SORPTION OF ACTINIDES (Th, U, Np, Pu, Am) ON OPALINUS CLAY IN SYNTHETIC POREWATER

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Clay formations are under consideration in several countries as a potential host rock for high-level nuclear waste repositories. Opalinus Clay (OPA) from Mont Terri, Switzerland, has been selected as a representative for natural clay to study the sorption of actinides. The results of such studies are important for the development of a sorption data base required for the performance assessment of a radioactive waste repository.

The aim of this study was to investigate the sorption behaviour of Th(IV), U(VI), Np(V), Pu(III/IV) and Am(III) on OPA equilibrated with synthetic porewater at pH 7.6. Sorption isotherms were measured and K_d values for different solid-to-liquid ratios were determined. The experiments were performed under ambient air conditions, except for Pu(III) that was studied under argon atmosphere.

The total concentrations of Th, Pu, and Am in the OPA suspensions were 8×10^{-9}, 1×10^{-7}, and 9×10^{-9} mol/L, respectively. The total concentrations of U(VI) and Np(V) were varied between 10^{-8}-10^{-4} and 10^{-11}-10^{-4} mol/L, respectively.

For U(VI) and Np(V) the K_d values were obtained from sorption isotherm measurements that were analyzed using a Freundlich adsorption isotherm.

The Freundlich isotherm is expressed as follows:

$$x/m = K \cdot [An]_{eq}^{n} \qquad (1)$$

where x/m is the weight of the sorbate devided by the weight of the sorbent (mg/g) and $[An]_{eq}$ is the equilibrium concentration in solution (g/L). The constants K and n were determined from a fit of the logarithmic form of eq. (1) to the experimental data.

$$\log(x/m) = \log(K) + n \cdot \log[An]_{eq} \qquad (2)$$

When n = 1 in eq. (1), K = K_d, the so-called distribution coefficient, which in the slope of the isotherm at the origin.

For the other actinides, average K_d values were calculated according to eq. (3) from a series of measurements, where the solid-to-liquid ratio was varied, typically between 2-20 g/L.

$$K_d = \frac{x}{m} \cdot \frac{1}{[An]_{eq}} \qquad (3)$$

The determined K_d values in comparison with literature values are shown in Table 1.

TABLE 1. *K_d values of Th(IV), U(VI), Np(V), Pu(III/IV) and Am(III) sorbed on OPA in comparison to published data [1].*

		K_d (m^3/kg)		
		This work	Ref. [1]	
An	[An] mol/L	pH 7.6	pH 7.2	pH 7.8
Am(III)	9×10^{-9}	30	17.0	63.0
Pu(III)	1×10^{-7}	> 6	22.6	75.2
Th(IV)	8×10^{-9}	56	55.4	55.4
Pu(IV)	1×10^{-7}	48	-	-
Np(V)	10^{-11} - 10^{-4}	0.05 - 0.031	-	-
U(VI)	10^{-8} - 10^{-4}	~ 0.03	-	-

The measurements showed that the K_d values for the tri- and tetravalent actinides are of the order of 30-50 m^3/kg, indicating strong sorption on OPA in porewater at pH 7.6. The K_d values for Th(IV) and Am(III) are comparable to those reported in [1]. Uranium and neptunium in oxidation states six and five, respectively, are weakly sorbed on OPA with a K_d value of about 0.03 m^3/kg.

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References

[1] Bradbury, M. and Baeyens, B. (2003): Far Field Sorption Data Bases for Performance Assessment of a High-Level Radioactive Waste Repository in an Undisturbed Opalinus Clay Host Rock. PSI Bericht Nr. 03-08. Paul Scherrer Institut, Villigen, Switzerland.