Effect of dissolved silica concentration on dissolution rate of smectite under highly alkaline condition

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The stability of smectites (i.e. dissolution behavior) has been the primary focus of numerous studies in the safety assessment of subsurface high level radioactive waste repositories. The dissolution rate of smectites depends on several factors such as pH, temperature and deviation from equilibrium. Amongst these factors, the effect of deviation from equilibrium under highly alkaline condition on the dissolution rate has not been sufficiently investigated.

In this study, the effect of dissolved silica on the dissolution kinetics and rate of smectite under highly alkaline conditions was investigated. Flow-through experiments were carried out at 50 deg C and 70 deg C. Dissolved silica concentration in the solutions range from none to 0.5mM (at 50 deg C) and 0.05 to 0.5mM (at 70 deg C). This sets the saturation indices from -1 to -7 in the reacting solution. The Si concentration was analyzed with a UV-visible spectrophotometer following the molybdate blue method. The Al concentrations were measured by Inductively-Couple Plasma Mass Spectrometry (ICP-MS). Samples were taken from the reaction vessels for ex situ Atomic Force Microscopy (AFM) observation to detect changes in surface area and volume of particles.

In flow-through experiments at 50 deg C and 70 deg C, high Si concentrations are observed at the onset. The rise in Si concentration steadily decreased until a steady state condition was achieved. The measured silica concentrations from output solutions are lower than the dissolved silica initially added in the reacting solutions. Polymerization of silica could have been responsible at highly alkaline pH. The dissolution rate was instead calculated based on the dissolved Al concentrations in the output solutions. However, dissolution rates based on dissolved aluminum concentrations is met by difficulty (i.e. underestimated dissolution rates) due to the possibility of co-polymerization with dissolved silica.

Based on ex situ AFM observations on particles from the flow-through setup at 70 deg C, the dissolution rates calculated are slightly slower with an initial dissolved Si concentration of 0.05 to 0.25mM. Significant particle volume decrease at 0.5mM initial dissolved silica concentrations was not detected by AFM observation which makes the computation of dissolution rate very difficult. However, unpaired t-test indicates that the decrease in particle volume between 0.25 and 0.5 mM initial dissolved silica concentrations are drastically slower than at lower initial dissolved silica concentrations (e.g. 0.05 to 0.25mM). This suggests that at very high dissolved silica concentrations in reacting solutions retards the dissolution of smectite. Furthermore, as the delta G of the solution increases the retardation factor of dissolved silica on the dissolution rate of smectites at highly alkaline conditions approximates the predictions from the Transition State Theory (TST)