

## Nanogeoscience: There's plenty of room at the ground

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Nanogeoscience is emerging as a new discipline bringing together two very distinct scales of length: the micro (atomic at nanoscale) and the macro World. In our group at Kyoto University, we have focused on the possible applications of Nanogeoscience on the Mining and Oil & Gas industry by studying the fundamental interactions of water-oil-rocks interfaces under controlled and realistic conditions. By using First Principles calculations where the systems are treated through Quantum Mechanics to the use of Molecular Dynamics, we have been able to address and explore several issues on Petroleum Technology from Upstream to Downstream. We will review our efforts to apply molecular modeling in the understanding of oil-water-rock interactions at nano scale and present some effective applications of Nanogeoscience on problems related with the Oil and Gas industry. We illustrate such applications through two distinct case studies. First, we have modeled the interaction of a nanodroplet of oil on  $\alpha$ -quartz and amorphous  $\text{SiO}_2$  surfaces under  $\text{H}_2\text{O}$  solution in order to determine the surface tension and the contact angle to study the three-phase wettability phenomena. The oil droplet was modeled based on realistic crude oil data including the most representative hydrocarbon molecules for light and heavy oil systems. The hydrocarbon molecules were described by the well-tested Charmm force field with partial charges obtained by quantum chemistry calculations. The interaction between the oil molecules with the  $\text{SiO}_2$  systems were determined by fitting the ab-initio potential energy surface of isolated hydrocarbon molecules on the  $\text{SiO}_2$  surfaces. The diffusivity of each hydrocarbon molecule on the mixed oil interfaced with  $\text{H}_2\text{O}$  and  $\text{SiO}_2$  was determined under different environmental conditions (temperature, pressure and salinity). Such information is essential to improve the Enhanced Oil Recovery (EOR). In particular, to explore non-conventional fossil-fuel resources such as oil-sand and oil-shale. Additionally, we have studied the interaction and diffusion of  $\text{CO}_2$  within cementitious materials. This is also valuable information to EOR combined with  $\text{CO}_2$  geological sequestration to estimate and tuning cementitious materials to prevent  $\text{CO}_2$  leakage.

## Structure and coordination of aluminum in aqueous solution and on mineral surfaces

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The chemical reactivity of soil surfaces can be significantly altered by the adsorption of metals and the formation of clay coatings. The unique chemistry of the  $\text{Al}^{3+}$  ion plays a central role in clay nucleation and growth as it sorbs to soil surfaces. However mechanism governing these processes remains largely unknown. Elucidating these mechanisms requires a detailed understanding of the structure and coordination of Al, both in solution and at the mineral-water interface.

The geometric and electronic structures of aqueous Al complexes were studied using Al K-edge X-ray absorption near-edge structure (XANES) spectroscopy and Density Functional Theory (DFT). Al solution spectra confirmed the expected presence of octahedral  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  at low pH and tetrahedral  $\text{Al}(\text{OH})_4^-$  at high pH. Spectral comparisons also revealed subtle electronic structure differences among various 6-coordinate complexes. The spectra of Al-organic structures, dominated by a single Al 3p – O 2p orbital contribution, appeared narrower than the  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  spectrum, which included Al 3p – O 2s and split O 2p contributions. Mixed aquo-organic complexes exhibited features intermediate between full-aquo and full-organic ligation, illustrating the utility of this technique in assessing aqueous Al complexation.

Aqueous Al results were then applied to the study of Al adsorption on Fe-oxide (goethite, ferrihydrite) and Si-oxide (silicic acid, quartz) substrates under different physicochemical conditions. The coordination geometry of sorbed Al was found to be highly sensitive to pH (4.0 – 9.0), aqueous Al concentration (100 – 1000  $\mu\text{m}$ ), and reaction time (minutes to months). At low pH, Al sorbed to silica exhibited tetrahedral coordination. As pH and Al loadings were increased, Al on crystalline silica converted to octahedral coordination, while Al on amorphous silica remained tetrahedral. In contrast, Al coordination on Fe-oxides was primarily octahedral for all pH values and Al concentrations examined. We are also using scanning transmission X-ray microscopy (STXM) and micro-diffraction ( $\mu$ -XRD) to understand the distribution and mineralogy of Al phases on reacted substrates. Details of these results and their implications will be discussed.