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Surface Reaction Kinetics of O_2(aq) Reduction by Ferrous Silicate Minerals

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Laboratory studies of O_2(aq) reduction have been carried out in support of a large international programme on the fate of dissolved oxygen during geological disposal of high level nuclear waste. Dissolved oxygen trapped in a waste repository at the time of closure is a concern due to the possibility of corrosion of engineered barriers and the higher solubility and thus mobility of several long-lived radionuclides (Np, Tc) under oxic conditions. The reactivity of naturally-occurring fracture-filling minerals towards reduction of O_2(aq) was studied in order to better elucidate reaction mechanisms that affect the redox performance of the geological barrier. Samples were taken from a number of hydraulically conductive fractures at the Äspö Hard Rock Laboratory (Sweden), an underground research laboratory for the study of spent nuclear fuel disposal.

Rapid removal (within days) of O_2(aq) was observed in closed laboratory batch reactors containing fracture-fillings and an aqueous solution initially in equilibrium with atmospheric PO_2(g). The observed decay curve for O_2(aq) fits a second-order rate law.

The total concentration of Fe(II) surface sites and the value of the rate constant were estimated by regression analysis of the time series for dissolved oxygen concentration obtained during the experiments. The rate constants obtained fall within the range $-4 < \log k < 2$ (units for k, L $mole^{-1}$ s^{-1}), with the bulk of the experiments demonstrating a rate constant near $\log k = 1$. These rate constants were compared with the corresponding values for oxygenation of aqueous Fe(II) species in solution, and with values obtained by applying the regression analysis to other data sets available in the literature. These comparisons showed the naturally occurring fracture minerals to have a kinetic reactivity towards O^2(aq) reduction that was slightly less than that for the mono-hydroxo ferrous species in solution ($Fe(OH)^+$), but significantly greater than that of the ferrous ion (Fe^{2+}). The reactivity of the fracture minerals was also found to be similar to that previously reported in the literature for hornblende, augite, biotite and basalt (White and Yee 1985, White, Yee and Flexser1985), and for Fe(II) surface complexes on iron oxide minerals (Wehrli 1990).

The rate constants were also applied to the Linear Free Energy Relation of Wehrli (1990) that relates Fe(II) oxidation rates to the redox potential for the one-electron transfer according to the Marcus Theory for outer-sphere electron transfer. The associated redox potentials for the range of rate constants obtained from these experiments and those previously reported falls within the range $0.33 < Eh < 0.52$ V independently reported for ferrous silicate minerals by White and Yee (1985) based on thermodynamic considerations. The theoretical framework outlined by Wherli (1990) now appears to explain a broader range of mineral surface redox reactions than previously proposed, namely outer-sphere electron-transfer reactions occurring between structural Fe(II) in pure minerals or polymineralic mixtures, and solution species.

In addition to an improved understanding of reaction mechanisms, the experiments reported here have the potential to provide a relatively simple laboratory assay for the reactivity of geological materials towards oxygen. The regression analysis applied to the decay curve for O_2(aq) provided estimates of both the second-order reaction constant and the total number of Fe(II) sites on the mineral surfaces. These values are of direct relevance, respectively, to the rate and the capacity of O_2(aq) removal in performance assessment modeling.

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