

	Experiment title: XAS investigations of the influence of reducing conditions on clay properties	Experiment number: 01-01-858
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Report:

In the safety case for high-level radioactive waste repositories redox phenomena play an important role in radionuclide retention. Virtually all deep underground repository concepts contain large amounts of iron, and reducing conditions will prevail in the long-term. In the near field, the corrosion processes of metallic iron and production of H₂ will control the redox potential. Through the corrosion of steel canisters large amounts of ferrous iron (Fe(II)) are produced and released into the engineered barrier system (bentonite, consisting predominantly of the clay material montmorillonite) as well as into the argillaceous host rocks. The presence of high concentrations of ferrous iron in the interstitial porewaters in the near- and far fields could have a significant influence on the sorption behaviour of radionuclides.

The aim of this XAS study was to determine the local structural environment of Fe(II) sorbed onto montmorillonite under anoxic conditions.

Preliminary results

Macroscopic Fe(II) sorption experiments on a synthetic iron free montmorillonite (IFM) were carried out under anoxic conditions (O₂ < 0.1 ppm). The sorption data on IFM agree well with a modelled Fe(II) edge using the 2 Site Protolysis Non Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) sorption model [1]. One of the main features in the modelled data is that there are two sorption edge sites with different capacities, i.e. the strong and weak sites. Due to their sorption characteristics, it was expected that the structural environment of the Fe(II) surface complexes on the two sites would be differ.

EXAFS analysis of sorbed Fe(II) on synthetic montmorillonite

On the basis of the sorption data on the syntetic IFM, Fe uptake samples were prepared in which the metal was predominantly sorbed onto either the strong or the weak edge sites at the clay mineral. The experimental conditions used for the preparation of some selected EXAFS clay samples are summarized in Table 1.

Table 1. EXAFS clay samples description: S/L ratio = 7.5 g·l⁻¹.

Sample	pH	NaClO ₄ (M)	[Fe(II)] _i (M)	Fe(II) sorbed (mmol·kg ⁻¹)	log R _d (L·kg ⁻¹)
1	6.7	0.1	1.57·10 ⁻⁰⁵	1.74	2.78
2	6.7	0.1	2.52·10 ⁻⁰⁵	2.69	2.73
3	6.7	0.1	1.66·10 ⁻⁰⁴	12.3	2.23
4	6.7	0.1	2.68·10 ⁻⁰⁴	17.0	2.09

EXAFS spectra were analyzed and fitted using WINXAS and IFEFFIT software package. Backscattering phases and amplitudes were obtained from FEFF8.0 calculations. The Fe(II) loaded clays samples were measured at the Fe K-edges (7112 eV) in fluorescence mode. The observed multifrequency waveshape of all spectra indicated that Fe atoms are surrounded by more than one neighboring shell, confirming that outer-sphere complexation (cation exchange) is not the predominant binding mode. The corresponding radial structure functions (RSF) of IFM samples at low and high Fe loadings show similar backscattering features. The fit results show that sorbed Fe is surrounded by 4.0 O at 2.01 Å, 2.3 Al at 3.04 Å and 3.4 Si₂ at 3.20 Å (Fe sorbed ~ 1.7 mmolkg⁻¹). The structural parameters are characteristic of bivalent metals located in the octahedral sheet of a 1:2 phyllosilicate [2,3]. The fact that Fe is surrounded by ~ 3 Al atoms gives evidence that Fe is not occupying the empty cis site from the dioctahedral sheet. There are two significant spectroscopic differences among the measured IFM samples suggesting the existence of different Fe binding sites on montmorillonite. First, Fe-Al and Fe-Si₂ bond distances slightly increase with increasing metal loadings, i.e. R_{Fe-Al} = 3.04 Å to 3.09 Å, and R_{Fe-Si2} = 3.20 Å to 3.25 Å. This finding is consistent with the hypothesis that iron complexes at high loadings (weak sites) exhibit a stronger structural disorder and are less crystallographically defined than iron sorbed at low loadings (strong sites). Second, a splitting of the oscillations in the FT⁻¹ EXAFS data at 8 k(Å⁻¹) is strongly attenuated in the spectra of IFM with higher Fe loadings, i.e. in the weak site samples as observed in previous study.

XANES data indicated that a partial oxidation of the sorbed Fe(II) occurred in the synthetic IFM system, suggesting an electron transfer to other reactive sites, since no structural Fe(III) is present in the clay lattice. Future investigations should therefore address the reactive sites responsible for the oxidation of sorbed Fe(II) on IFM. The results of this study will help to better understand the role of Fe(II) in retention processes in radioactive waste repositories and contribute to an improved molecular understanding of the Fe(II)-clay interaction at the solid-liquid interface under anoxic conditions. Finally, the results provide a solid basis for further XAS investigations about the sorption competition between Fe(II) and other safety-relevant radionuclides.

References

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