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Wechselwirkungen von Actiniden mit Anorgano-Huminkolloiden

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Summary

The present report is a continuation of our study [1, 2] on the generation and characterization of actinide pseudocolloids, in particular, the influence of humic acid (HA) on the formation of hydroxyaluminosilicate (HAS) colloid borne actinides. The following investigation is focused firstly on the humic acid itself as far its colloidal properties are concerned, then on the interaction of humic acid Gohy-573 (HA) with Ca(II), Al(III), Eu(III), Am(III) and Th(IV) ions and finally on the influence of HA on the dissolution kinetic of HAS colloids, as parts of the ultimate objective to predict the distribution and mobility of radionuclides in the environment.

In the first part of the work, the influence of pH, temperature and the concentration of the humic acid itself on its partition between the precipitate, colloids and solution is investigated. The effect of Ca, Al, Eu and Th ions on the destabilization of humic colloids is also examined. It is found that Eu is the most effective coagulant among other metal ions. The obtained results indicate that for any given pH, colloid HA possess to hold tri-, tetra and hexavalent cations in higher amounts than weakly coordinated divalent calcium ions if the metal concentration does not exceed the proton exchange capacity of HA. The stability of colloidal ^{14}C -radiolabelled humic substances is tested by filtration and ultrafiltration combined with liquid scintillation counting and UV/Vis spectroscopy. In one sample series the HA concentration is kept constant at 6 mg/l and the pH is varied from 4 to 9. A slightly elevated precipitate fraction is observed at $\text{pH} < 5.5$ due to the beginning of the protonation of the HA functional groups leading to aggregation. In the neutral pH region, the fraction regarded as humic colloids after a sample conditioning time of 35 days is found to reach approximately 75 - 80%. At longer conditioning time, however, slightly elevated precipitate and ionic fractions are observed. In another sample series the pH is kept constant at 6.6 in 0.01 M MOPS buffer and the HA concentration is gradually increased from 0.6 to 10 mg/l. A variation of the HA concentration has only negligible effects on the partition of HA. The impact of temperature on the stability of the HA is studied with solutions of 6 mg/l HA at pH 7.8 (10^{-2} M MOPS buffer). Solutions are kept in water bath for 4 days storage at different temperatures up to 90°C . The difference between UV/Vis absorption of HA solution stored at room temperature and the absorption of the HA solution stored at 90°C is small but well reproducible. At 90°C , the spectrum shows a slight change with an increase towards shorter wavelengths. This indicates that aggregation

of HA occurs which induces the increase in the UV absorbing properties of HA. The fractionation tests demonstrate that HA colloids are dissolved and precipitated at the same time. The result shows that rearrangement of HA takes place already at 40°C. With increasing temperature the expected increase in conversion velocity is found.

In the second part of the work, the stability of Th(IV) and Am(III) humate complexes are investigated using a competing ligand displacement method. The effects of initial [Th]/[HA] concentration ratio, predissociation equilibration time, and temperature on the rates of complex dissociation are studied. In a separate experiment the competition between Th and Am for generation of humate colloid-borne actinides is investigated. Solutions containing the metal humate complexes are spiked with appropriate amounts of EDTA. The differentiation between colloid-borne metal species and the metal – EDTA complexes formed as a function of time is carried out by sequential filtration, first at 450 nm pore size (Sartorius) and then the resulting filtrate at about 1.5 nm nominal pore size (Centricon YM-10, Millipore). The dissociation kinetics and the apparent equilibrium of the exchange reactions are used for operational characterization of the kinetic stability of the metal species of interest. These experiments imply that although metals bind rapidly to humic acid, the aqueous-phase metal humate complex formation reaction is still proceeding over a long period of time (up to several years) which promotes formation of more stable complexes and retarded subsequent dissociation. In general, increasing predissociation equilibration time decreases Th-HA complex dissociation rates. Increasing Th/HA ratio increases Th-HA dissociation rates. Overall results indicate that Th-humic acid binding strength increases with increasing temperature. A separate experiment investigates the competition between Th and Am for generation of humate colloid-borne actinides. The Th-Am competition experiment performed at quite low actinide concentrations shows significant effects of Th in reducing Am-HA binding strength. Thus Am(III) is desorbed faster in presence of Th(IV). In contrast, the desorption kinetics of Th(IV) complexed with HA does not change in presence of Am(III). The lability of the Am(III) humate complexes in the presence of Th(IV) is the result of a successful competition of Th with Am for strong binding sites of the humic acid. The ligand exchange reactions are shown to be an efficient method for the specification of labile and inert metal species in aquatic HS samples.