

Influence of ionic strength on neptunium(V) sorption onto kaolinite in the presence and absence of CO₂

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Neptunium is one of the most important elements from the safety point of view due to its hazardous nuclide Np-237 with a half-life of $2.1 \cdot 10^6$ years. The risk assessment of future nuclear waste repositories requires knowledge on the migration behavior of neptunium in potential host rock formations such as the clay mineral kaolinite.

The aim of this study is to derive basic sorption data (dependency of the sorption isotherm on pH, metal ion concentration and ionic strength) as a complement to the direct spectroscopic speciation (EXAFS and XPS). The neptunium/kaolinite system has been selected to provide a basic understanding of the reactions at the mineral-water interface and to derive experimental results that will be used for the development of appropriate thermodynamic models.

The adsorption of Np(V) on the reference kaolinite KGa-1b (Source Clay Repository, Washington Country, Georgia, USA) was examined by batch experiments carried out in the presence and in the absence of ambient CO₂ at two different ionic strengths 0.1 M and 0.01 M NaClO₄ in pH range 6.0 to 10.5.

The batch experiments were done with a Np(V) concentration of $8.0 \cdot 10^{-6}$ mol/L, 4 g kaolinite/L, and 60 h equilibration. All experimental conditions are summarized in [1].

The sorption curves for $8.0 \cdot 10^{-6}$ mol/L Np(V) obtained in the presence of CO₂ at ionic strength 0.1 M and 0.01 M NaClO₄ show that the adsorption edge occurs at pH 8.0 (Fig. 1). The uptake of Np(V) by kaolinite strongly increased above pH 6.5 and reached its sorption maximum at pH 9.0 with 70 % sorption at I=0.1 M and 47 % sorption at I=0.01 M. Above pH 9.0, the amount of Np(V) sorbed onto kaolinite decreased to 10 % at pH 10.5.

Np sorption was strongly reduced relative to the CO₂-free system for the pH value greater than 9.0 due to the formation of neptunyl carbonate solution complexes. Speciation calculation of $8.0 \cdot 10^{-6}$ mol/L Np(V)-solution with pCO₂= $10^{-3.5}$ atm using the thermodynamic code Medusa [2] and NEA-data bank [3] shows that the [NpO₂CO₃]-species (with 83%) dominated the speciation of Np(V) at pH 9.0.

In the CO₂-free system at both ionic strengths, the sorption of Np(V) increased continuously with the pH until the sorption maximum of 90 % was reached at pH 10.5.

Our EXAFS investigations of Np(V) sorbed onto kaolinite (at pH 9.0, Np(V) concentration of $8.0 \cdot 10^{-6}$ mol/L, ambient CO₂) confirmed the formation of Np(V)-carbonate species on the surface of kaolinite [4]. The solubility of NaNpO₂CO₃-species depends on the ionic strength [5]. This can explain the lower sorption of Np(V) on kaolinite at 0.01 M NaClO₄.

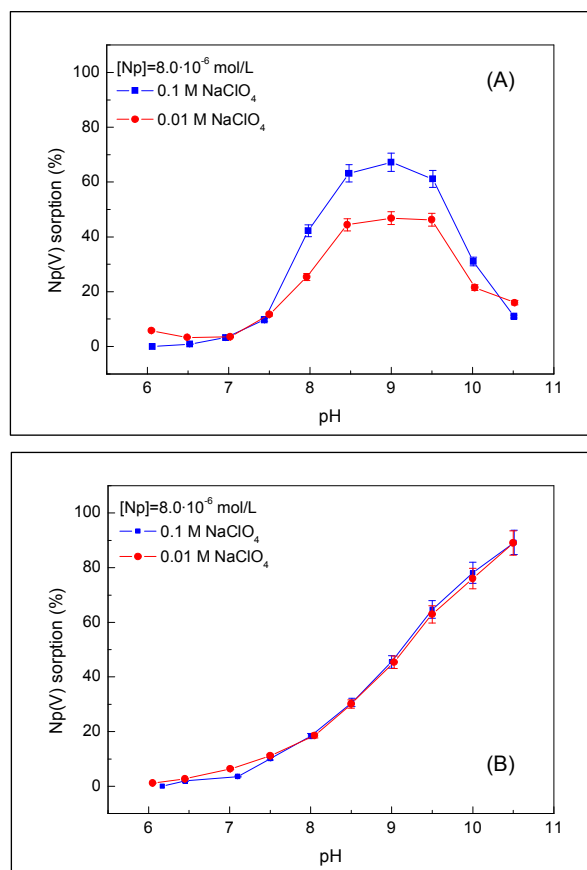


Figure 1: Np(V) adsorbed on kaolinite in the presence of CO₂ (A), absence of CO₂ (B)

Acknowledgments

This work was supported by the BMWA grant No. 02E9653.

References

- [1] S. Amayri et al., Institut für Kernchemie, Annual Report C2 (2004).
- [2] I. Puigdomenech, Chemical equilibrium software, Royal Inst. of Chem., Stockholm, Sweden (1994).
- [3] R. J. Lemire, et al., Chemical thermodynamics of neptunium and plutonium, Elsevier Science, Amsterdam (2001).
- [4] T. Reich et al., Institut für Kernchemie, Annual Report C4 (2004).
- [5] V. Neck, et al., Radiochimica. Acta **65**, 29 (1994).