
**Introduction:** It is estimated that since the late 1950’s, high level nuclear waste containing 1 to 2 million curies of radiation has leaked into the sediments beneath the U.S. Department of Energy’s Hanford Site in southeast Washington [1]. To predict the fate of the radionuclides released into the environment, the thermodynamics and kinetics of reactions that may have occurred between leaked fluids and Hanford sediments (dominantly quartz and feldspar sands) must be known. In this study the kinetics of quartz dissolution in fluids similar to the leaked waste has been investigated.

Many of the leaked fluids contained Al, and were characterized by high pH (9-14), high ionic strength, and relatively high temperature (some were self-boiling) [1]. Quartz dissolves quickly in high pH solutions, but the effect of dissolved Al on the dissolution rate of quartz has not been well characterized, especially at Al concentrations below the solubility of Al oxyhydroxides [2]. Here, we demonstrate that dissolved Al in the form of Al(OH)$_4^-$, in concentrations below gibbsite and boehmite solubility, significantly depresses the rate of quartz dissolution. Furthermore, the observed rate depression is consistent with the hypothesis that Al(OH)$_4^-$ adsors as inner-sphere complexes to silanol groups on the quartz surface, inhibiting the dissolution process.

**Methods:** Batch chemical experiments were performed in which high ionic strength, alkaline, Al-bearing solutions reacted with quartz.

**Batch Experiments.** In each experiment, quartz sand ~0.3 mm in diameter was placed in plastic bottles, which were filled with solution. The bottles were placed in a constant temperature bath (59.2, 75.0, and 88.7 °C), and one bottle at a time was removed for measurement of pH and Si and Al concentrations.

Most solutions investigated were 2 m NaNO$_3$, with 0.0001, 0.001, 0.005, or 0.01 m Al(NO$_3$)$_3$. A free OH$^-$ concentration of 1 m or 0.1 m was obtained by adding enough NaOH, taking into account the formation of Al(OH)$_i$ complexes in solution. Also, solutions with 0.005 m Al(NO$_3$)$_3$ and 0.1 m free OH$^-$ were made with 0.5, 1.0, 2.0, and 4.0 m NaNO$_3$.

**Solution model.** The Geochemist’s Workbench 3.0 [3] (GWB) was used to model the speciation of the reacting solutions. Equilibrium constants for reactions among the solution components and interaction parameters for Pitzer’s model were taken from the literature and incorporated into a GWB database.

**Rate calculations.** Initial, rather than final, rates of silica release were calculated from the solution data because an aluminosilicate (nitrate-cancrinite) formed on the quartz surfaces in many experiments decreasing the observed Si release rate at later times.

**Results and Discussion:** Some general observations can be made about the dissolution rate data. First, the ionic strength of the solutions did not significantly affect the baseline dissolution rate or the degree to which Al(OH)$_i$ in solution depressed that rate. Second, the degree of dissolution rate depression, expressed as a fraction of the dissolution rate at the same pH and temperature without Al in solution, appears to depend solely on the in situ pH and Al(OH)$_4^-$ concentration. Third, the degree of rate depression increases as the pH is lowered. Fourth, the maximum rate depression under these conditions is ~80%.

These data are being interpreted within the paradigm of Dove and coworkers [4-6]. In their work, dissolved cations affected the dissolution rate of quartz in proportion to the fraction of surface sites on which the cations sorbed. In Na$^+$ solutions, Dove [4] showed that the quartz dissolution rate at high pH is proportional to the fraction of >SiOH$^-$ and >SiO$^-$Na$^+$ sites on the surface, as predicted by a Triple-Layer Model (TLM). Surface speciation was assumed to depend on the in situ pH and Na$^+$ concentration in solution. We are extending this model to include the surface reaction:

\[ >\text{SiOH} + \text{Al(OH)}_4^- + \text{Na}^+ \leftrightarrow >\text{SiOAl(OH)}_3^- \cdot \text{Na}^+ + \text{H}_2\text{O} \]

This proposed reaction is consistent with our data because at lower pH the number of >SiOH sites would be greater, allowing for more adsorption of Al(OH)$_i$. Similarly, the fact that the degree of rate depression depends solely on the in situ pH and Al(OH)$_i$ concentration is consistent with the model proposed by Dove [4] for rate enhancement by adsorbed cations. If we assume that the quartz dissolution rate at surface sites where Al(OH)$_i$ is sorbed is much lower than that at >SiO$^-$ and >SiO$^-$Na$^+$ sites, reaction (1) can be incorporated into the TLM described in [4], and an intrinsic equilibrium constant for the reaction can be extracted.

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