

SORPTION PROPERTIES OF BENTONITE CLAYS TOWARDS SEVERAL RADIONUCLIDES

Sabodina M.N., Kalmykov St.N., Sapozhnikov Yu.A.

Radiochemistry div., Chemistry dept., Lomonosov Moscow State University
maria_sab@rambler.ru, phone: (095) 939-3220

Key words: bentonite, sorption, surface complexation, colloidal particles

Introduction

Bentonite is a natural clay mineral that with high sorption properties towards cations and could be used to create isolation barriers at the toxic and nuclear waste repository sites. Sorption of radionuclides, their solubility in pore waters of bentonite and diffusion properties of radionuclides is the major factors that define bentonite as a geochemical barrier. Published data on mechanisms of cation sorption, role of different sorption sites and stability constants of surface complexes is quite contradictory. The aim of this work was a molecular level understanding of ^{137}Cs , Pu (IV) and Np (V) sorption by bentonite.

Materials and methods

Characterization of the sample. Bentonite (Khakassiya deposit) used in the experiments was taken in Na-form and characterized by powder X-ray diffraction. According to the mineralogical composition the main component of the sample was montmorillonite – clay mineral with layered structure. The sample was characterized by scanning electron microscopy, potentiometric titration and elemental analysis. The surface area and pore distribution according to their size was determined by N_2 adsorption technique using BET equation.

Sorption experiments were performed in plastic vessels to avoid radionuclide adsorption by walls under inert atmosphere. All the solutions were degassed by passing N_2 to avoid carbonate complexation of actinides. Bentonite samples were left in the working solutions to swell for few days before sorption experiments were performed. After the required concentration of radionuclide (^{238}Pu , ^{239}Pu , ^{237}Np , ^{239}Np) was added to the suspension the required pH value was established and samples were left until the equilibrium was reached. Separation of suspended matter after the sorption was performed using micro- and ultrafiltration techniques.

Study of colloid formation in the water-bentonite suspension

In order to study the formation of colloid particles of different origin (clay colloids vs. true actinide colloids) the sorption experiment was performed using different water / bentonite ratios. Different methods of suspended matter separation was used – centrifugation (4.000 RPM), microfiltration (0.45 μm) and ultrafiltration (10 kD). Experiment was performed at pH=8 and trace actinide concentration of 2.69×10^{-9} M and 6.00×10^{-10} M for Pu and Np correspondingly.

Results and discussions

Sorption of cations by bentonite is governed by two mechanisms including ion exchange with interlayer cations and formation of surface complexes with either silanol or aluminol groups. Depending on the mechanism of sorption both kinetics and pH dependence should differ significantly.

For ^{137}Cs sorption equilibrium reached for 1.5 h while for Pu (IV) and Np (V) rather slow kinetics was observed. The kinetic curve for Pu (IV) and Np (V) indicate complex interaction with the surface. The equilibration time at low pHs was less than for neutral or alkaline solutions. For pH values of 3.25, 5.45 and 8.45 these values were 5 and 7-8 days correspondingly. The same dependence was established for Pu (IV) – the equilibration time at pH=2.95 were 7 days while for pH=5.95 and 8.65 it was about 10 days. The slow kinetics of Pu (IV) and Np (V) was due to their interaction with the surface hydroxyl groups and effects in the double electric layer.

The pH sorption curves for ^{137}Cs , Pu (IV) and Np (V) are presented in Fig. 1. If compared to Pu (IV) and Np (V) the sorption of ^{137}Cs was less pH dependant that indicates predominant ion exchange mechanism of sorption. The decrease in ^{137}Cs sorption occur only at pH values less than $\text{pH}_{\text{pzc}}=1.7$. The maximum of Np (V) sorption was established at pH=8.5 ($K_d=1.4 \times 10^4$ ml/g) while at higher pH values the decrease of sorption was observed due to carbonate complexation. Despite the experiment

was performed under N₂ atmosphere the carbonate concentration in bentonite (in the form of calcite) was rather high. The same behavior was found for Pu (IV) for which maximum of sorption was observed at pH about 7.

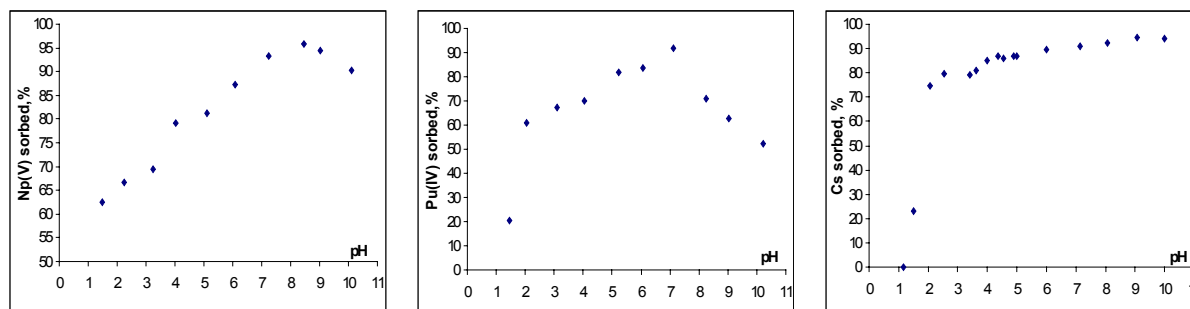
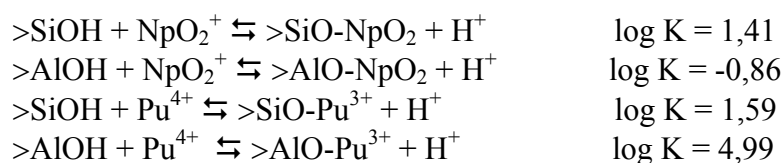


Fig. 1. Sorption of radionuclides on bentonite as function of pH

Formation of true actinide colloids results in the non-linear dependence of K_d on solution / bentonite ratio. However it was found that under the experimental conditions the linear dependence was found using either centrifugation, microfiltration or ultrafiltration to separate solid matter and solution. The K_d values obtained using ultrafiltration both for Pu and Np were significantly (up to about one order of magnitude) higher than using microfiltration. These indicate sorption of radionuclides to bentonite nano-colloids.

Surface complexation modeling was performed using FITEQL software by applying diffuse layer model. The input parameters were stability constants of actinide complexation in solution, sample characteristics and pH sorption dependence. The complexation of actinides with both silanol and aluminol groups were considered. The following complexation constants were obtained:



Conclusions

1. It was established that ¹³⁷Cs is predominantly bound to bentonite by ion exchange with interlayered cations while Pu (IV) and Np (V) form surface complexes.
2. Radionuclide sorption to bentonite nano-colloids is found to be significant.
3. Actinides are predominantly bound to aluminol groups but not silanol groups.