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Eu(III)/Cm(III) sorption onto kaolinite

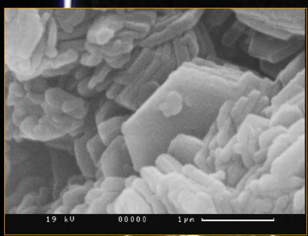
Introduction

Clay minerals are considered as buffer and backfill materials in geological repositories for nuclear waste and are present as alteration products in crystalline bedrock. The sorption behaviour and speciation of trivalent actinides on the 1:1 layered clay mineral, kaolinite, was investigated by means of batch experiments and time-resolved laser fluorescence spectroscopy (TRLFS).

Kaolinite synthesis

Natural kaolinite minerals often contain impurities like e.g. illite, mica, and iron oxides. To reduce the possible effect of such impurities on the sorption and speciation studies, a batch of kaolinite was synthesized from pure reagents by hydrothermal treatment of $Si_2Al_2O_7$ at 220°C for 14 weeks.

Teflon reactors used for kaolinite synthesis



SEM image of synthetic kaolinite

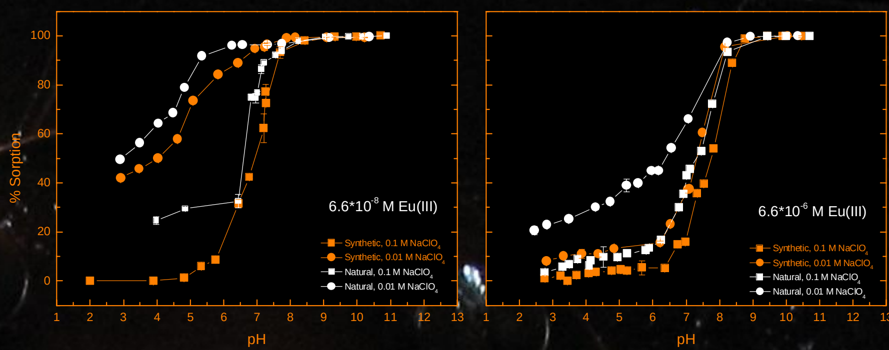
Both the synthetic product and a natural kaolinite mineral from St. Austell (UK) ,that was used for comparison in batch and TRLFS experiments, were characterized.

Kaolinite properties	St. Austell kaolinite	Synthetic kaolinite
Chemical composition (XRF)	46.51 % SiO_2 39.62 % Al_2O_3 *	N/A
Specific surface area (N_2-BET)	11.7 m²/g *	22.2 m²/g
Grain size (SEM)	0.2 µm thickness 0.4-1.0 µm diameter *	0.2µm thickness 0.4-1.1 µm diameter
Elemental composition [atom%] (SEM-EDX)	O - 68.27 ± 3.40 % Al - 15.26 ± 1.50 % Si - 16.47 ± 1.90 % Traces (< 1%) of K, Na, In, Sb, Fe	O - 68.21±2.00 % Al- 15.81±0.80 % Si- 15.98±1.30 %
HI (XRD) (measure of crystallinity)	1.34	1.01

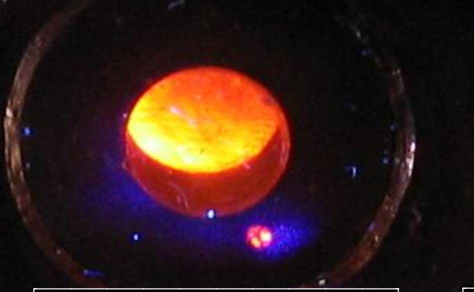
* Bauer, A. and Berger, G., Appl. Geochem. 13, 905-916 (1998)

Eu(III) batch sorption study

Batch sorption studies provide information on the sorption capacity of a mineral or soil and, thus, on the retention behaviour of the metal ion in the studied environment. The batch experiments with europium were conducted under Ar-atmosphere in a glove box, to exclude the influence of carbon dioxide. Different pH values, metal ion concentrations and ionic strengths were used to study the sorption behaviour.

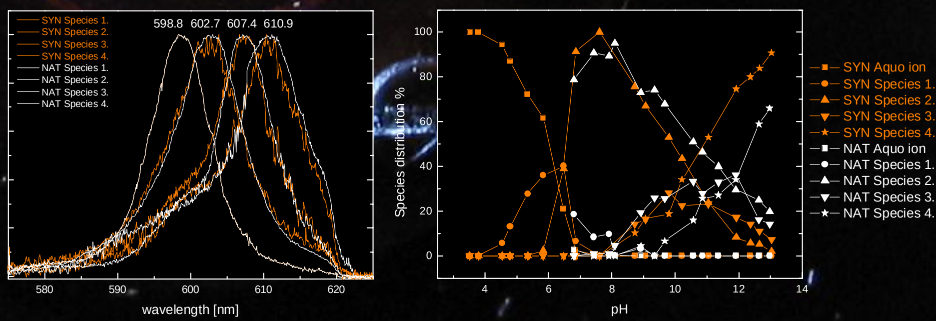


pH edges for Eu(III) sorption onto synthetic and natural kaolinite, respectively. The two minerals show different uptake behaviour towards Eu(III), especially at low ionic strength, 0.01 M $NaClO_4$.



Cm(III) TRLFS

Cm(III) sorption onto synthetic and natural kaolinite, respectively, was investigated from CO_2-free kaolinite suspensions in the pH range 4-13 with TRLFS.



Four curium species could be identified in both systems from the recorded emission spectra. Proposed Cm(III) complexes on the kaolinite surface are:

Species 1. = ≡S-O-Cm$(H_2O)_5^{2+}$ *Species 2.* = ≡S-O-Cm(OH)$(H_2O)_4^+$ *Species 3.* = ≡S-O-Cm$(OH)_2(H_2O)_3$
Species 4. = ≡S-O-Cm$(OH)_x$-silicate

Summary

Outer-sphere sorption of Eu(III) is more pronounced in the natural clay mineral system than in the synthetic one, especially at low ionic strength.
Four curium inner-sphere complexes on the kaolinite surface are found in the investigated pH-range 4-13. The fourth complex is assumed to form between surface-bound curium and dissolved silicates in solution, forming a ternary or quaternary Cm-silicate surface complex.

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