Investigation of the Sorption of Pu(III) onto Kaolinite in the Presence of Aldrich Humic Acid

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It was demonstrated that Aldrich humic acid (AHA) has a strong influence on the sorption of Pu(III) onto kaolinite (K) [1].The question whether the metal ion (M) is directly sorbed onto kaolinite or a humate complex sorption takes place is difficult to answer. The following possibilities were considered:

- the sorption of metal ion (M) and humic substances are independent of each other
- a K-AHA-M bridge is formed
- a K-M-AHA bridge is formed

Several authors have concluded that the metal complex with humic substances already sorbed on mineral surfaces is stronger than humate complexation in solution [2, 3], so the first possibility is less likely.

Attempts to determine chemically the form of binding to the solid surface were performed. It was proven in previous experiments that at pH ~ 1 Pu(III) is almost completely desorbed from kaolinite, while at pH > 10 it remains strongly fixed. On the other hand, humic acid is strongly sorbed onto kaolinite at lower pH values, but desorbed at pH > 10. Assuming that no other interactions take part, if a K-AHA-M bridge is formed, the AHA-M complex should be desorbed from the kaolinite when the pH of the solution is > 10. On the contrary, when a K-M-AHA bridge is formed, M-AHA will remain fixed at pH > 10 and will only be desorbed when the pH is lowered.

In a first experiment (I), plutonium was sorbed onto kaolinite, and AHA was added after 48 hours, and in the second one (II), AHA was mixed with Pu(III) and subsequently K was added following a contact period of 28 days. After determining the sorption of AHA and Pu(III) onto kaolinite in the pH range 2-10, the pH of the solutions was first increased to pH ~ 11.5 by adding NaOH. The reaction vials were agitated for 48 hours, the suspension centrifuged and the activity of the supernatant determined (“basic desorption”). Afterwards, the supernatant was ultrafiltrated to determine whether the desorbed plutonium is complexed by AHA or not. A fresh solution of 0.1 M $NaClO_4$ with pH < 1 was mixed with the separated solid phase from the earlier experiment. After another 48 hours of agitating, the solution was again centrifuged, and the activity of the liquid phase was determined by LSC providing information on the desorption in acidic conditions (“acid desorption”). The supernatant was also ultrafiltrated and the free plutonium ion content was determined by LSC in the filtrate. It was found that the sorption takes place differently in the two cases, as shown in Fig. 1.

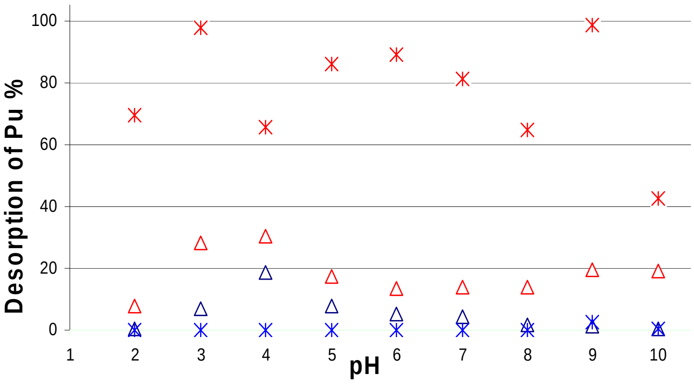

Figure 1: Influence of the adding sequence of the components on the desorption of Pu(III) and Pu(III)-AHA complexes from kaolinite; blue crosses - “basic desorption” exp. I, red crosses - “acid desorption” exp. I, blue triangles “basic desorption” exp. II, red triangles – “acid desorption” exp. II

From the obtained data it can be concluded that plutonium is sorbed onto kaolinite in case II not as a complex but as a metal ion, as the sorption was appreciably lower compared to case I [1], thus it is easily desorbed at pH < 1. This was also sustained by the fact that the entire amount of plutonium desorbed was found in the filtrate after ultrafiltration. Only a small part of plutonium sorbed as a humate complex is desorbed at either basic or acidic pH.

So far, it was not possible to determine in which form plutonium and the humic acid are sorbed onto kaolinite in the ternary system. This answer could be given by EXAFS/XANES, and therefore future experiments are planed with the XAS technique.

References:

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