

Sorption behavior of U(VI) on a reference montmorillonite (SWy-2)

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Introduction

Sorption to mineral surfaces is a main retardation mechanism of radionuclide migration in the mineral-water reaction system (Payne et al., 1994; Thomson et al., 1986). It is an important part of the performance assessment to insure long-term safety in the geological disposal of radioactive wastes. Especially, actinide elements are important in the geological disposal because of their long half-lives (Ringwood, 1985). However, even their chemistry is not clearly known at present.

In this work, batch type experiments of U(VI) sorption on a reference montmorillonite (SWy-2) were carried out over various pH, total U(VI) concentration and ionic strength conditions. Montmorillonite is a representative expandable 2:1 type clay mineral that has been known to have both fixed and variable charge sites for a metal cation sorption. It is the major constituent mineral of bentonite that is a strong candidate for the back-fill material used in the radioactive waste disposal. However, the sorption mechanism of radionuclides on montmorillonite has not been clearly understood till now. Uranium(VI) was selected as a model sorbate because of its relatively well-known chemistry among actinides and its environmental significance. A surface complexation model (SCM) based on the batch sorption data and the analysis of the factors affecting sorption was established to obtain macroscopic information on the mechanism of U(VI) sorption on montmorillonite.

Materials and Methods

The sorption experiments were conducted over the pH range of 2 – 10 in 0.1, 0.01, and 0.001 M sodium nitrate (NaNO₃) solutions. Initial U(VI) concentrations were 10⁻⁴, 10⁻⁵, 10⁻⁶, and 10⁻⁷ M. The experiments were conducted in a closed system, where no attempts were made to exclude dissolved carbonate. The appropriate admixtures of montmorillonite suspension, background electrolyte, acid (HNO₃)/base (NaOH) and U(VI) solution were kept in reaction in 15 ml LDPE (low density polyethylene) bottles (Nalgene) for 3 days in a shaking incubator at 25°C. After enough reaction time of 3 days, the final pH was measured (Orion EA940 pH meter and Sure-flow pH electrode) and the separation of solution from solid was conducted by the centrifugation at 41,000 or 90,000 rpm for 30 minutes using a Beckman XL-90 or an Optima™ TLX Ultracentrifuge. The separated solution was analyzed for U(VI) by ICP-AES (Shimadzu ICPS-1000III) or ICP-MS (VG Elemental PQ3).

Results and Discussion

Sorption in 0.001 M NaNO₃ Solution

To examine the influence of the total U(VI) concentration on sorption, the U(VI) sorption data under the same ionic strength conditions were plotted together. In Fig. 1(a), the results of U(VI) sorption on montmorillonite in 0.001 M NaNO₃ solution are plotted as a function of pH for four different initial U(VI) concentrations. The sorption curves as a function of pH showed no low pH sorption edge. Instead, fair amounts of total U(VI) were sorbed in all pH ranges studied. At higher pH values than around 6, the amount sorbed decreased as a function of pH.

Sorption in 0.1 M NaNO₃ Solution

U(VI) sorption on montmorillonite in 0.1M NaNO₃ solution as a function of pH for four different U(VI) concentrations is presented in Fig. 1(b). In this figure we can observe an oxide-like sorption pH edge where the amount sorbed rapidly increased as a function of pH in a narrow pH range of about 2 pH unit. The slope of increase in the extent of sorption as a function of pH decreased and the sorption pH edge shifted to a higher pH with increasing total U(VI) concentrations. This behavior matches the general trend of sorption as a function of metal concentration where no surface precipitation occurs.

SCM Results

Figs 2 and 3 show the SCM results of U(VI) sorption on montmorillonite in different electrolyte concentrations. The U(VI) sorption on montmorillonite showed a distinct dependence on the ionic strength. In 0.001 M NaNO₃ solution, the ion exchange prevails at low pH conditions and then its contribution decreases with increasing pH where the strong binding of U(VI) by the surface complexation reaction occurs (Figs 2(a) and 3(a)). On the other hand, the sorption by ion exchange reaction is never a dominant mechanism over the whole pH range in 0.1M NaNO₃ solution (Figs 2(b) and 3(b)). Instead, the surface complexation is the dominant mechanism of U(VI) sorption, which shows similar feature to the case of oxide minerals. The U(VI) sorbed by ion exchange is bound to the interlayer site by the electrostatic attraction between the positive charge of UO₂²⁺ and the permanent negative charge of the montmorillonite lattice. As our previous spectroscopic study shows the binding strength is so weak that the metal cations bound to the interlayer site are readily exchangeable by the competing metal cations, in the experimental condition, Na⁺ (Hyun et al., 2000). As the solution pH is increased, the edge complexed U(VI) increased, but the ion exchanged U(VI) decreased though the permanent lattice charge is independent of pH. U(VI) is mainly bound through the surface complexation to hydroxyls on the edge surface at high pH condition.

Conclusion

The batch sorption data of U(VI) on montmorillonite were successfully interpreted by analyzing the influences of factors affecting sorption, such as pH, ionic strength, and total U(VI) concentration. A mechanistic model was established based on these findings, which successfully simulated the U(VI) sorption on montmorillonite. The model describes the sorption behavior as simultaneous and competitive reactions of ion exchange and surface complexation. At a low ionic strength and low pH condition, ion exchange is the dominant mechanism for U(VI) sorption on montmorillonite. At high ionic strength and high pH condition, surface complexation is the dominant mechanism. In the intermediate condition for pH and ionic strength, ion exchange and surface complexation contribute to the total U(VI) sorption in a varying ratio.

References

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