Aqueous leachability of metakaolin-based geopolymers with molar ratios of Si/Al = 1.5–4

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ABSTRACT

The leachability in water of metakaolin based geopolymers with molar ratios of Na/Al = 1 and Si/Al = 1.5–4.0 has been investigated in order to optimise the composition for the immobilisation of nuclear waste. Formulations with Si/Al of around 2 are the most suitable using the ASTM/PCT leach test method. The variability of the leach results is discussed with reference to the microstructure, compressive strength and the degree of polymerisation of the geopolymers as observed here by solid state nuclear magnetic resonance, XRD and infrared measurements.

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1. Introduction

Inorganic polymers formed from the reaction of naturally occurring aluminosilicates with alkaline solutions have been termed geopolymers (GP) by Davidovits [1]. They have been known for over 60 years and are also described as inorganic cements or polysilates. GPs are basically aluminosilicate inorganic polymers composed of chains with three dimensional repeat structures of $(Si–O–Al–O–)_n$ and $(Si–O–Al–Si–O–)_n$ units. Normally Na^+ is used to maintain the charge balance required when Al^{3+} replaces Si^{4+}, but monovalent ions other than Na^+ may be used. To a rough approximation, the structure can be described as a nanoporous aluminosilicate glass [2,3].

Sources of Si and Al ions in reactive glassy or amorphous phases are added to concentrated alkaline solutions for dissolution and polymerisation to take place [4]. Typical precursors used are flyash, ground granulated blast furnace slag, and metakaolin made from thermal treatment of kaolin to render it X-ray amorphous and thus more reactive. The concentrated alkali solutions are typically a mixture of NaOH, KOH, Na_2SiO_3 and K_2SiO_3. The mechanism of the reaction with aluminosilicates involves dissolution of Si and Al ions to form $Si(OH)_4$ and $Al(OH)_4^-$ oligomers in solution. Condensation involves the OH ions on neighbouring molecules interacting to form oxide linkages between the molecules and hence releasing a molecule of water [4]. Further polycondensation at curing temperatures of between 20 °C and 90 °C results in a rigid polymer with unbound interstitial water. Thus GPs consist mainly of porous amorphous and semi crystalline three dimensional aluminosilicate networks.

The rigidity and flexibility of GPs depend very much on the Si/Al molar ratio [4]. If this ratio increases beyond a value of ~3:1, the GP becomes less rigid and therefore more flexible. If the ratio is below ~3:1, the three dimensional network structure forms and is suitable as a structural material as well as a structure for incorporating waste ions . If the Si/Al ratio is above 3:1 and as high as 35:1, the resulting two dimensional structure is more suited for use as an adhesive, or as an impregnating resin for forming fibre mat composites [4].

The physical behaviour of GPs is similar to that of Portland cement and they have been considered as an improvement on cement with respect to their compressive strength, resistance to fire, heat and acidity, and as noted above, as a medium for encapsulation of radioactive and hazardous waste [5–10]. For radioactive waste, Cs and Sr are amongst the most difficult radionuclides to immobilise. Attempts have been made to immobilise Cs and Sr in GPs previously [5–9,11–12] and their leach resistance was studied using the MCC-1 [13] test for qualification of high level nuclear waste. According to that test, leach rates for Na, Cs and Sr were high, in the order of tens of g/m^2/day (tens of μm/day) for the first few weeks, decreasing with increasing time [14]. Such behaviour is unsatisfactory for the immobilisation of high level nuclear waste, which is basically liquid waste derived from reprocessing of spent nuclear power plant fuel, or production of plutonium for nuclear weapons.

To assess the suitability of a material for the immobilisation of intermediate level nuclear waste (ILW), there is no universal test. Since the MCC-1 test is primarily for high level nuclear waste, it was decided to test only metakaolin-based GPs using the PCT-B method [15] which uses Environmental Assessment (EA) glass as a reference. This method is applicable to both high level nuclear waste (HLW) and low level nuclear waste (LLW), although the criterion for passing the test does vary depending on the class of

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the nuclear waste. Intermediate level nuclear waste (ILW) is not recognised as such in the United States, but it is recognised in Europe and by the IAEA. Examples of such wastes are those from radioisotope production having activities of >100 MBq/kg.

For assessing suitability of LLW immobilisation, the ANSI/ANS – 16.1-2003 test [16] is normally used, mainly in Europe. However, some countries, especially Slovakia, which already has a nuclear waste repository, use this test to assess mixed LLW/ILW [17], in addition to testing the surface activity of the drum containing the waste package for acceptability.

The formation and leaching behaviour in water of GPs with compositions having molar ratios of Si/Al = 1.0–3.0 and Na/Al = 0.8–1.0 were reported earlier [5]. These were made using commercial sodium silicate solution or adding fumed silica to metakaolin and mixing with NaOH solution. It was deduced from this study that the fumed silica did not dissolve appreciably, and that high Si samples needed pre-digestion of the fumed silica [18] to minimise leachability. Such samples actually showed better leach resistance than comparable samples made with alkaline commercial silicate solutions and metakaolin, and it was concluded that the optimal leach resistant composition of metakaolin-based geopolymers probably lay at a Si/Al molar ratio substantially in excess of 2; hence the range of Si/Al molar ratios chosen for this study.

So for the present study, a series of metakaolin-based geopolymers with differing molar ratios of Si/Al 1.5–4.0 and Na/Al = 1 were made using fumed silica, sodium hydroxide and metakaolin.

2. Methods and procedures

2.1. Samples

Samples were prepared using ingredients as shown in Tables 1 and 2. Fumed silica was pre-dissolved in ~8 M NaOH solution and heated to ~75 °C for 16 h prior to mixing with metakaolin. The solution was sealed while being heated to prevent atmospheric carbonation and water loss. The metakaolin was added to this solution after it was cooled to ambient and was processed in a dental mixer for ~5 min under vacuum at 300 rpm. The H_2O/Na molar ratio was ~7 for most samples, but some compositions required more water to render them workable, up to a molar ratio of ~10. Nonetheless, the general aim was to minimise the water content. All samples contained small amounts of Sr and Cs added as hydroxides. These elements are very important performance indicators for nuclear wasteforms, being relatively soluble in water, especially Cs. If these elements are effectively immobilised, less soluble radionuclides should be unlikely to pose a problem. This is of utmost importance if GPs are considered as candidates for the immobilisation of radioactive waste [11,12].

The slurry was poured into a 40 mm internal diameter polycarbonate container and sealed with a screw top lid. It was de-aerated by holding it for 5 min on a vibrating platform. Samples were cured for 2 h at ambient followed by 24 h at 60 °C. After cooling to ambient, the lids were opened after the fifth day and the samples removed from the moulds on the seventh day.

All the cured samples were heated to 400 °C/2 h to remove free water. In samples containing actual radioactive waste, this step is crucial in order to minimise the production of hazardous H_2 by radiolysis [11]. The samples were then crushed, sieved, and a fraction (75–150) μm collected for each sample, followed by methanol treatment to remove fines (see below).

2.2. ASTM/ PCT-B leach test [15]

Leach testing was carried out using the PCT-B test protocol in which a (75–150) μm sized powdered sample is usually washed with water using an ultrasonic bath in order to remove adherent finer particles. For GP samples this is not an option, since washing of samples with water tends to dissolve the soluble components of the sample prior to the test; and the use of the ultrasonic bath may alter the particle size of the sample by inducing fracture. Washing of GP samples with non polar cyclohexane showed that though it prevented loss of water soluble analytes from the geopolymer matrix, it certainly did not easily remove all the adherent finer particles from the main particle size fraction, according to scanning electron microscope (SEM) studies. The presence of adherent finer particles results in elevated and erroneous PCT-B results. In this study, the samples were washed in methanol for 1.5 min (without the aid of an ultrasonic bath) so as to remove adherent finer particles, and then dried at 90 °C overnight before the PCT-B leach test was carried out. SEM confirmed the substantial removal of fines.

Table 2
GP sample compositions containing Si/Al molar ratios = 1.5–4.0

Number	Si/Al molar ratio	Fabrication details
1	1.5	MK = 24.54 g, FS = 6.64 g, NaOH = 8.82 g, DIW = 19.75 g (BD = 1.08)
2	2.0	MK = 13.92 g, D = 26.08 g, DIW = 0.0 g (BD = 1.44)
3	2.5	MK = 12.72 g, D = 23.84 g, FS = 3.44 g, DIW = 1.44 g (BD = 1.54)
4	3.0	MK = 11.72 g, D = 21.96 g, FS = 6.34 g, DIW = 0.0 g (BD = 1.77)
5	3.5	MK = 14.75 g, FS = 19.93 g, NaOH = 5.32 g, DIW = 13.74 g (BD = 1.42)
6	4.0	MK = 13.41 g, FS = 21.75 g, NaOH = 4.84 g, DIW = 13.46 g (BD = 1.61)

MK = Metakaolin, D = Sodium silicate 'D' solution, FS = Fumed silica, DIW = Deionised water, BD = Bulk density.
One equivalent wt% of Cs and Sr added as hydroxides.

Fig. 1. Time dependence of DIW pH after immersion of GP (8 mm cube) with Si/Al molar ratio = 2 and containing 1 wt% each of Ca^{2+} and Fe^{3+} in 30 mL of DIW.

Table 1
Precursors used to make GPs

Precursor	Supplier
NaOH	Ajax Finechem Pty Ltd., Sydney, Australia.
Kaolin[a]	Kingwhite80, Unimin Australia Ltd., Sydney, Australia.
Fumed silica[b]	Australian Fused Materials, Perth, Western Australia.
Water	Deionised water, Milli-Q system.

[a] Kaolin heated to 750 °C for 15 h in air to form metakaolin ($Al_2O_3 \cdot 2SiO_2$). The XRD analysis showed an amorphous phase with trace amounts of anatase and quartz. The clay contained ~1 mass% quartz, TiO_2 and Fe_2O_3 according to the supplier.
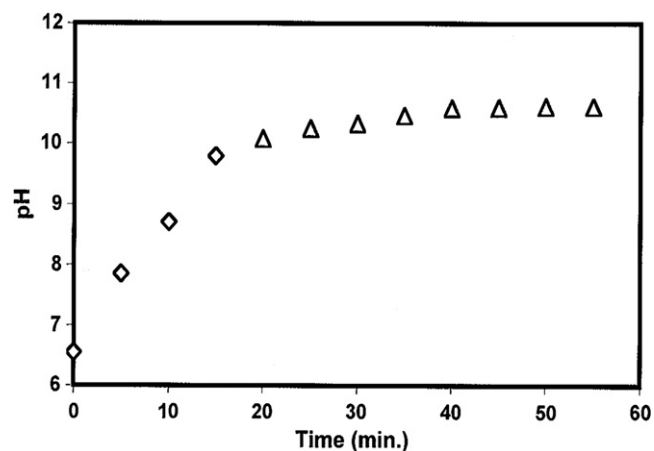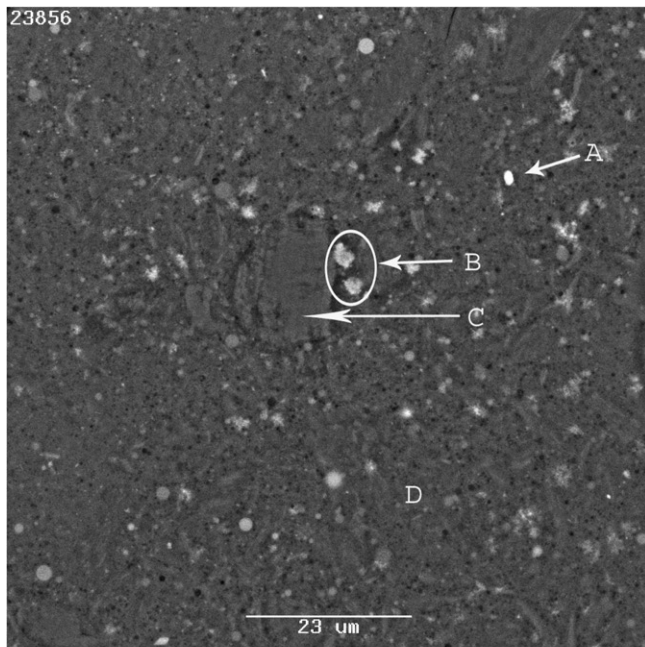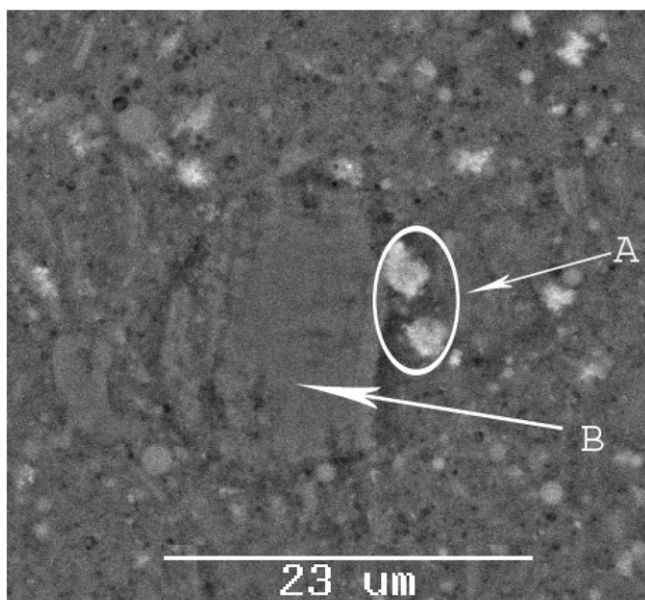[b] Fumed silica contained about 7 wt% impurity of zirconia and hafnia.

Table 3
PCT-B normalised releases of GPs – g/L (±5%)

Si/Al molar ratio	Al	Si	Na	Cs	Sr
1.5	0.10	1.8	9.3	0.8	0.01
2.0	0.24	1.3	11	0.3	0.01
2.5	0.4	1.0	11	0.3	0.02
3.0	0.02	8.9	27	0.4	0.18
3.5	0.02	11	29	0.6	0.39
4.0	0.02	12	32	0.5	0.42

PCT-B leach tests were undertaken using 1.0 g of washed and dried sample in 10 mL of deionised water (DIW) as per the ASTM/PCT-B protocol. Duplicate blanks were also included into each PCT-B batch of samples; and all samples were examined in triplicate.

Once the leaching test period (7 days at 90 °C) was completed, the samples were taken out and cooled before being re-weighed to gauge any mass loss. If the mass loss was greater than 5% (from evaporation consequent upon poor vessel sealing) of the original leachant mass, then the test sample was disregarded.
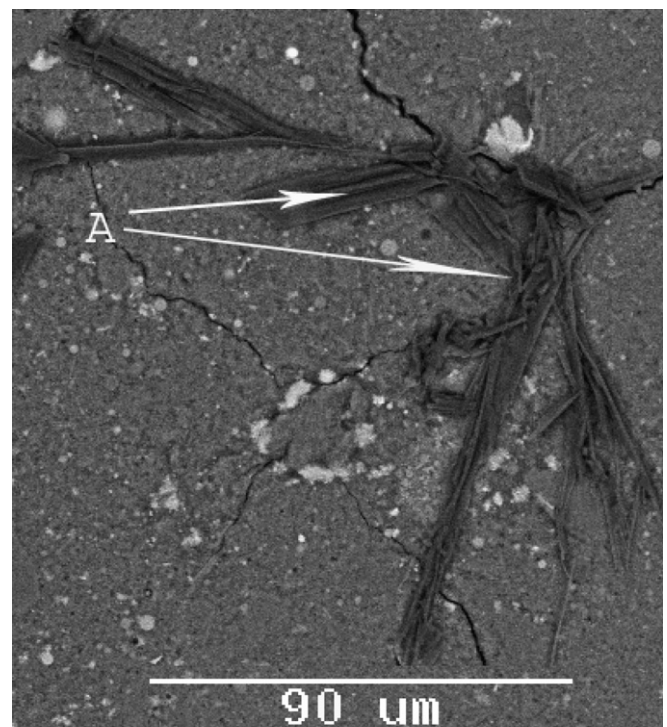
The samples were filtered immediately after cooling using sterile 0.45 μm filters mounted onto sterile syringes into clean, dry and labelled polypropylene containers. This ensured that there was no further equilibration between the powdered sample and the leachant, and also prevented any solid particulates from being introduced into the analytical system.

2.3. Dilution and sample preparation for analyses

Portions of GP leachate samples were diluted and acidified to prevent any possible hydrolysis and precipitation of metal cations. These samples were used for cation analyses, except silicon, employing a combination of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Perkin-Elmer Optima 3000DV, USA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin-Elmer Elan 6000, USA).

The remaining non-diluted, non-acidified samples were used for pH determination (aliquot discarded afterwards) and analysed for silicon using ICP-OES, with appropriate standards prepared in water. Any dilutions of samples for silicon analyses were made in deionised water only, so as to prevent precipitation of silica which occurs at lower pH values.

For quality control of analyses, internal controls and international standards were inserted in the analytical batch for validation purposes.

A = TiO₂ impurities from kaolin
B = Strontium precipitate region
C = unreacted or partially reacted metakaolin
D = GP matrix

A = Strontium precipitate region
B = Partially reacted or unreacted metakaolin

Fig. 2. Backscattered electron SEM image of GP with Si/Al molar ratio = 3.0. Inset: close up of backscattered SEM image of GP with Si/Al molar ratio = 3.0.

A = Sodium based dendritic crystal growth after exposure of GP to air

Fig. 3. Backscattered electron SEM image of GP with Si/Al molar ratio = 3.0.

2.4. Scanning Electron Microscopy (SEM)

GP microstructures were examined using a JEOL JSM-6400 SEM with an attached Noran Instruments Voyager Series IV X-ray microanalysis system. Samples were cut into thin cross-sections and mounted in an epoxy resin and polished to a 1 μm diamond finish. A carbon film (~3 nm) was deposited onto the polished surfaces of samples under vacuum to prevent charging.

The SEM was operated at an accelerating voltage of 15 kV. A combination of backscattered electron imaging and qualitative X-ray microanalysis (EDS) was used to study GP microstructures.

2.5. Solid state NMR measurements

High resolution solid state ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired at ambient temperatures using an MSL-400 NMR spectrometer (B_o = 9.4 T) operating at the ^{29}Si frequency of 79.48 MHz. ^{29}Si MAS NMR data were acquired using a Bruker 7 mm double-air-bearing probe with single pulse (Bloch decay) methods which utilised high-power ^1H decoupling during data acquisition. The MAS frequencies implemented for these measurements were ~5 kHz. For these ^{29}Si MAS single pulse/high-power ^1H decoupling measurements, a single ^{29}Si $\pi/4$ pulse width of 2.5 μs and a pre-acquisition delay of

10 μs were used in conjunction with recycle delays of 30–60 s for quantitative ^{29}Si speciation analysis. All ^{29}Si MAS chemical shifts were externally referenced to tetramethylsilane (TMS) at δ = 0 ppm via a high purity sample of kaolinite (δ = −91.2 ppm).

2.6. Infrared measurements

Diffuse reflectance (DRIFT) spectra of the samples were recorded in KBr (10% w/w) in the range 4000–650 cm^{-1} with a Nicolet Nexus 8700 FT-IR spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector and a thermo electron diffuse reflectance (DRIFT) accessory. Decomposition of the spectra was undertaken using the GRAMS/Al (Version 8.0) software suite.

3. Results and discussion

The most leachable species in GPs are the alkali ions. Previous work [14] has shown that the pH of the leaching solution stabilises at values >10 within only a few tens of minutes of leaching at 90 °C – see Fig. 1.

PCT-B normalised releases of GP samples at 90 °C over 7 days are shown in Table 3. Only samples containing Si/Al 1.5, 2.0, and 2.5 passed the PCT-B test for HLW for Na. The Na releases (alkali, most leachable element) for these samples were <13 g/L. Normali-
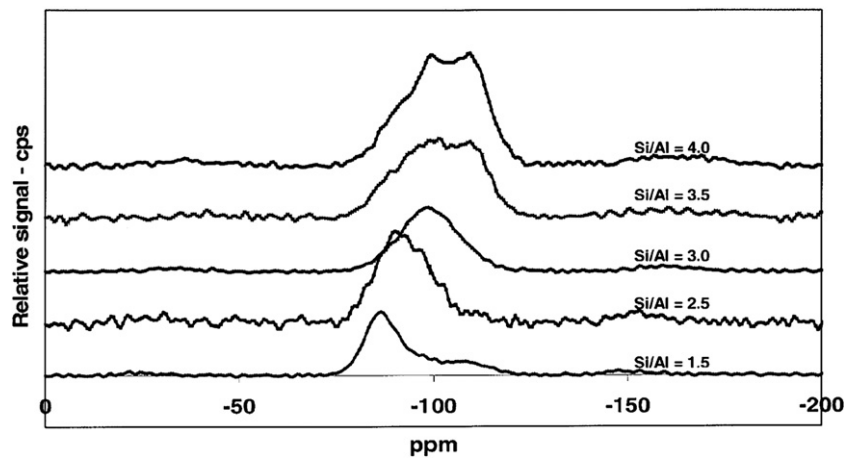

Fig. 4. ^{29}Si MAS NMR of GP as a function of Si/Al molar ratios. Data offset for clarity.
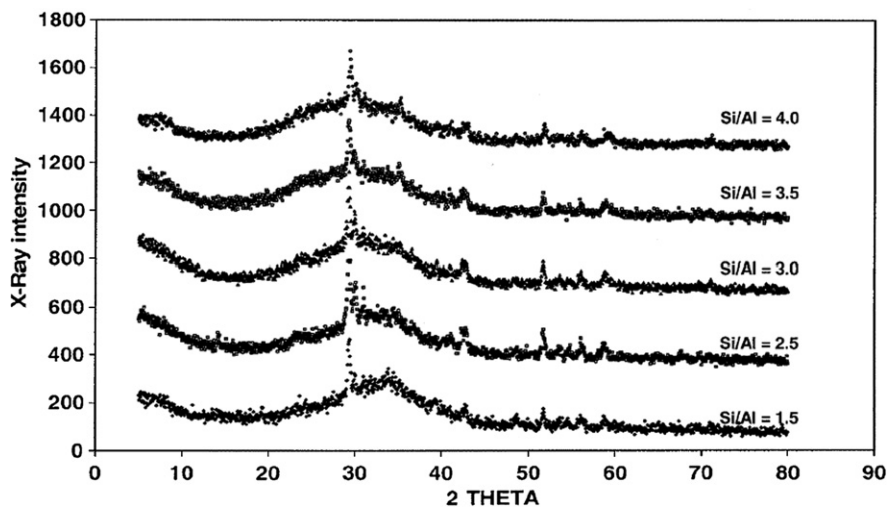

Fig. 5. XRD traces of GPs with Si/Al molar ratios = 1.5–4.0 (CoKα radiation, data offset for clarity).

sation of the releases were calculated and reported to standardise PCT-B releases by taking into account the formulation differences between GPs i.e. [(concentration of element g/L)/weight fraction of element in solid]. This results in figures which are independent of formulation ingredients and which are normalised to 100% for complete elemental release. So the maximum normalised release of a particular element is 100 g/L. Releases for elements other than Na were also tracked and these were well below 13 g/L in most cases, except for Si which had releases of ~10 g/L for those samples which failed the PCT-B test. (see Table 3).

Integrated Na releases (over 7 days) for GPs with molar ratios 1.5, 2.0 and 2.5 were 1.80, 3.00 and 3.20 g/m². Only the wasteform with Si/Al = 1.5 met the PCT-B criterion of <2 g/m² for near surface disposal for LLW [19].

As the PCT-B leaching procedure is a static leaching process, it is envisaged that leaching of the constituents of the pore water will predominate since the deionised water comes in direct contact with the pores initially. This will be concurrent with the reaction of alkali rich leachate with the unreacted metakaolin in the GP matrix (see Fig. 2) and the GP matrix itself. However, calculating the relative contributions of these two effects to the total leachability remains to be done, and no easy way immediately suggests itself to us. Both effects will contribute to the pH increase, with the framework dissolution giving rise to ion exchange between Na and H_3O^+.

Nevertheless, it has been previously observed that the fractional extraction of Na, Al and Si ions into water from the amorphous GP structure is strongly dependent on the ratio R of solid/water, increasing with decreasing R [20]. If pore water was the sole contributor to elemental release, the elemental fractional (normalised)

release would be expected to be approximately independent of the solid/water ratio, especially at low solid/water ratios. Hence this strong dependence of dissolved Na on R, which would be expected to be independent of pH, is indicative of Na dissolution derived mainly from the framework dissolution rather than pore water transfer to the leach solution. This idea agrees with the solid state NMR measurements which show that Na ions are significantly coupled to the GP aluminosilicate framework [21].

Normally during the geopolymerisation process, Al takes on a coordination of 4 [4] i.e. $[Al(OH)_4]^-$, and Na^+ maintains the charge balance in the GP matrix. If the geopolymerisation reaction is incomplete, excess Na^+ is deposited into the pores to form a saturated solution and some of it is deposited on the GP surface. When exposed to air, sodium based dendritic crystal growth is observed – most probably sodium carbonate (solubility 29.4 g/100 g H_2O)], or
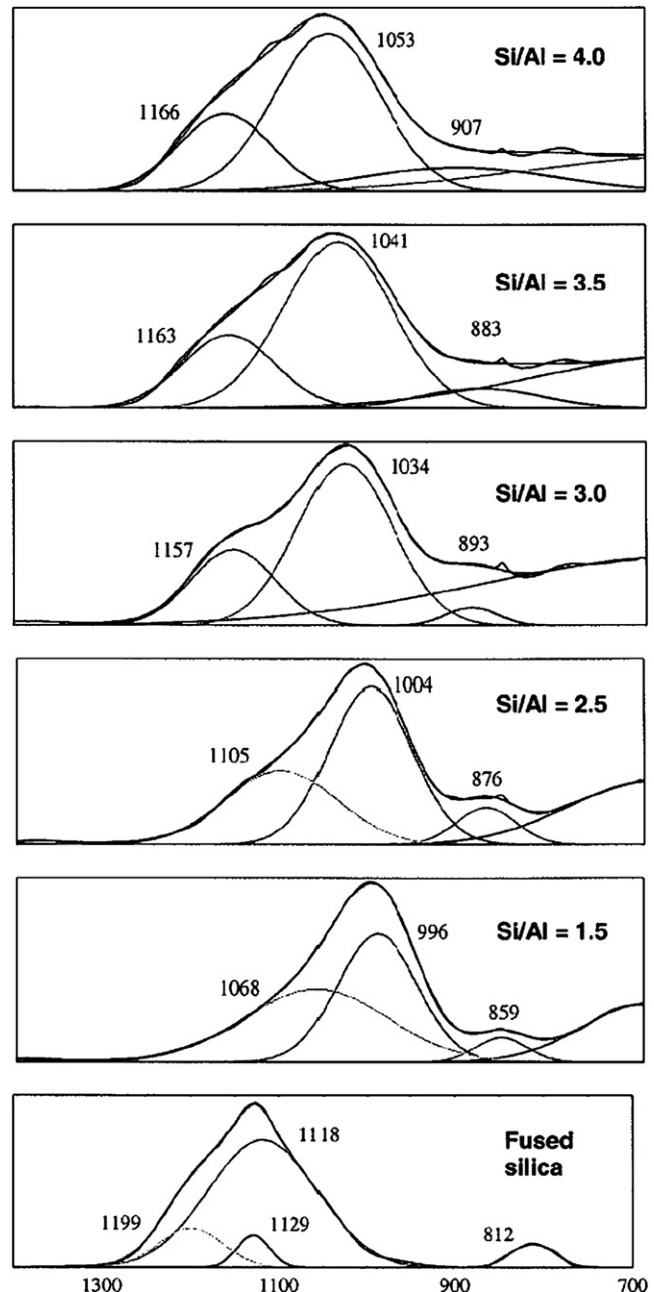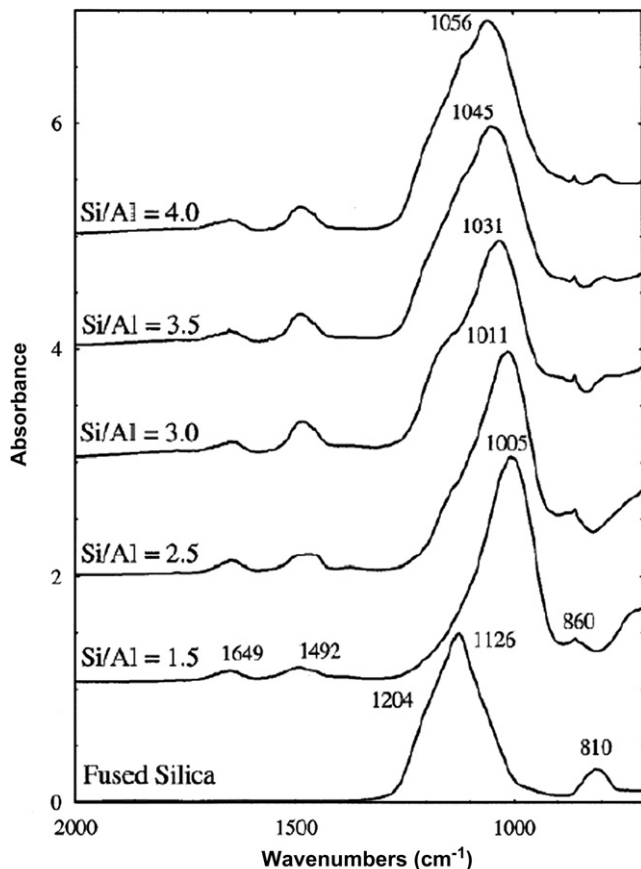
Fig. 6. DRIFT spectra of GPs with varying molar ratios of Si/Al for the region 2000–700 cm⁻¹. Spectra offset for clarity.

Fig. 7. Decomposition of DRIFT spectra of GPs with Si/Al molar ratio = 1.5–4.0 in the 1400–700 cm⁻¹ region.

sodium bicarbonate (solubility 10.3 g/100 g H_2O; rather than sodium silicate which is very soluble [22]. This can be seen clearly from SEM micrographs – see Fig. 3. Of course, SEM cannot identify the anion characterising the sodium based deposits.

In an attempt to confirm the hypothesis of a lower degree of polymerisation (3-D) at higher Si/Al ratios (see Section 1) as a way to explain the higher elemental releases of GPs upon exposure to water, ^{29}Si and ^{27}Al MAS NMR, FTIR and XRD studies were carried out. The ^{29}Si MAS NMR data in Fig. 4 show that heterogeneous products were formed across the Si/Al range of 1.5–4.0. Each spectrum was dominated by the characteristic ^{29}Si GP resonance which appeared at a chemical shift of ~-86 ppm for the Si/Al = 1.5 preparation, and then moved progressively upfield to ~-90 ppm and ~-98 ppm for the Si/Al = 2.5 and 3.0 samples, respectively. Samples of Si/Al ratios greater than 3.0 (i.e. 3.5 and 4.0) also exhibited ^{29}Si shifts that appeared to have stabilised at around ~-98 ppm. The monotonic upfield movement of this chemical shift is consistent with the changing nearest neighbour aluminium coordination number (m) influencing the Q^4 Si sites, i.e. $Q^4(m$Al$)$. An increase in the Si/Al ratio of the nominal composition leads to a corresponding decrease in the m number, thus reflecting a reduced Al influence on the average Si coordination sphere. In other words, as the GP network becomes dealuminated, there is less influence from the more electropositive Al^{3+} which subsequently induces an upfield movement of the GP ^{29}Si chemical shift towards that expected for amor-phous condensed Q_4 silica. This behaviour has been reported previously in other studies on the bonding character of metakaolin-based GP preparations [23]. For the Si/Al = 3.5 and 4.0 preparations, another resonance of similar intensity was observed at ~-110 ppm which has been assigned to a presence of condensed amorphous silica. This is a consequence of competing Si polymerisation processes initiated by insufficient Al in those nominal compositions. The modest post-curing heating temperature of 400 °C would not be sufficient to ensure a complete condensation of all excess Si to purely Q_4 species, and some residual colloidal silica and unreacted silica fume appear to exist in these preparations. The ^{29}Si resonances for these latter Si species cannot be resolved from the main geopolymer resonance [23]. However, the increased Si releases for the higher Si/Al ratios (see above) are probably derived from the Si species that have not transformed to fully condensed Q_4 amorphous silica. In contrast, the resonance at ~-108 ppm in the Si/Al = 1.5 preparation has been assigned to the presence of incompletely reacted metakaolin, promoted by the Si-poor conditions of that nominal composition.

XRD data (Fig. 5) showed the presence of a prominent diffuse peak in the 20–40° range of 2θ, moving to more characteristic positions for amorphous silica at Si/Al ~ 3, i.e. smaller 2θ values; the peak for amorphous silica occurs at $2\theta \sim 28°$ for CoKα radiation [24]. Sharp peaks in Fig. 5 are due to both anatase and quartz as previously noted.
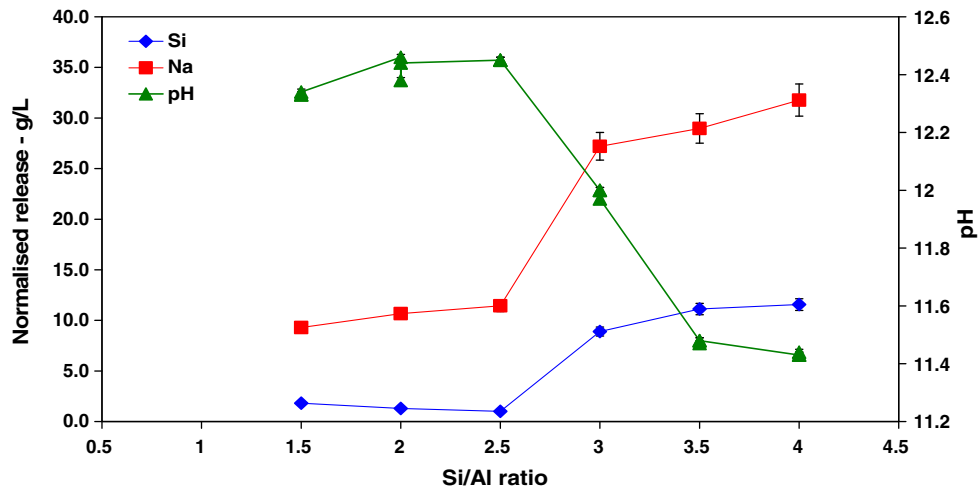

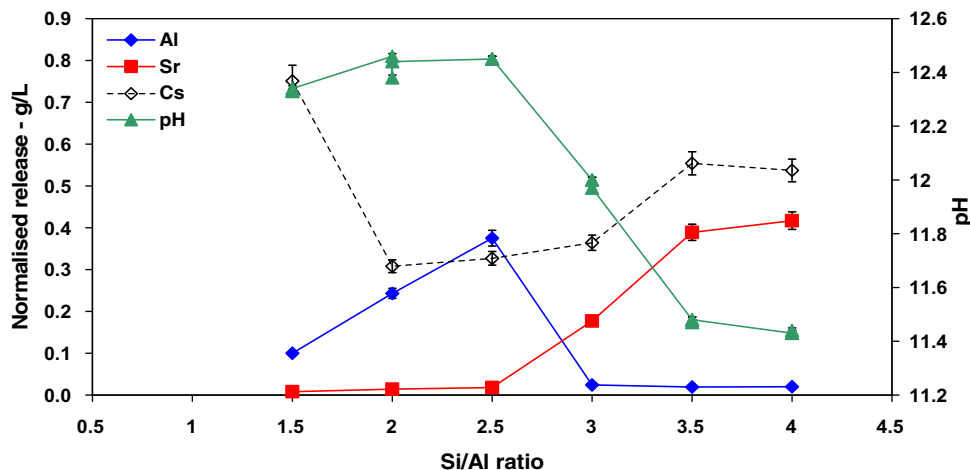Fig. 8. Si and Na PCT-B releases of GPs as a function of Si/Al molar ratios.

Fig. 9. Al, Sr, and Cs PCT-B releases of GPs as a function of Si/Al molar ratios.

The diffuse reflectance IR data also supported the presence of amorphous silica via the increased absorption in the 1100–1200 cm^{-1} region for samples with Si/Al $\geqslant$ 2.5 (see Fig. 6). Decomposition of the fused silica spectrum shows two bands at 1204 and 1106 cm^{-1}, and centred at 1150 cm^{-1} (see Fig. 7). Decomposition of the GP sample spectra of Si/Al = 3.0–4.0 (Fig. 7), shows the development of an extra band (a shoulder) between 1150 and 1160 cm^{-1}, which indicates the presence of amorphous silica. In all spectra, there is also the presence of a small absorption band at ~1500 cm^{-1} relating to the presence of anti-symmetric stretch of CO_3^{2-} ions. The fact that these are of low intensity suggest that GPs are less prone to atmospheric carbonation than ordinary Portland cement.

Thus all data sets suggest less polymerisation at higher Si/Al ratios, in agreement with the interpretation of the compressive strength data of Rowles et al. [18], and in line with the data showing increasing leachability at high Si/Al ratios for Na and Si.

3.1. Cs, Sr and Al releases

As Al occupies positions within the network, it might be expected that it would exhibit similar leaching behaviour to that of Si, but this is not observed, as shown in Figs. 8 and 9. This is probably indicative that all Al is in the 3-D polymerised phase at higher Si/Al values, which would account for the low normalised Al releases. As Si/Al increases from 1.5 to 4.0, Si leachability increases sharply at Si/Al = 2.5, whereas Al leachability decreases sharply. Normalised Si releases are 10 times higher than normalised Al releases for these GPs, and most probably include dissolution of unpolymerised (amorphous) silica [25] as well as some silicon from the GP framework. This is backed up by the NMR and IR studies which also indicated the presence of amorphous silica at higher (>2.5) Si/Al molar ratios (see above).

SEM EDS and TEM studies indicated that Cs is present within the GP matrix [21], at least for Si/Al molar ratios of 2. Lower Cs releases are observed at lower Si/Al molar ratios (higher degree of polymerisation) – see Fig. 9, because the GP matrix accomodates the Cs ions which are more strongly coupled to the framework than Na [11,21].

From TEM measurements, it was shown that Sr was partly incorporated in the amorphous phase and partly as $SrCO_3$ [21]. The presence of the $SrCO_3$ precipitate is very probably what limits the Sr normalised releases to quite low values.

At higher Si/Al molar ratios (3.0, 3.5, 4.0), the normalised Sr releases are relatively higher than those at the lower Si/Al molar ratios – see Fig. 9, and this may be due to particulates of $SrCO_3$ (less than ~0.45 μ) physically disengaging from the GP during leaching, followed by subsequent dissolution of Sr after acidification of leachates.

PCT-B leachates (90 °C test, over 7 days) of samples showed variations in pH values as seen in Table 4. The most leachable species in geopolymers are the Na ions from (alkaline) pore water transfer to leachates, and framework dissolution by alkali/H_3O^+ ion exchange (see above). At higher Si/Al molar ratios, where there tends to be 2-D rather than 3-D polymerisation, there may be, rel-

atively, more pore water transfer to the leachate, thus increasing its pH more than is the case for samples with the lower Si/Al molar ratios. However, as the alkaline leachate attacks the unreacted constituents and the GP framework to form $Si(OH)_4$ monomer species in solution, OH^- ions are consumed, offsetting the pH rise. The process probably stops or proceeds extremely slowly afterwards due to saturation. Overall, the balance of the reactions giving rise to pH changes is complex and not very well understood.

4. Conclusions

The following conclusions can be drawn from this study:

(a) Na release is the major leaching process in deionised water, and lower normalised Na releases at lower Si/Al molar ratios (1.5, 2.0, 2.5) are consistent with higher degree of 3-D polymerisation (as against 2-D) as shown by MAS NMR, FT-IR and XRD studies.

(b) Only GPs with Si/Al molar ratios of 1.5, 2.0 and 2.5 passed the ASTM/PCT-B test for deep disposal (>500 m underground) for HLW in terms of Na releases which were < 13 g/L. Only GP with Si/Al molar ratio of 1.5 passed the criterion for near surface disposal of LLW (<2.0 g/m^2).

(c) The principal leaching mechanisms in GP with Si/Al molar ratio ~2 which gives rise to Na being the most leachable species, appear to be framework dissolution and pore water dissolution; but it is difficult to decide which process is more important in deionised water at temperatures $\leqslant$90 °C.

(d) GPs with Na/Al molar ratio ~1 and Si/Al molar ratio ~2 may be considered as serious candidates for LLW/ILW immobilisation based on their PCT-B performance. Some European countries, notably Slovakia, have already placed GPs in a repository since 2003. Possible improvements in the fabrication of GPs could include high-shear mixing and lower water contents which are currently under investigation. Further details and advantages of GPs over other candidate materials are discussed in an upcoming book chapter [26].

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Table 4
pH variations of GP leachates (initial pH = 5.50)

Si/Al molar ratio	Final av. pH of leachates
1.5	12.33 ± 0.01
2.0	12.43 ± 0.03
2.5	12.45 ± 0.01
3.0	11.99 ± 0.02
3.5	11.48 ± 0.01
4.0	11.43 ± 0.01

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