

Reactive surface area measurements using a solid-state NMR probe molecule

R.L. SANDERS^{1*} AND K.T. MUELLER²

¹Department of Chemistry, Pennsylvania State University, University Park, PA 16802

(*correspondence: rls410@psu.edu)

²Department of Chemistry, Pennsylvania State University, University Park, PA 16802 (ktm2@psu.edu)

An understanding of the surface reactivity of solids, such as volcanic glasses or clay minerals, is crucial for characterizing numerous environmental processes, including dissolution rates or sorption capacities. The release rate during dissolution or concentration of metal species during sorption is scaled to remove differences in the available solid surface area. Typically, BET or geometric surface area measurements are the convention to calculate surface area. However, these methods do not necessarily report on the *reactive surface area* of a material, which provides a chemically-sensitive measure of surface area. To measure reactive surface area, the probe molecule (3, 3, 3-trifluoropropyl)dimethylchlorosilane (TFS) is attached to lone Q³Si hydroxyl sites and the ¹⁹F spins in the TFS-treated samples are then quantified using ¹⁹F magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The quantification of the number of reactive hydroxyl sites per gram of sample is proportional to the reactive surface area of each solid, which in the case of a set of volcanic glasses has been shown to be proportional to their acid-mediated dissolution rate.

We report here on our on-going studies into reactive surface area using NMR-sensitive probe molecules. In one study, sets of experiments have been conducted on kaolinite to utilize the selective nature of TFS attachment to probe changes in reactive surface area during proton-promoted dissolution. Batch dissolution experiments of kaolinite (KGa-1b) were conducted at 21 °C and pH 3. During the course of three months of dissolution, the reactive surface area of KGa-1b decreased while the BET surface area remained unchanged. These changes in reactive surface area correlate with decreases in the release rates of Si and Al into solution. In on-going experiments, this method is also being utilized to quantify changes in the number of TFS reaction sites upon equilibrium sorption of Cd²⁺, Pb²⁺, and other metal species. The utility of this tool to study competitive ion adsorption on mineral surfaces, which cannot be quantitatively explained or predicted based on single-metal-solid component additivity models, will be evaluated.

Geochemistry and speciation of trace elements captured by various activated carbons in a Canadian coal-fired power plant

HAMED SANEI¹, FRANK HUGGINS² AND FARI GOODARZI¹

¹Geological Survey of Canada, Calgary, AB, T2L 2A7, Canada (hsanei@nrcan.gc.ca)

²Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky, USA

The coal-fired power plants in Canada are required to reduce the emission of Hg up to 80% by 2018 and beyond to meet the national and regional regulatory targets. Activated carbon is considered by industry as an efficient sorbent to capture Hg from the flue gas during the combustion process. A widespread use of activated carbon is anticipated by the coal-fired power plants to reduce the emission of Hg and meet their regulatory obligations.

This study provides the preliminary results of a comprehensive study on the geochemistry of ESP fly ash and related feed coal samples during an experiment trial by a full-scale coal-fired power plant in Western Canada. The study investigates the efficiency of capture of Hg and other trace elements by 5 different commercial activated carbons and effects of various parameters such as geochemistry of coal and combustion variables during various activated carbon injection episodes. Furthermore, the study examines the speciation of trace elements using X-ray Absorption Fine Structure (XAFS) spectroscopy and X-ray absorption near-edge structure (XANES).

While the significant amount of Hg is being captured by activated carbons, the ultimate fate of Hg after capture and possible environmental impacts related to handling and use of Hg-rich fly ash has been a major concern. This study investigates revolatilization of Hg at various thermal treatment and the leachability of Hg and other elements from the captured fly ash.