Excess near-critical adsorption of carbon dioxide in porous silica: Linking theory, simulations, and experiment

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Underground injection and storage of carbon dioxide has been proposed as a key element in the effort to reduce the impact of greenhouse gases emissions. Thorough and quantitative understanding of CO_2 adsorption in various mineral environments at thermodynamic conditions expected at potential sequestration sites is a prerequisite for the assessment of their viability.

In the presented study we use simulation as a molecular link between recent small-angle neutron scattering (SANS) results on the behavior of supercritical carbon dioxide confined in silica aerogel [1] and a general theoretical interpretation based on a fundamental statistical thermodynamic solvation formalism [2]. In particular, we investigate the effect of confinement and surface hydroxylation on the excess adsorption of near-critical carbon dioxide in porous amorphous silica, from liquid-like to zero limiting fluid density. The excess adsorption profiles along near-critical isotherms, derived from axial density distribution functions, are compared to the results of SANS experiments. Special attention is paid to the limit of zero CO_2 density, at which the surface adsorption can be described by an equivalent of Henry's constant, which may serve as a simple quantitative characteristic of the surface, as well as a check of thermodynamic consistency.

[1] Rother, G. Melnichenko Y.B. Cole, D.R. Frielinghaus, H. Wignall, G.D. *Phys. Chem. C* **111** (2007) 15736. [2] Cole, D.R. Chialvo, A.A. Rother, G. Vlcek, L. *Phil. Mag.* (2010) in press.

Isotopic Reference Materials: New frontiers leading to new opportunities

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NIST has produced the first of a new series of isotopic Reference Materials (RM) that have been designed to address the present and future needs of the isotope ratio measurement community. The latest generation of thermal and ICP multicollector mass spectrometers are capable of producing isotope ratio measurements with precisions approaching 10 to 100 ppm. However, published data involving different measurement protocols, as well as different instrumentation suggest that significant biases remain and that the accuracy of isotope ratios is drastically less than measurement precision. However, there is good evidence that these same multicollector instruments are capable of measuring absolute differences between two samples with an accuracy approaching measurement precision.

These new isotopic RMs capitalize on this fact by providing high purity solutions that are isotopically homogeneous at the ppm level and are suitable as zeros for delta scale measurements for different elements. Discussion will focus on the new isotopic RMs for Hg (RM 8333), Tl (RM 8358), and Lead (RM 8328). The experimental design for the characterization and utilization of these new isotopic RMs together with provisions for their long term availability will be covered.