SORPTION OF NP(V), U(VI) AND CS ONTO BENTONITE AND CLAYEY SOILS

M.N. Sabodina1,2, St.N. Kalmykov3, K.A. Artem’eva3, E.V. Zakharova1

1. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Science, Moscow, Russia
2 Chemisty dept., Lomonosov Moscow State University, Moscow, Russia
e-mail: maria_sab@radio.chem.msu.ru

INTRODUCTION

Low-level nuclear wastes containing transuranium elements (TRU nuclides) such as neptunium and uranium are generated in spent nuclear fuel treatment procedure. The safe disposal of radioactive waste in geological formations is based on what is known as multi-barrier concept. Bentonite is a natural clay mineral that has high sorption capacity towards cations and is proposed in several countries as a main component of isolation barriers at the nuclear waste repository sites. However, the possible use of sandy soils with high clay content is considered for this purpose as well.

The presence of colloid particles is essential for radionuclide transport and should be considered in design of such barriers. For bentonite pore waters that have reducing Eh values actinides could be present in the form of intrinsic hydroxocolloids or sorbed onto natural aquatic colloids forming so-called pseudocolloids. Presence of surface coatings on colloidal particles may change their coagulation properties (e.g. Fe(III) oxide coating or humic coating). The aim of this work was to study actinide speciation in bentonite pore waters and sorption of 237Np(V), 137Cs, 238U(VI) by clayey soils including possible role of surface coatings on it.

EXPERIMENT

Bentonite (Khakassiya deposit, Russia) was taken in Na-form for all experiments. The mineralogical composition of the sample was characterized by powder X-ray diffraction, particle topology was studied by SEM and TEM. The average particle size was 3 μm as determined by dynamic light scattering technique however according to TEM the presence of clay nanocolloids was detected as well. Bentonite pore waters were separated by ultrafiltration under inert (N2) atmosphere and analyzed by AAS, AES and ion chromatography. The pore waters were found to be reductive with Eh=-100 mV due to presence of Fe(II) or organic matter. The major complexing ligand are CO32−/HCO3− and SO42−. Sorption experiments were performed under N2 atmosphere in plastic vials to avoid radionuclide adsorption onto walls. Bentonite samples were left in the working solutions to swell for few days before sorption experiments were performed. After the desired concentration of radionuclide was added to the suspension, the required pH values were established and samples were left until the equilibrium was reached. Separation of suspended matter after the sorption was performed using microfiltration techniques.

For experiments with natural clayey soils, samples were fractionated granulometrically (0.5 – 0.25mm; 0.25 – 50μm; 50μm – 10μm and <10μm). For each fraction specific surface area and porosity were determined. All samples were characterized by SEM and TEM. The sorption of radionuclides was studied by initial clayey soil samples and by samples after extraction of Fe amorphous compounds (by Tamm methods described by Vorob’eva, 1998).

RESULTS AND DISCUSSION

The sorption of U(VI) and Np(V) on bentonite was found to be pH dependant that indicate predominant surface complexation mechanism of their sorption. For 137Cs the pH dependence of sorption was less
pronounced that indicate the ion exchange as the major mechanism. The equilibrium constant of Na\(^+\)/Cs\(^+\) exchange reaction calculated from sorption isotherms and pH dependences:

\[
\text{NaX} + \text{Cs}^+ \leftrightarrow \text{CsX} + \text{Na}^+ \quad \log K = 1.7
\]

For Cs\(^+\) sorption depended upon ionic strength as studied in the range from 0.001 to 0.1 M (NaClO\(_3\)). The same effect is observed for Np(V) and U(VI) at pH<5. In case of neptunium and uranium ion exchange contributes to their sorption at low pH values while at neutral and slightly alkaline solutions the sorption is defined by surface complexation reactions.

The desorption of radionuclides by deionized water, 1M KCl and 1M HCl was studied. The largest fraction of Cs was desorbed by 1M KCl while for of Np and U the largest fraction were extracted by 1M HCl that supports the assumption on different sorption mechanisms. Only minor fraction of radionuclides was desorbed by deionized water.

For natural clayey soils the highest sorption of actinides (Np and U) correlated with Fe(III) content and was highest for the largest fraction (0.5 – 0.25 mm) and the finest fraction (<10\(\mu\)m). The extraction of Fe(III) from the samples result in significant decrease of actinide sorption. Indicating, that sorption of actinides is defined by presence of surface coatings of Fe(III) compounds. Earlier it was established by SEM, that Fe is present both in the form of separate hematite particles, and in the form of surface coatings. Presence of Fe(III) surface coatings did not effect on Cs sorption.

References:
Vorob'eva L.A. Chemical analysis of sandy soils. Moscow State University, 1998, 272 P.

This research was supported by the RFBR (grant 05-03-33028).