^{39}K NMR OF FREE POTASSIUM IN GEOPOLYMERS

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Introduction

^{39}K MAS NMR is technically difficult due to the low frequency of the NMR-active isotope, and corresponding low sensitivity. The only known ^{39}K NMR study of geopolymers showed a single resonance at -44 ppm for a specimen with Si/Al ratio close to unity, and -92 ppm for a specimen with Si/Al ratio close to 2. 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 recent advances in solid-state NMR technology, significant improvements in signal to noise and spectral resolution is anticipated. In an extension of the previous work we report the results of a ^{39}K NMR study of several potassium-bearing geopolymer gels to determine the speciation of potassium in specimens with Si/Al ratio from close to unity up to approximately 2.

Experimental

The gels were prepared by reaction of metakaolin ($2.3 \cdot SiO_2.Al_2O_3$) in alkali solution (SiO_2/M_2O = 0, 1, 2), $H2O/M_2O$ = 11, M = (1:1)NaK or K). Specimens were cured at 40°C for 24 hours and crushed and dried to remove isotropic contributions from water for use in NMR. ^{39}K solid-state NMR spectroscopy was performed at 19.6 T (38.70 MHz) at the National High Magnetic Field Laboratory (Tallahassee, Florida), using a Bruker (Karlsruhe, Germany) DRX spectrometer and a 4-mm MAS probe. All ^{39}K 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 RF field was 25 kHz (5 µs 90° pulse considering (S+1/2) factor). A recycle time of 0.1 s was used and 102,400 scans were acquired.

Results and Discussion

Figure 1a 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. Also, an additional isotropic peak at 0 ppm was present only in the K1.15 specimen. The peak at 13-16 ppm in these spectra result from potassium acting as a charge balancing cation for aluminum in the tetrahedral network of the gel, while 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 Si/Al ratio close to unity as has been implied previously.[1] The ^{39}K MAS NMR spectra of mixed alkali (sodium and potassium) geopolymers are shown in Figure 1b. As no evidence of K^+(aq) in the pores of the NaK1.15 specimen (i.e., no peak at 0 ppm) 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 by ^{23}Na MAS NMR.

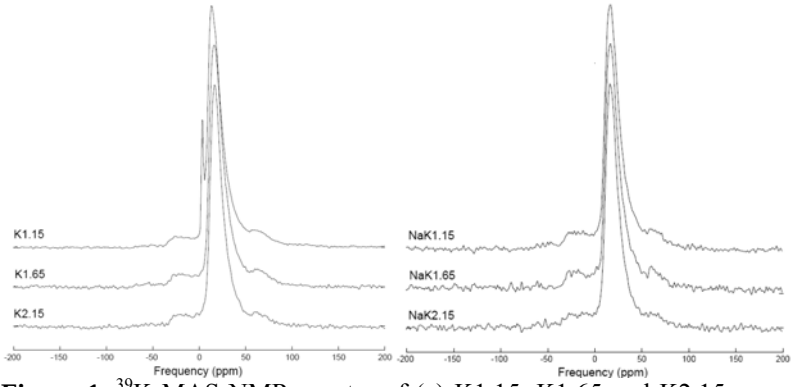

Figure 1. ^{39}K MAS NMR spectra of (a) K1.15, K1.65 and K2.15 geopolymer specimens, and (b) NaK1.15, NaK1.65 and NaK2.15 geopolymer specimens.

Conclusions

Clear evidence has been presented to show that free K^+(aq) is present in the pore solution of the potassium geopolymer with Si/Al ratio close to unity, which must charge-balance the framework aluminate sites. However, the absence of observable K^+(aq) in the NaK specimens indicates that potassium is preferentially incorporated into the gel phase compared to sodium.

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