

Reactive Surface Area In the Environment

Reactivity of minerals, whether via dissolution or adsorption processes, is controlled by the interfacial region between the bulk mineral and the surrounding solution/environment. A critical element for understanding the mechanisms and kinetics of adsorption and dissolution is the quantification of reactive sites, or more generally, the determination of *reactive surface area*.

Currently, two competing models are in use for the normalization of dissolution kinetic data from glasses, clays, and minerals. These models employ either the geometric surface area or the Brunauer, Emmett, Teller (BET) gas adsorption isotherm (Figure 1). The advantage that BET has over geometric surface area is that it includes roughness in the overall measurement. However, questions exist over the utility of including internal surface area (e.g., mesoporosity) in the specific surface area. We have proposed an alternative scaling factor for the comparison of reaction rates in the environment, which involves chemical reactions on the surface of a material, following by spectroscopic analysis of the resulting surface complexes (Figure 1, right). In-depth reaction studies with model gel systems (Figure 2) provide a model for attachment to specific reactive hydroxyl groups (those not part of strongly hydrogen-bonded networks), and results from a suite of natural aluminosilicate glasses demonstrate a linear correlation between glass dissolution rate and hydroxyl numbers measured with our method.

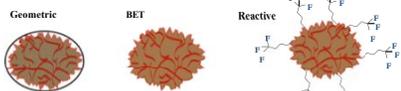


Figure 1. Surface area models used for scaling environmental reaction rates.

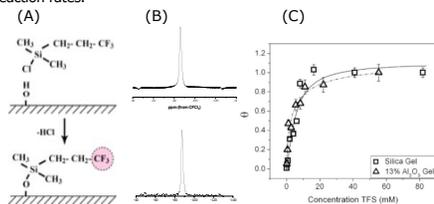


Figure 2. (A) Oxide surface attachment of a fluorine containing silane, 3,3,3-(trifluoropropyl)dimethylchlorosilane, also known as TFS. (B) Quantitative ¹⁹F detection via NMR on silica gel (top) and a mesoporous alumina (bottom). (C) Adsorption isotherm curves for TFS attachment to silica gel and 13% Al₂O₃ weight percent aluminosilicate gel, demonstrating similar uptake of the TFS probe.

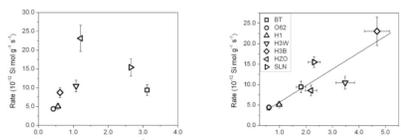


Figure 3. Mass normalized dissolution rate plotted as a function of BET surface area (left) and the number of reactive hydroxyls per gram (right) for a suite of seven low-surface-area rhyolitic and dacitic volcanic glasses.

High-Field NMR and Kinetic Analysis

Our preliminary studies have focused on the identification and quantification of neophases formed in a kaolinite/simulated tank waste leachate (STWL) system as a function of reaction time, where variable-field ²⁷Al magic-angle spinning (MAS) NMR provides kinetic data for the formation of four aluminum-containing neophases (Figures 4 and 5). Further experiments have now been performed on Hanford sediment samples (Figure 6).

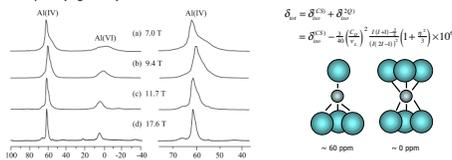


Figure 4. ²⁷Al MAS NMR data demonstrate line shifting and narrowing in both the four-coordinate and six-coordinate Al regions of the spectra as a function of magnetic field strength. The equation for total measured shift (upper right) allows extraction of quadrupolar NMR parameters describing the local symmetry and strength of the electric field gradient experienced by the Al nuclei in each phase.

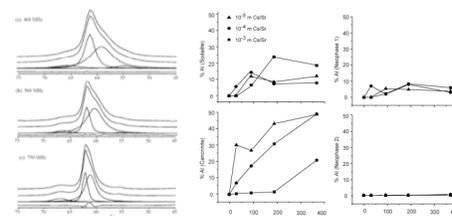


Figure 5. The spectral deconvolution of NMR resonances from four neophases in the kaolinite/STWL system as a function of time and Cs/Sr concentration provides details of the kinetics of kaolinite dissolution and neophase formation. At the right, the evolution of sodalite and cancrinite phases are followed, as well as the evolution of two as of yet unidentified phases. Note the formation of increasing quantities of cancrinite as a function of reaction time, at the expense of the sodalite in the system. Adapted from G. S. Crosson, S. Choi, J. Chorover, M. K. Amistadi, P. A. O'Day, and K. T. Mueller, *J. Phys. Chem. B* **110**, 723-732 (2006).

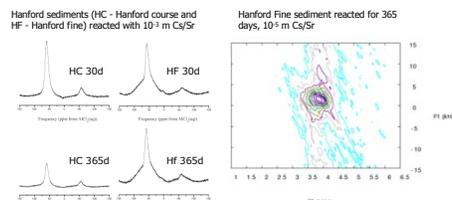


Figure 6. A set of reacted Hanford sediments have also been studied with ²⁷Al MAS and multiple-quantum magic-angle spinning (MQMAS) NMR. The latter technique simplifies the spectral analysis from complex mixtures of phases.

Strontium-87 Solid-State NMR

Solid-state NMR is extremely useful for exploring local cation binding structures. However, applications involving solid-state ⁸⁷Sr NMR have been quite limited to date, primarily due to the extreme sensitivity limitations of NMR when applied to the ⁸⁷Sr nucleus. We first demonstrated that use of the quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) method, coupled with data acquisition at 21.14 T magnetic field strength, provides excellent sensitivity enhancement (Figure 7).

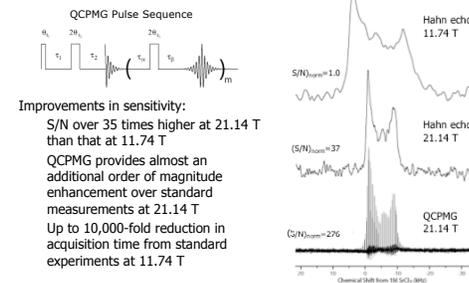


Figure 7. Adapted from G. M. Bowers, A. S. Lipton, and K. T. Mueller, *Solid-State NMR*, **29**, 95-103 (2006).

We then utilized ⁸⁷Sr NMR to study Sr sequestered in a designer fluoromica (Figure 8), again made possible by using advanced methods at the highest magnetic field available to us (the 21.14 Tesla instrument at EMSL). Here, the acquisition time of just over two days is orders of magnitude shorter than if we had acquired these data on a conventional, lower field NMR.

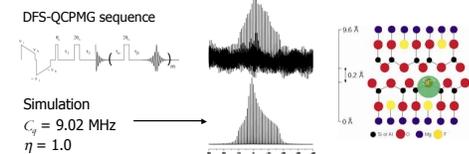


Figure 8. Adapted from G. M. Bowers, R. Ravella, S. Komarneni, and K. T. Mueller, *Journal of Physical Chemistry B* **110**, 7159-7164 (2006).

Acknowledgements

Collaborators: Jon Chorover, Peggy O'Day, Carl Steefel and Jeff Serne
United States Department of Energy
DE-FG07-99ER15012 and DE-FG02-06ER64191
Penn State Center for Environmental Kinetics Analysis
NSF CHE-0431328
Major Research Instrumentation Awards for NMR Spectrometers at PSU
NSF CHE-9601572 and NSF DMR-9413674

Andy Lipton, Joe Ford, and David Hoyt at EMSL/PNNL
A significant portion of the research described here was performed at the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.