

Np(V) sorption onto hematite ($\alpha\text{-Fe}_2\text{O}_3$) in the presence and absence of CO_2

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The fate and transport of neptunium from nuclear waste repositories in rock systems may be affected by adsorption onto mineral surfaces such as the iron mineral hematite ($\alpha\text{-Fe}_2\text{O}_3$). Therefore, detailed studies of important interaction processes of actinides released from a repository into the aquifer with the engineered barriers and the host rock formation of a nuclear waste repository are needed for its performance assessment. Our aim is to study the sorption of Np(V) on hematite using batch experiments as a function of pH in the presence and absence of ambient CO_2 . These macroscopic studies were combined with extended X-ray absorption fine structure (EXAFS) spectroscopy to determine the speciation of Np(V) at the hematite surface [1].

Hematite powders used in batch experiments were synthesized from 0.2 M $\text{Fe}(\text{ClO}_4)_3$ solution at 98 °C for 7 days following the method of Schwertmann and Cornell [2]. The synthesized hematite was purified by repeated intensive washing with Milli-Q water. Separation of the phases was achieved by centrifugation. With this procedure clean hematite was produced. Hematite surfaces have only Fe, O, and a trace amount of adventitious carbon, as measured by XPS (X-ray photoelectron spectroscopy) (Fig. 1). Photoelectron spectra were collected under UHV conditions ($<10^{-9}$ mbar) on SPECS X-ray photoelectron spectrometer using Al $K\alpha$ radiation. N_2 BET surface areas of the dried powders were 41.1 ± 0.4 m^2/g . The Powder XRD (X-ray diffraction) pattern agreed with the structural data of Maslen et al. [3] for crystalline $\alpha\text{-Fe}_2\text{O}_3$. There was no evidence for goethite or other impurity phases.

The sorption of Np(V) on synthetic hematite was examined by batch experiments carried out in the presence and in the absence of ambient CO_2 at an ionic strength of 0.1 M NaClO_4 in the pH range 4.0 to 10.0. The batch experiments were done with a Np(V) concentration of $8.0 \cdot 10^{-6}$ mol/L. The solid to liquid ratio was 0.5 g/L, and the equilibration time was 60 h. The neptunium uptake by hematite was determined by liquid scintillation counting (LSC) and γ -spectrometry of the supernatant. All experimental conditions are summarized in the [4]. The results of the sorption experiments on hematite are summarized in Fig. 2.

In the air-equilibrated system, the uptake of Np(V) by hematite increases from pH 6.5 to 8.5 (83 % sorption) and decreases, due to the formation of strong carbonato complexes in aqueous solution, above pH 8.5 to 0 % at pH 10.0. No decrease in uptake is observed in the absence of CO_2 . The sorption maximum is 100 % in the pH range 9.5 to 10.5. The adsorption edge occurs at pH 7.0 and 7.5 in both atmospheres, respectively (see Fig 2.). As a next step the nature of Np(V) surface species was studied by EXAFS spectroscopy [1].

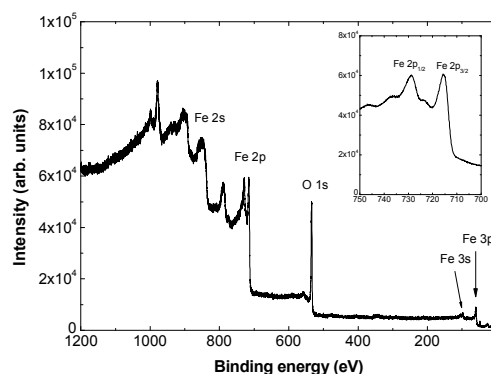


FIGURE 1. XPS spectra of synthetic hematite.

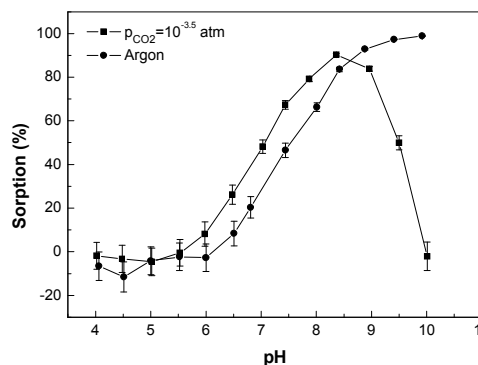


FIGURE 2. Sorption of 8.0 μM Np(V) on hematite.

Acknowledgment

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

References

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