

RESEARCH NOTES

³⁹K NMR of Free Potassium in Geopolymers**P. Duxson, J. L. Provis, G. C. Lukey, and J. S. J. van Deventer****Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia***F. Separovic***School of Chemistry, The University of Melbourne, Victoria 3010, Australia***Z. H. Gan***Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310*

Nuclear magnetic resonance (NMR) studies of geopolymer gels have shown directly that free Na cations are present in the pore solution of some specimens. Furthermore, it has been suggested previously but not directly proven that potassium is incorporated into these materials, in preference to sodium. Here, the presence of free potassium in the pore solution of geopolymeric gels prepared without sodium hydroxide was confirmed by ³⁹K NMR. The preferential incorporation of potassium was directly shown by the absence of free potassium in the mixed-alkali geopolymer gel.

Introduction

In a previous report by the authors,¹ 15 geopolymers were synthesized using sodium, potassium, and mixed-alkali silicate activators of different silicon concentrations, and then were characterized by magic angle spinning (MAS) multinuclear nuclear magnetic resonance (NMR). The role of alkali cations and the soluble silicon concentration in the incorporation of aluminum in geopolymers was investigated using ²⁷Al and ²³Na MAS NMR. Al(OH)₄⁻(aq) was identified in all geopolymer samples with a Si/Al ratio of ≤1.40, irrespective of the alkali composition. ²³Na MAS NMR distinguished Na⁺(aq) in the pores of the sodium and mixed-alkali geopolymers, where Na⁺(aq) would provide a charge balancing role for Al(OH)₄⁻(aq). Because Al(OH)₄⁻(aq) was identified in the pores of the potassium geopolymer, it was postulated that K⁺(aq) also would be present, although the authors did not have access to ³⁹K NMR analysis for confirmation.

The presence of aqueous aluminum in geopolymers is believed to be due to the Si/Al ratio in the solution phase being less than unity during synthesis.² Geopolymers with a Si/Al ratio of ≥1.65 did not exhibit a resonance for Al(OH)₄⁻(aq) in the ²⁷Al MAS NMR spectra, which clearly demonstrated that there is a link between the composition of the activator solution and the incorporation of dissolved aluminum in the binder.¹ The broad resonance for sodium that was associated with aluminum in the ²³Na MAS NMR spectra of sodium-containing geopolymers does not exhibit a change in chemical shift as the Si/Al ratio is varied, from which it can be inferred that the mechanism of sodium incorporation is unaffected by the Si/Al ratio. The preferential incorporation of sodium over potassium was inferred

from the proportionally higher intensity of Na⁺(aq) in the ²³Na spectrum of a mixed-alkali geopolymer, compared with the resonance of Na⁺ cations in the charge-balancing site.

³⁹K MAS NMR analysis is technically difficult, because of the low frequency of the NMR-active isotope and the corresponding low sensitivity. The only known ³⁹K NMR study of geopolymers showed a single resonance at -44 ppm for a specimen with a Si/Al ratio close to unity, and -92 ppm for a specimen with a Si/Al ratio close to 2.³ The spectra of these earlier samples, which were heated to 1400 °C, were collected at 23.236 MHz and over a very large spectral window. With the recent advances in solid-state NMR technology, significant improvements in signal-to-noise and spectral resolution are anticipated. In an extension of the previous work by Duxson et al.,¹ here, we report the results of a ³⁹K NMR study of several potassium-bearing geopolymer gels to determine the speciation of potassium in specimens with a Si/Al ratio from close to unity up to ~2.

Experimental Methods

NMR Spectroscopy. Solid-state ³⁹K NMR spectroscopy was performed in a magnetic field of 19.6 T (38.70 MHz) at the National High Magnetic Field Laboratory (Tallahassee, FL), using a Bruker (Karlsruhe, Germany) DRX spectrometer and a 4-mm MAS probe. All ³⁹K chemical shifts were referenced to the secondary standard of solid KBr at 0 ppm. The spinning speed for all MAS experiments was 10 kHz. A rotor synchronized spin-echo pulse sequence was used (5 μs pulse-92.5 μs delay-10 μs pulse-92.5 μs delay-acquisition). The radio frequency (RF) field was 25 kHz (5 μs and a 90° pulse, considering a factor of (S + 1/2)). A recycle time of 0.1 s was used and 102 400 scans were acquired.

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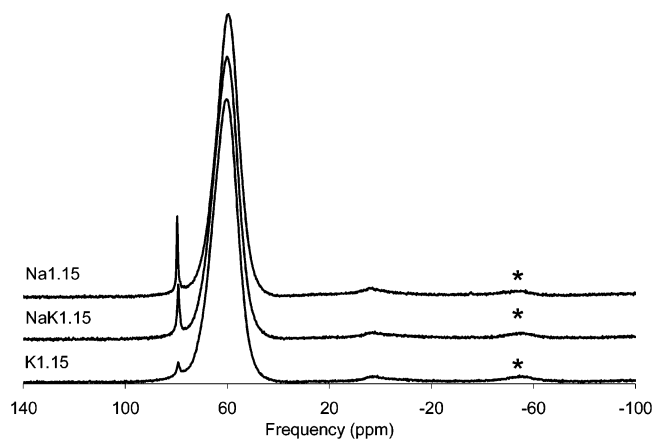


Figure 1. ^{27}Al MAS NMR spectra of Na1.15, NaK1.15, and K1.15 geopolimer gels. Asterisk symbol (*) indicates MAS sidebands. Data taken from Duxson et al.¹

Materials. Metakaolin was purchased under the brand name of Metastar 402 from Imerys Minerals, U.K. The metakaolin contains a small amount of a high-temperature form of muscovite (Powder Diffraction File (PDF) Card No. 46-0741) as an impurity. The chemical composition of metakaolin, as determined by X-ray fluorescence (XRF), was (2.3:1) $\text{SiO}_2/\text{Al}_2\text{O}_3$. The Brunauer–Emmett–Teller (BET) surface area of the metakaolin, as determined by nitrogen adsorption on a Micromeritics (Norcross, GA) ASAP2000 instrument, was $12.7 \text{ m}^2/\text{g}$ and the mean particle size (d_{50}) was $1.58 \mu\text{m}$.

Alkaline and alkaline silicate solutions that were based on three ratios of alkali metal ($\text{Na}/(\text{Na} + \text{K}) = M$, where $M = 0.0, 0.5, \text{ and } 1.0$) with a composition of $\text{SiO}_2/\text{M}_2\text{O} = R$ (where $R = 0.0, 1.0, \text{ and } 2.0$) and $\text{H}_2\text{O}/\text{M}_2\text{O} = 11$ were prepared by dissolving amorphous silica (99.8%, Cabot Corp., Billerica, MA) in appropriate alkaline solutions until clear. Solutions were stored for a minimum of 24 h prior to use, to allow equilibration at ambient temperature.

Geopolymer Synthesis. Geopolymer samples were prepared by mechanically mixing stoichiometric amounts of metakaolin and alkaline solution with an $\text{Al}_2\text{O}_3/\text{M}_2\text{O}$ ratio of 1 to form a homogeneous slurry. After 15 min of mechanical mixing, the slurry was vibrated for an additional 15 min, to remove entrapped air before the slurry was transferred to Teflon molds and sealed from the atmosphere. Samples were cured in a laboratory oven at $40 \text{ }^\circ\text{C}$ and ambient pressure for 20 h before being transferred from molds into sealed storage vessels at ambient temperature and pressure for two weeks prior to pulverization for use in NMR experiments. To reflect the different Si/Al compositions, samples synthesized from Na, Na/K, and K alkaline solutions are referenced in the text as NaX, NaKX, and KX, respectively (where X is the nominal Si/Al ratio).

Results and Discussion

^{27}Al MAS NMR spectra, adapted from a previous study,¹ of the three geopolymers studied in the present work are shown in Figure 1. Three resonances can be observed in each spectrum, at ~ 0 , ~ 60 , and 80 ppm . The peak at 0 ppm is due to unreacted aluminum(VI) from metakaolin, whereas the peak at 60 ppm is comprised of resonances from both unreacted aluminum(IV) in metakaolin and aluminum(IV) in the newly formed geopolymer gel. The peak at 80 ppm is from free $\text{Al}(\text{OH})_4^-$ (aq).⁴ The size of the peak at 80 ppm clearly decreases in the following order: Na1.15 > NaK1.15 > K1.15.

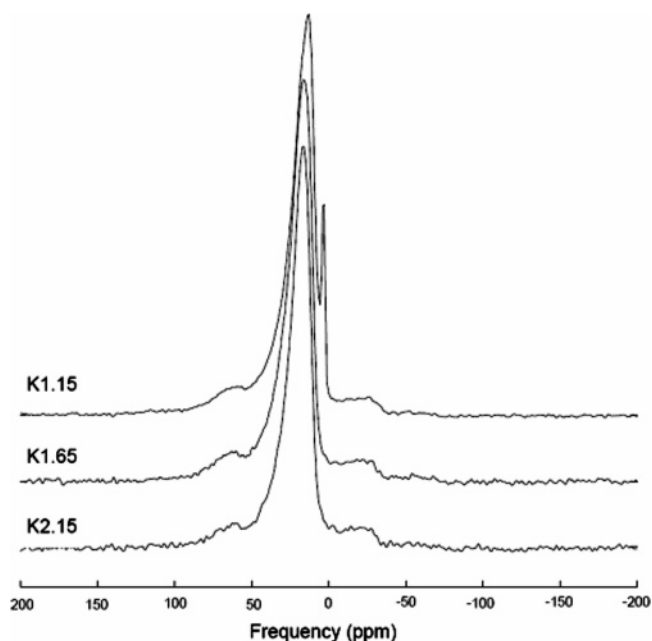


Figure 2. ^{39}K MAS NMR spectra of K1.15, K1.65, and K2.15 geopolimer specimens.

Figure 2 shows the ^{39}K MAS NMR spectra of geopolymers with only potassium as the charge-balancing cation. A single large resonance was observed for each specimen, although the position of this peak is shifted slightly from 13.5 ppm in the K1.15 specimen to 16.5 ppm in the K1.65 and K2.15 specimens. The shape of the spectra is due to the quadrupolar nature of the ^{39}K species. Also, an additional isotropic peak at 0 ppm was present only in the K1.15 specimen. The peak at $13\text{--}16 \text{ ppm}$ in these spectra results from potassium acting as a charge-balancing cation for aluminum in the tetrahedral network of the gel, whereas the peak observed at 0 ppm is from K^+ (aq). This provides clear and direct evidence of the existence of free potassium in the pores of geopolymers with a Si/Al ratio that is close to unity, as has been implied previously.¹ The slight shift in the resonance of the main peak between the K1.15 and K1.65 specimens is likely to be related to the presence of free potassium. The several-orders-of-magnitude improvement in the signal-to-noise ratio and half-height peak width of the resonances in these spectra, compared to the previous work of Barbosa and MacKenzie,³ allows us to distinguish these peaks.

The ^{39}K MAS NMR spectra of mixed-alkali (sodium and potassium) geopolymers are shown in Figure 3. Only a single resonance at 17 ppm is present in each spectrum, indicating that there is little change in the environment of potassium in the mixed-alkali specimens. Because there is no evidence of K^+ (aq) in the pores of the NaK1.15 specimen (i.e., no peak at 0 ppm), this provides a clear indication that potassium is preferentially incorporated into the solid phase of mixed-alkali geopolymer specimens, as free Na^+ (aq) was observed previously in the pore solution of these specimens using ^{23}Na MAS NMR.¹

This observation—that K^+ is preferentially associated with the geopolymer gel phase, rather than remaining free in the pore solution—may also be correlated with the observations of McCormick et al.,^{5,6} in regard to the effects of cation size on the strength of ion pairing interactions in silicate and aluminosilicate solutions. Smaller alkali cations were observed to pair more strongly with less highly connected anionic species in both silicate and aluminosilicate systems, whereas larger cations had a tendency to be associated primarily with more highly connected anions. Given that the tetrahedral framework sites

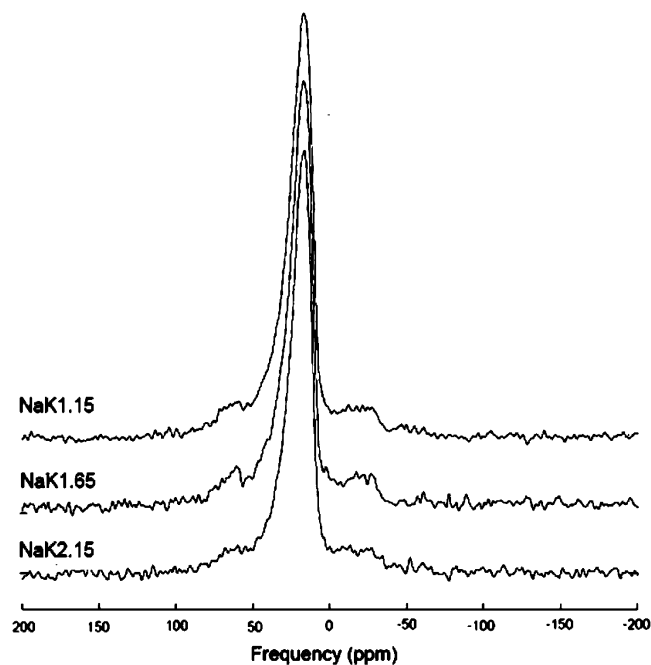


Figure 3. ^{39}K MAS NMR spectra of NaK1.15, NaK1.65, and NaK2.15 geopolymer specimens.

in the geopolymer gel will obviously show a higher degree of connectivity than the aluminate monomers present in solution, the observation that, in a mixed NaK-geopolymer, K^+ has a tendency to be incorporated into the gel, while Na^+ is inclined to remain dissolved may, therefore, be rationalized. The preferential incorporation of potassium over sodium may also relate to differences in the solubility of these species, in terms of the Gibbs free energies. These results indicate a need to clarify how the sodium and potassium levels in solution evolve throughout the reaction process.

Conclusions

New experimental ^{39}K MAS NMR spectra of potassium-containing and mixed-alkali metakaolin-derived geopolymers are presented. Given the advances in solid-state NMR, the

spectra are of significantly higher quality than those previously available in the literature and show the presence of free potassium in geopolymer gels made without NaOH. Earlier data shows that the amount of free $\text{Al}(\text{OH})_4^-$ present in geopolymers with a Si/Al ratio that is close to unity decreases in the following order: $\text{Na} > \text{NaK} > \text{K}$. Clear evidence has been presented to show that free K^+ is present in the pore solution of the potassium geopolymer with a Si/Al ratio that is close to unity, which must charge-balance the framework aluminate sites. However, the absence of observable K^+ in the NaK specimens indicates that potassium is preferentially incorporated into the gel phase, compared to sodium.

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