# Local Environments of Slags:
# The First Application of $^{43}$Ca 3QMAS NMR Technique

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We first applied $^{43}$Ca 3QMAS NMR spectroscopy for $^{43}$Ca-enriched model slags. Local environments of $Ca^{2+}$ ions in slow- and rapid-quench model slags were found to be different each other. The slow-quench slag has well-defined $CaO_8$ polyhedra in a crystalline form, although the rapid-quench slag is considered to have $CaO_6$ octahedral species as a main component.

Alkaline earth metals such as Ca and Mg play an important role in many organic and inorganic compounds. However, local environments around these modifier ions have never been well investigated in detail. NMR spectroscopy is one of robust structural analysis tools focused on a specific element, and has an advantage over XAS (X-ray absorption spectroscopy) at the point that site distributions can be observed for the given atomic species. NMR studies on $^{25}$Mg in inorganic compounds have been reported by several workers.[1–4] On the other hand, solid-state $^{43}$Ca NMR measurement has been difficult because of a low natural abundance (0.135%) and very low Larmor frequency (20.2 MHz at 7.0 Tesla). Moreover, second-order quadrupolar interaction ($I = 7/2$) results in a signal broadening, and, therefore, prevents the detailed determination of the Ca local environments. MQMAS (multiple quantum magic angle spinning) technique[5] is a very effective method for obtaining intimate structural information on half-integer quadrupolar nuclei in solids by virtue of averaging out the second-order quadrupolar broadening. However, MQMAS has lower signal sensitivity in compensation for the higher spectral resolution. In this study, we overcome the problems by using high magnetic field, a developed and specialized high-power radio frequency resistant probe, and $^{43}$Ca isotope labeling. We successfully have demonstrated the first $^{43}$Ca 3QMAS spectra for $^{43}$Ca-enriched model slags, and discussed the local environments of $Ca^{2+}$ ion in the slag structures.

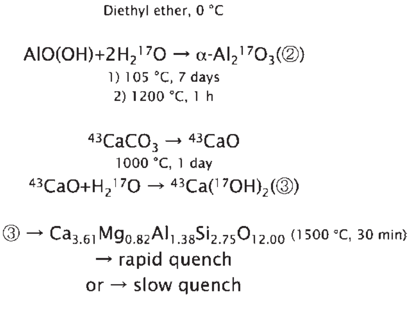

**Figure 1.** Synthesis schemes of the isotope-labeled starting materials.

Inorganic materials in $CaO–MgO–Al_2O_3–SiO_2$ (CMAS) join, such as a slag, are of great importance for industrial resources. Chemical composition of model slag is the same as typical blast-furnace slag (43.0 wt% CaO, 7.0 wt% MgO, 15.0 wt% $Al_2O_3$, 35.0 wt% $SiO_2$). We used $^{43}$Ca- (66 wt%-enriched) and $^{17}$O-labeled $^{43}Ca(^{17}OH)_2$ synthesized from $^{43}CaCO_3$ (Trace Sciences International Inc.) and $H_2{}^{17}O$, $Mg(OH)_2$, $Al_2{}^{17}O_3$, and $Si^{17}O_2$ powders as starting materials (Figure 1). $^{17}$O-Labeling will be effective in next works. Two slags were prepared with different quenching rate. Rapid-quench slag was prepared by melting a mixture of reagents at 1500 °C for 30 min and subsequent quenching on a copper plate. Slow-quench slag was prepared in same manner but quenched by $-20\,°C/min$ in a furnace. The obtained rapid- and slow-quench slags were transparent and opaque, respectively.

$^{43}$Ca NMR spectra were acquired on a JEOL model JNM-ECA700 spectrometer (16.4 Tesla) at 47.1 MHz. A home-built 4-mm MAS probe was used, which endures a very high power rf field. The actual 90° pulse width at ca. 1 kW is 2.0 µs for both slags. Samples were spun at 18 kHz. $^{43}$Ca chemical shifts were referenced to saturated $CaCl_2$ solution at 0.0 ppm. All MAS spectra were acquired with a pulse width of 1.0 µs, which corresponds to 18° pulse for aqueous $CaCl_2$. The pulse delays were 25 and 50 s and the total acquisition times for 3QMAS measurements were 38 and 75 h for rapid- and slow-quench slags, respectively. In 3QMAS, z-filter sequence[4] was applied, which is easily adjustable compared to other sophisticated and effective sequences such as FAM. Each 4.2 µs length for excitation pulse and 1.5 µs length for conversion pulse were optimized.

Figure 2 shows $^{43}$Ca MAS spectra of rapid- and slow-quench slags along with $Ca(OH)_2$. This indicates that Ca environments in synthesized slags are clearly different from the source, $Ca(OH)_2$. $Ca(OH)_2$ has a doublet peak, which is due to second-order quadrupolar interaction.[6] For rapid-quench slag the MAS spectrum represents a broad signal (FWHM ≈ 73 ppm) centered at 19.1 ppm, implying that $Ca^{2+}$ ions are in disordered phase. On the other hand, slow-quench slag has a rather sharp peak (FWHM ≈ 20 ppm) at −13.4 ppm with a subtle shoulder at ca. 13 ppm. The relatively sharp peaks suggest well-defined Ca sites in some crystalline phases. Dupree et al.[7] reported natural abundance $^{43}$Ca MAS spectra for several minerals, and suggested a relationship between isotropic chemical shifts and average Ca–O distances. The isotropic shifts can be determined to 64.1 and 1.6 ppm from the MAS chemical shifts for rapid- and slow-quench slags, and average Ca–O distances are estimated to be 2.30 and 2.58 Å, respectively. These values correspond to six- and eightfold Ca sites, respectively. It is well known that $Ca^{2+}$ ions mainly locate octahedral sites in silicate glasses.[8] Therefore, the octahedral $Ca^{2+}$ species in rapid-quench

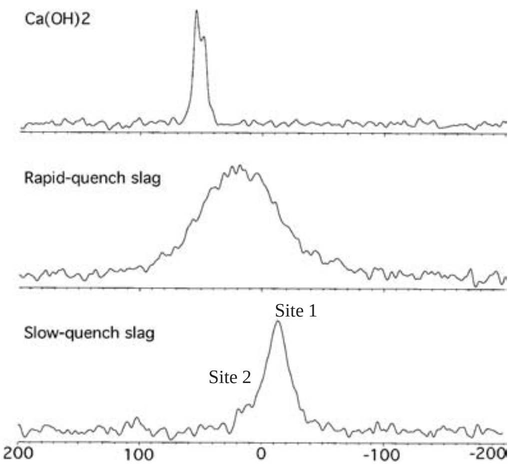

**Figure 2.** $^{43}$Ca MAS NMR spectra of $Ca(OH)_2$, and two slags with distinct quench speed. Horizontal axis is relative frequency in ppm unit.

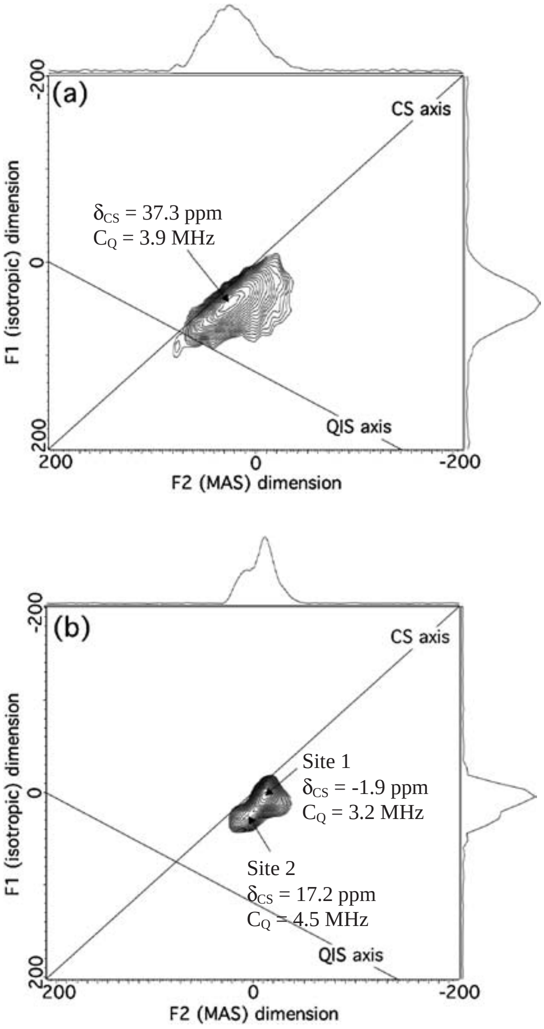

**Figure 3.** $^{43}$Ca 3QMAS NMR spectra of (a) rapid- and (b) slow-quench slags. Vertical and horizontal axes show relative frequency in ppm.

slag is very convincing. The broad peak distribution in rapid-quench slag may suggest a minor existence of the several species with lower- or higher-coordination polyhedra. Saturation recovery provides $T_1$ relaxation delays of ca. 5 and 13 s for rapid- and slow-quench slags, respectively. This result also indicates that the $Ca^{2+}$ ions in slow-quench slag locate in relatively regular sites compared with that in rapid-quench slag. An additional XRD measurement determined that the crystalline phase occurred in slow-quench slag should be in åkermanite–gehlenite solid solution, where $Ca^{2+}$ is eight-coordinated. An examination of average Ca–O distances and $CaO_8$ polyhedral distortions in åkermanite and gehlenite allows an assignment of sites 1 and 2 to Ca environments in åkermanite and gehlenite, respectively. Relative intensity in the MAS spectrum estimated the ratio of åkermanite/gehlenite to be ca. 4.5.

Figures 3a and 3b represent 3QMAS spectra of rapid- and slow-quench slags, respectively. The $\delta_{CS}$ and $C_Q$ were calculated from the 2D spectra.[9] These results are the first practical application of $^{43}$Ca MQMAS for inorganic materials. The 3QMAS spectrum of rapid-quench slag has a broad distribution as in the corresponding MAS spectrum. In 3QMAS experiment, the broadened single Ca site is found, although there is a subtle indication of multiple sites from the asymmetric contour peak shape. On the other hand, the slow-quench slag shows two distinct sites at least with a hint of additional site. The two-dimensional distributions of both slags run along the chemical shift (CS) axis. The lower frequency tail in the distribution of rapid-quench slag overlaps with the site 2 in slow-quench slag, suggesting that a part of Ca sites in the amorphous phase may be in a relatively regular environment similar to gehlenite structure.

In conclusion, we successfully demonstrated the first observation of $^{43}$Ca 3QMAS NMR spectra with excellent S/N ratio, by virtue of high magnetic field, a high power rf-resistant probe, and $^{43}$Ca-labeling technique. This study gives a new practical information on $Ca^{2+}$ ion in the amorphous structure, which has never been well determined. $^{43}$Ca MQMAS NMR should provide novel and useful information on chemical environments of various Ca-containing solid materials with complex structures.

## References

1 N. G. Dowell, S. E. Ashbrook, and S. Wimperis, *J. Phys. Chem. B*, **108**, 13292 (2004).
2 P. S. Fiske and J. F. Stebbins, *Am. Mineral.*, **79**, 848 (1994).
3 K. J. D. MacKenzie and R. H. Meinhold, *Am. Mineral.*, **79**, 250 (1994).
4 M. Hatakeyama, T. Nemoto, K. Kanehashi, and K. Saito, *Chem. Lett.*, **34**, 864 (2005).
5 L. Frydman and J. S. Harwood, *J. Am. Chem. Soc.*, **117**, 5367 (1995).
6 Z. Lin, M. E. Smith, F. E. Sowrey, and R. J. Newport, *Phys. Rev. B*, **69**, 224107 (2004).
7 R. Dupree, A. P. Howes, and S. C. Kohn, *Chem. Phys. Lett.*, **276**, 399 (1997).
8 P. H. Gaskell, M. C. Eckersley, A. C. Barnes, and P. Chieux, *Nature*, **350**, 675 (1991).
9 C. Fernandez and M. Pruski, 10th Annual Varian/Chemagnetics Solid-State NMR Workshop, Varian publisher, Palo Alto (1999).

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