^{17}O MAS-NMR Investigation of Geopolymer Binder Structure

J.L. Provis, P. Duxson, C.E. White, J.S.J. van Deventer (U. Melbourne, Chemical & Biomolecular Engineering); J.D. Gehman, F. Separovic (U. Melbourne, Chemistry/Bio21 Institute); Z. Gan (NHMFL)

Introduction

NMR study of ^{17}O-enriched geopolymers provides a unique opportunity to directly observe gel structure without interference from (non-enriched) unreacted aluminosilicate precursors. The study of low-silica (Si/Al ~ 1) geopolymers by ^{17}O 3QMAS is based on predictions from ^{29}Si MAS NMR and computational modeling [1,2]. However, the full analysis of these data requires the availability of spectra for samples synthesized across a wider range of Si/Al ratios, up to Si/Al = 2, to determine trends in peak shape, position and width. These spectra were obtained using a 19.6 T spectrometer at NHMFL, giving a very high signal-to-noise ratio and enabling clear identification of the different oxygen environments in these materials.

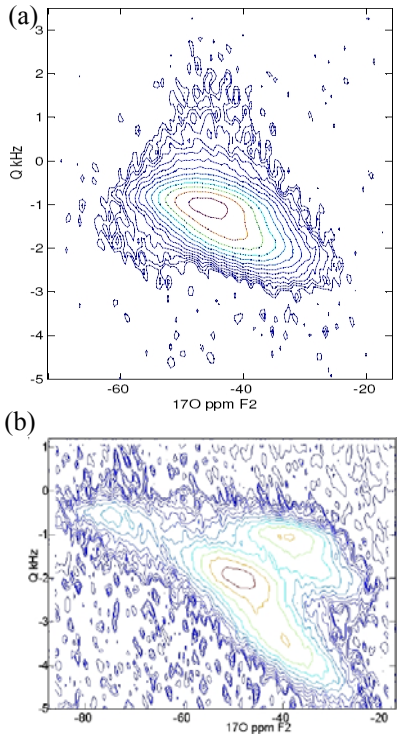

Figure 1. *^{17}O 3QMAS NMR spectra of geopolymers with: (a) Si/Al = 1.25, and (b) Si/Al = 2.0*

Experimental

Samples were prepared from a synthetic aluminosilicate powder using the polyvinyl alcohol method [2]. This aluminosilicate solid was mixed with potassium hydroxide or silicate solution enriched in ^{17}O. The samples were then cured at 40°C for 24 hours. Prior to NMR analysis, the samples were dried to ensure no free water was present. Solid-state NMR spectroscopy was performed at 19.6 T (112.43 MHz for ^{17}O nuclei) at the National High Magnetic Field Laboratory (Tallahassee, FL), using a Bruker (Karlsruhe, Germany) DRX spectrometer and a 4-mm MAS probe spinning at 10 kHz. All ^{17}O chemical shifts were referenced to H_2O at 0 ppm. ^{17}O 3QMAS NMR spectra were collected using a shifted-echo pulse sequence composed of two hard pulses with durations of 3.5 µs and 1.5 µs, followed by a soft pulse of 10µs. The recycle time for all experiments was 0.2 s. MQMAS spectra were analyzed by performing 2D Fourier transformations sheared by a factor of 3 to provide a pure quadrupolar component along the F1 axis.

Results and Discussion

Figure 1 presents the ^{17}O 3QMAS NMR spectra of geopolymers with Si/Al = 1.25 and 2.0. Figure 1(a) shows that the sample with Si/Al = 1.25 is dominated by the Si-O-Al bonding environment with a relatively low quadrupolar parameter. Figure 1(b) shows that at Si/Al = 2.0 the sample exhibits a large Si-O-Si peak, a Si-O-Al peak in a similar location to that in the lower-silica sample, as well as a small peak attributed to the Si-O-H environment. This is the first time these non-bridging oxygen sites have explicitly been observed in geopolymers. Quantification and simulation of these spectra, as well as those obtained at intermediate Si/Al ratios (1.5 and 1.75), is ongoing and is expected to provide detailed data for comparison with theoretical models of the framework bonding environment of geopolymers [3].

Conclusions

^{17}O 3QMAS NMR spectra showing the changes in Si-O-Al and Si-O-Si bond environments in geopolymers across the range Si/Al = 1.25 to 2.0 were obtained, and provide key information relating the chemical shift, lineshape and peak intensities to the sample compositions. Ongoing work is aimed at quantifying and simulating these spectra, which will provide detailed information for comparison with the results of previous ^{29}Si MAS NMR studies and statistical thermodynamic modeling.

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References

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