

KINETICS AND MECHANISMS OF ANION ADSORPTION AND DESORPTION AT THE GOETHITE-WATER INTERFACE USING PRESSURE-JUMP RELAXATION (CHEMICAL KINETICS)

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Abstract

The mechanism(s) and chemical kinetics of adsorption and desorption of inorganic ions on soils and soil constituents cannot be determined by the traditional kinetic methods such as batch, miscible displacement, and stirred-flow techniques. A pressure-jump (p-jump) relaxation apparatus with conductivity detection was employed to investigate the mechanism(s) and chemical kinetics of MoO_4 , SO_4 and SeO_3 adsorption/desorption on goethite in aqueous suspensions. Single relaxations were observed in the SO_4 goethite and SeO_4 goethite systems. The mechanism for adsorption of SO_4 and SeO_4 on goethite involved simultaneous protonation of surface functional OH group and adsorption of the anion on this surface. The intrinsic rate constants showed that the adsorption process, ($\log k_{ads\ \text{SO}_4}^{int} = 8.3$, $\log k_{ads\ \text{SeO}_4}^{int} = 8.55$), was much faster than the desorption process ($\log k_{ads\ \text{SO}_4}^{int} = -0.84$, $\log k_{ads\ \text{SeO}_4}^{int} = 0.52$).

Double relaxations were observed for the MoO_4 and SeO_3 goethite systems. The overall reaction for both systems consisted of two steps. An outer-sphere surface complex forms during the first step and occurs at the β layer, in which the intrinsic forward rate constants, ($\log k_{1,\text{MoO}_4}^{int} = 3.6$, $\log k_{1,\text{SeO}_3}^{int} = 10.6$), are much larger than those for the second step ($\log k_{2,\text{MoO}_4}^{int} = 0.28$, $\log k_{2,\text{SeO}_3}^{int} = -4.0$). A ligand exchange process occurred in the second step resulting in the formation of inner-sphere surface complexes.

The modified triple layer model was successfully used to describe the adsorption of MoO_4 , SO_4 , SeO_4 , and SeO_3 on goethite with the assumption that adsorbed ions may be located at either the α or β layer. Electrostatic parameters, such as surface potentials computed from the model were employed in the relaxation equations to derive the intrinsic rate constants. Excellent agreement was found between the intrinsic equilibrium constants determined from TLM model calculations ($\log k_{\text{SO}_4,model}^{int} = 9.6$, $\log k_{\text{SeO}_4,model}^{int} = 8.64$, $\log k_{\text{MoO}_4,model}^{int} = -0.47$, $\log k_{\text{SeO}_3,model}^{int} = 20.42$ for HSeO_3 and 15.48 for SeO_3). These results indicate that a combination of equilibrium and kinetic studies can and must be

used to ascertain mechanisms for anion adsorption/desorption on soil constituents.