NEPTUNIUM(V) SORPTION ONTO KAOLINITE IN THE PRESENCE AND ABCENCE OF CO_2

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Kaolinite, $Al_2Si_2O_5(OH)_4$, is a clay mineral that has a strong affinity for the sorption of radionuclides and heavy metals. It has been proposed as a backfill material for geologic repositories for nuclear waste. The adsorption of heavy metals on kaolinite is an important process that affects the migration and retardation of neptunium and other actinides in the geosphere. Unfortunately, there is not enough information available on neptunium sorption onto kaolinite. Therefore, detailed studies of the sorption and migration behavior of neptunium from nuclear waste repository are necessary for safety assessments. We investigated the sorption of Np(V) onto the reference clay mineral kaolinite KGa-1b both by batch experiments and EXAFS measurements [1].

The batch experiments were done under relevant environmental Np(V) concentrations of $1.1 \cdot 10^{-11}$ and $9{,}1 \cdot 10^{-13}$ mol/L and compared to sorption experiments at $2.0 \cdot 10^{-5}$ and $8.0 \cdot 10^{-6}$ mol/L Np(V). Sorption samples were prepared in $NaClO_4$ solution, pH 6.0 to 10.5, presence and absence of ambient CO_2. All experimental conditions of Np(V) sorption on kaolinite are summarized in Table 1.

The sorption curves for $1.1 \cdot 10^{-11}$ and $9.1 \cdot 10^{-13}$ mol/L mol/L Np(V) obtained in presence and absence of CO_2, respectively, show that the adsorption edge occurs at pH 8.5. The uptake of Np(V) by kaolinite strongly increased above pH 6.5 and reached its sorption maximum (70 %) at the pH 9.0. Above pH 9.0, the amount of Np(V) sorbed onto kaolinite decreased due to the formation of the Np(V) carbonato species in aqueous solution, to 30 % at pH 10.5.

In the CO_2-free system, the sorption of Np(V) increased continuously with the pH until the sorption maximum of 100 % was reached at pH 10.5. The same sorption behavior was found in batch experiments in the CO_2 equilibrated system with 10 µmol/L Np(V) concentration.

EXAFS experiments on some of these batch samples indicated the formation of Np(V) carbonato species at the kaolinite surface at pH 9.0 where the uptake of Np(V) by kaolinite reached its maximum [1].

Table 1: Experimental conditions of Np(V) sorption on kaolinite

Method: batch experiment
Vessel: 10 ml polypropylene centrifuge tube
Solid/liquid: 4 g/L
Electrolyte: 0.1 mol/L $NaClO_4$
Np(V) concentration: $2.0 \cdot 10^{-5}$, $8.0 \cdot 10^{-6}$, $1.1 \cdot 10^{-11}$ and $9{,}1 \cdot 10^{-13}$ mol/L
p_{CO_2}: $10^{-3.5}$ atm, CO_2 free
Temperature: 25 °C
pH-range: 6.0-10.5
Pre-equilibration: 72 h
Separation: centrifugation 5000 rpm for 7 min
Contact time neptunium/kaolinite: 60 h
Agitation: overhead shaking 16 rpm
Chemical analysis: γ-measurement of solid phase and solution (tracer: Np-239 (103 keV, 106 keV)

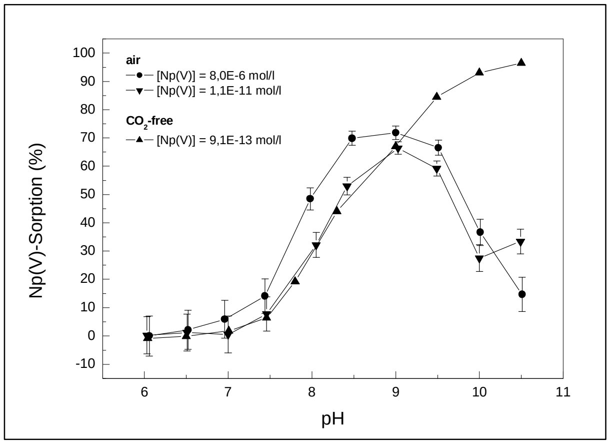

Figure 1: Np(V) adsorbed on kaolinite in the presence and absence of CO_2

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REFERENCES

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