Sorption isotherms for [241]Am(III) on kaolinite

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Plutonium is of major concern for the long-term safety of high-level nuclear waste repositories due to the high radiotoxicity and long half-life of Pu. Therefore, the knowledge of the migration behavior of Pu in the geosphere is essential for the design and safety assessment of nuclear waste repositories. Under reducing conditions, Pu(III) is an important oxidation state of Pu in aqueous solution. Since this oxidation state is difficult to stabilize in environmentally-relevant solutions, Am(III) is used as the redox-stable chemical analogue of Pu.

The sorption isotherm for 8×10^{-9} M [241]Am(III) on the reference clay mineral kaolinite KGa-1b (Source Clay Repository) in 0.1 M $NaClO_4$ was measured under ambient air conditions by varying the solid-to-liquid ratio from 0.5-22 g/L. The pH was fixed at 9.0 using a carbonate buffer (HCO_3^-/CO_3^{2-}). After a contact time of three days, the solid and liquid phases were separated by centrifugation at 81,000 g for 1 h. The concentration of [241]Am in the supernatant was determined by ICP-MS (Agilent 7500ce) and γ spectroscopy (59.5 keV, Ortec GAMMA-X HPGe Coaxial Photon Detector). The detection limits for [241]Am, determined experimentally by dilution of a [241]Am stock solution, were two orders of magnitude lower for ICP-MS ($\sim 10^{-12}$ mol/L) than for γ spectroscopy ($\sim 10^{-10}$ mol/L, 0.5 mL sample, 1 h counting time). The percentage of Am(III) sorbed on kaolinite was calculated relative to a 8×10^{-9} M [241]Am(III) solution without clay (blank sample). In addition to the isotherm measurement, this study aimed also at estimating the usefulness of ICP-MS for measuring low Pu concentrations in future sorption studies, especially in combination with CE-ICP-MS for the speciation of Pu in the aqueous phase [1].

As can be seen, the results obtained by ICP-MS and γ spectroscopy coincide. The sorption data were analyzed using the linearized forms of *Freundlich* (eq. 1) and *Langmuir* (eq. 2) sorption isotherms (Figs. 1 and 2) [2]:

$$\log\left(\frac{x}{m}\right) = \log(K) + n \cdot \log(c) \qquad (1)$$

$$\frac{m}{x} = \frac{1}{N_{max}} + \frac{1}{b \cdot c \cdot N_{max}} \qquad (2)$$

where *x/m* is the weight of sorbate divided by weight of sorbent, *K* and *n* are constants, and *c* is the aqueous concentration. If *n* = 1 in eq. 1, $K = K_d$, the so-called distribution coefficient. In the *Langmuir* isotherm (eq. 2), *b* is a con-

stant. N_{max} is the maximum possible sorption by the solid due to the finite supply of sorption sites. In contrast, the *Freundlich* isotherm and K_d approaches assume an infinite supply of unreacted sorption sites.
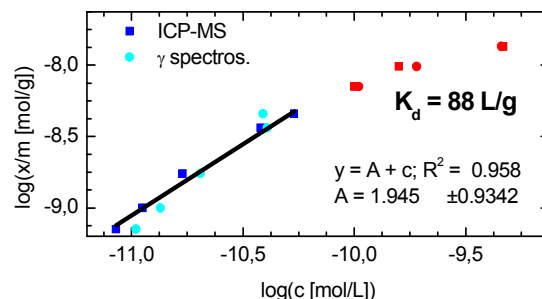

Fig. 1 *Freundlich fit to determine* K_d.

As can be seen from Fig. 1, the *Freundlich* isotherm describes the sorption data well up to an equilibrium concentration of $\sim 10^{-10}$ mol/L Am with *n* = 1.0 and $K_d \approx 88$ L/g .

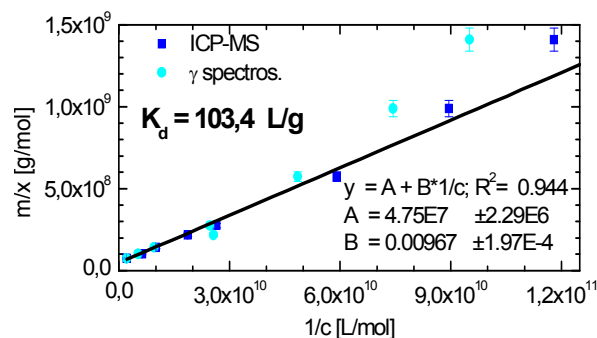Fig. 2 *Langmuir fit to determine* K_d.

The *Langmuir* isotherm can describe the sorption data over the entire range of this experiment (see Fig. 2). From $K_d = bN_{max}$, K_d equals 103 L/g.

It can be concluded that Am(III) is strongly sorbed onto kaolinite at pH 9.0 in the presence of ambient CO_2. ICP-MS is well suited as an analytical tool in sorption studies for determining actinide concentrations in aqueous solution as low as 10 pmol/L.

[1] B. Kuczewski, C.M. Marquardt, A. Seibert, H. Geckeis, J.V. Kratz, N. Trautmann, Anal. Chem. **75** (2003) 6769-6774.
[2] D. Langmuir, *Aqueous Environmental Geochemistry*, Prentice Hall, Inc., (1997) 355-361.