2.1.P01

Experimental study and modelling of adsorption of strontium on iron and manganese oxides

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Migration of radionuclides, in particular ^{90}Sr, in natural waters can be reduced by adsorption on the mineral surfaces. Our general research questions are to study and to compare the mechanisms of Sr adsorption at the hematite (α-Fe_2O_3) and birnessite (δ-MnO_2) surfaces.

The investigations have been carried out by the methods representing a combination of potentiometric acid-base titration and metal uptake experiments. Comparative study of acid-base properties and Sr adsorption on hematite and birnessite has been accomplished for wide range of pH, ionic strength, sorbate/sorbent ratio and temperature.

It was obtained that Sr adsorption on both hematite and birnessite increased with increasing pH as for most cations forming the inner-sphere complexes on mineral surfaces. However, adsorption of strontium takes place over a pH region above the point of zero charge where the surface is negatively charged. In contrast to hematite surface with pH_{pzc} 8.5, pH_{pzc} of birnessite is much lower (<3). So, adsorption of Sr on birnessite occurs against a background of the strong negative surface charge where a electrostatic force are significant. Besides, Sr adsorption on birnessite notably increases with decreasing ionic strength and this is probably due to a competing of Sr^{2+} with the electrolyte ions. Thus, there are indications that strontium may form inner-sphere as well as outer-sphere complexes.

To solve this problem experimental data were simulated using three various surface complexation models: the Constant Capacitance Model (*CCM*), the Extended Constant Capacitance Model (*ECCM*) and the Triple-Layer Model (*TLM*). Treatment of data included tests for formation of both inner-sphere and outer-sphere complexes of different stoichiometric composition. As a result it was shown that the model describing Sr adsorption on hematite surface consists of two surface complexes of inner-sphere type: $\equiv FeOHSr^{2+}$ and $\equiv FeOSrOH^0$. In the case of birnessite, the best fit to experimental data was obtained with the model consisting of three inner-sphere complexes ($\equiv MnOHSr^{2+}$, $\equiv MnOSr^+$ and $\equiv MnOSrOH^0$) and one outer-sphere complex ($\equiv MnO - Sr^+$). The corresponding intrinsic equilibrium constants of the formation of these complexes were calculated for 25, 50, and 75^0 C. Consequently, under condition of low ionic strength and negatively charged surface in the wide range of pH, strontium may form outer-sphere complexes along with inner-sphere complexes. In this case, right the outer-sphere complexation is responsible for the increasing the strontium adsorption near the neutral pH region.

2.1.P02

The energetics of selenite and iodate adsorption onto goethite

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The enthalpies of adsorption of biselenite and iodate onto goethite were measured calorimetrically at two pH conditions (4.6 and 6.0) along with the adsorption isotherms at 25°C and 60°C at the same pH values. We find that adsorption of selenite dramatically affects the energetics of Brønsted reactions on the goethite surface, whereas these enthalpies are unaffected by the presence of iodate. The enthalpies of proton adsorption in the presence of adsorbed iodate are virtually identical to those measured in an inert electrolyte. This effect requires that surface equilibria in the presence of adsorbed selenite be treated using a ternary set of surface complexes [e.g., $>SOH_2^+(s)$, $>SOH(s)$, and $(>SO)_2SeO(s)$] that interact with one another in a manner that cannot be practically treated by studying the separate binary system. Furthermore, the considerable differences between the enthalpies estimated calorimetrically and those estimated by modeling adsorption as a function of temperature indicate that nonidealities of adsorption contribute a large amount of heat to enthalpies determined in the microcalorimeter.