. A.; Mizina, L. V., Sorption of cesium, strontium, and yttrium radionuclides from the aqueous phase on layered double hydroxides. *Radiochem. (Moscow)* **2008**, *50* (5), 493-501.
11. Kang, M. J.; Chun, K. S.; Rhee, S. W.; Do, Y., Comparison of sorption behavior of I⁻ and TcO₄⁻ on Mg/Al layered double hydroxide. *Radiochim. Acta* **1999**, *85*(1-2), 57-63.
12. Nuclear Decommissioning Authority (NDA) *Waste stream 2D95.1: Magnox fuel storage pond sludge*; NDA: 2016.
13. Urwongse, L.; Sorrell, C. A., Phase relations in magnesium oxysulfate cements. *J. Am. Ceram. Soc.* **1980**, *63* (9-10), 523-526.
14. Walling, S.; Provis, J., Magnesia based cements - a journey of 150 years, and cements for the future? *Chem. Rev.* **2016**, *116*, 4170-4204.
15. Kingery, W. D., Fundamental study of phosphate bonding in refractories: II, Cold-setting properties. *J. Am. Ceram. Soc.* **1950**, *33* (8), 242-246.
16. Walling, S. A.; Kinoshita, H.; Bernal, S. A.; Collier, N. C.; Provis, J. L., Structure and properties of binder gels formed in the system Mg(OH)₂-SiO₂-H₂O for immobilisation of Magnox sludge. *Dalton Trans.* **2015**, *44*, 8126-8137.

- 1
2
3 17. Bertetti, J. W.; McCabe, W. L., Sodium hydroxide solutions. *Ind. Eng. Chem.* **1936**, 28 (2), 247-
4 248.
5
6 18. Lide, D. R., *CRC Handbook of Chemistry and Physics, 88th Edition*. CRC Press: Boca Raton, FL,
7 2007.
8
9 19. Engelhardt, G.; Felsche, J.; Sieger, P., The hydrosodalite system $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$:
10 Formation, phase composition, and de- and rehydration studied by ^1H , ^{23}Na , and ^{29}Si MAS-NMR
11 spectroscopy in tandem with thermal analysis, X-ray diffraction, and IR spectroscopy. *J. Am. Chem. Soc.*
12 **1992**, 114 (4), 1173-1182.
13
14 20. Subotić, B.; Škrtić, D.; Šmit, I.; Sekovanić, L., Transformation of zeolite A into hydroxysodalite:
15 I. An approach to the mechanism of transformation and its experimental evaluation. *J. Cryst. Growth*
16 **1980**, 50 (2), 498-508.
17
18 21. Walton, R. I.; Millange, F.; O'Hare, D.; Davies, A. T.; Sankar, G.; Catlow, C. R. A., An in situ
19 energy-dispersive x-ray diffraction study of the hydrothermal crystallization of zeolite A. 1. Influence of
20 reaction conditions and transformation into sodalite. *J. Phys. Chem. B* **2001**, 105 (1), 83-90.
21
22 22. Greer, H.; Wheatley, P. S.; Ashbrook, S. E.; Morris, R. E.; Zhou, W., Early stage reversed crystal
23 growth of zeolite A and its phase transformation to sodalite. *J. Am. Chem. Soc.* **2009**, 131 (49), 17986-
24 17992.
25
26 23. Subotić, B.; Šmit, I.; Madžija, O.; Sekovanić, L., Kinetic study of the transformation of zeolite A
27 into zeolite P. *Zeolites* **1982**, 2 (2), 135-142.
28
29 24. International Zeolite Association Structure Commission (IZA-SC), *Collection of simulated XRD*
30 *powder patterns for zeolites*. 4th ed.; Amsterdam, Netherlands, 2001.
31
32 25. Hansen, S.; Håkansson, U.; Landa-Canovas, A. R.; Falth, L., On the crystal chemistry of NaP
33 zeolites. *Zeolites* **1993**, 13 (4), 276-280.
34
35 26. Mills, S. J.; Christy, A. G.; Génin, J.-M. R.; Kameda, T.; Colombo, F., Nomenclature of the
36 hydrotalcite supergroup: natural layered double hydroxides. *Mineral. Mag.* **2012**, 76 (5), 1289-1336.
37
38 27. MacKenzie, K. J. D.; Meinhold, R. H., Thermal decomposition of brucite, $\text{Mg}(\text{OH})_2$: a ^{25}Mg
39 MAS NMR study. *Thermochim. Acta* **1993**, 230, 339-343.
40
41 28. Valente, J. S.; Pfeiffer, H.; Lima, E.; Prince, J.; Flores, J., Cyanoethylation of alcohols by
42 activated Mg–Al layered double hydroxides: Influence of rehydration conditions and Mg/Al molar ratio
43 on Brønsted basicity. *Journal of Catalysis* **2011**, 279 (1), 196-204.
44
45 29. Felsche, J.; Luger, S., Phases and thermal decomposition characteristics of hydro-sodalites
46 $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$. *Thermochim. Acta* **1987**, 118 (0), 35-55.
47
48 30. Joshi, U. D.; Joshi, P. N.; Tamhankar, S. S.; Joshi, V. P.; Idage, B. B.; Joshi, V. V.; Shiralkar, V. P.,
49 Influence of the size of extraframework monovalent cations in X-type zeolite on their thermal behavior.
50 *Thermochim. Acta* **2002**, 387 (2), 121-130.
51
52 31. Constantino, V. R. L.; Pinnavaia, T. J., Basic properties of $\text{Mg}^{2+1-x}\text{Al}^{3+x}$ layered double hydroxides
53 intercalated by carbonate, hydroxide, chloride, and sulfate anions. *Inorg. Chem.* **1995**, 34 (4), 883-892.
54
55
56
57
58
59
60

- 1
2
3 32. Klopogge, J. T.; Kristóf, J.; Frost, R. L., Thermogravimetric analysis-mass spectrometry (TGA-
4 MS) of hydrotalcites containing CO_3^{2-} , NO_3^- , Cl^- , SO_4^{2-} or ClO_4^- . In *2001. A clay odyssey. Proceedings of*
5 *the 12th international clay conference*, Bahía Blanca, Argentina, 2001.
6
7 33. Engelhardt, G., Solid state NMR spectroscopy applied to zeolites. In *Studies in Surface Science*
8 *and Catalysis*, van Bekkum, H.; Flanigen, E. M.; Jacobs, P. A.; Jansen, J. C., Eds. Elsevier: 2001; Vol.
9 Volume 137, pp 387-418.
10
11 34. MacKenzie, K. J. D.; Meinhold, R. H.; Sherriff, B. L.; Xu, Z., ^{27}Al and ^{25}Mg solid-state magic-
12 angle spinning nuclear magnetic resonance study of hydrotalcite and its thermal decomposition sequence.
13 *J. Mater. Chem.* **1993**, 3 (12), 1263-1269.
14
15 35. Lippmaa, E.; Maegi, M.; Samoson, A.; Tarmak, M.; Engelhardt, G., Investigation of the structure
16 of zeolites by solid-state high-resolution silicon-29 NMR spectroscopy. *J. Am. Chem. Soc.* **1981**, 103 (17),
17 4992-4996.
18
19 36. Newsam, J. M., Silicon-29 chemical shifts in sodalite materials. *J. Phys. Chem.* **1987**, 91 (5),
20 1259-1262.
21
22 37. Pallister, P. J.; Moudrakovski, I. L.; Ripmeester, J. A., Mg-25 ultra-high field solid state NMR
23 spectroscopy and first principles calculations of magnesium compounds. *Phys. Chem. Chem. Phys.* **2009**,
24 11 (48), 11487-11500.
25
26 38. Zhuravlev, L. T., The surface chemistry of amorphous silica. Zhuravlev model. *Colloids Surf., A*
27 **2000**, 173 (1-3), 1-38.
28
29 39. Nuclear Decommissioning Authority (NDA) *Geological Disposal: Radionuclide behaviour status*
30 *report*; NDA 2010.
31
32 40. Mon, J.; Deng, Y.; Flury, M.; Harsh, J., Cesium incorporation and diffusion in cancrinite, sodalite,
33 zeolite and allophane. *Microporous Mesoporous Mater.* **2005**, 86, 277-286.
34
35 41. Penilla, R. P.; Guerrero Bustos, A.; Goñi Elizalde, S., Immobilization of Cs, Cd, Pb and Cr by
36 synthetic zeolites from Spanish low-calcium coal fly ash. *Fuel* **2006**, 85 (5-6), 823-832.
37
38 42. Aggarwal, S.; Angus, M. J.; Ketchen, J. *Sorption of radionuclides onto specific mineral phases*
39 *present in repository cements*; AEA Technology: Windscale 2000.
40
41 43. Bontchev, R. P.; Liu, S.; Krumhansl, J. L.; Voigt, J.; Nenoff, T. M., Synthesis, characterization,
42 and ion exchange properties of hydrotalcite $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{A})_x(\text{A}')_{2-x}\cdot 4\text{H}_2\text{O}$ ($\text{A}, \text{A}' = \text{Cl}^-, \text{Br}^-, \text{I}^-$, and NO_3^- ,
43 $2 \geq x \geq 0$) derivatives. *Chem. Mater.* **2003**, 15 (19), 3669-3675.
44
45 44. Wall, N. A.; Minai, Y., Adsorption of $^{99}\text{TcO}_4^-$ onto hydrotalcite and calcined hydrotalcite under
46 basic conditions: influence of humic acids and anions. *J. Radioanal. Nucl. Chem.* **2014**, 301 (1), 221-225.
47
48 45. Miyata, S., The syntheses of hydrotalcite-like compounds and their structures and physico-
49 chemical properties - I: The systems $\text{Mg}^{2+}\text{-Al}^{3+}\text{-NO}_3^-$, $\text{Mg}^{2+}\text{-Al}^{3+}\text{-Cl}^-$, $\text{Mg}^{2+}\text{-Al}^{3+}\text{-ClO}_4^-$, $\text{Ni}^{2+}\text{-Al}^{3+}\text{-Cl}^-$ and
50 $\text{Zn}^{2+}\text{-Al}^{3+}\text{-Cl}^-$. *Clays Clay Miner.* **1975**, 23 (5), 369-375.
51
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54
55
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