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Uptake mechanisms of Ni(II) on montmorillonite as determined by X-ray absorption spectroscopy

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The uptake of metals and radiocontaminants in most natural systems, e.g. bentonites and argillaceous rocks, is inherently complex and multi-faced and, therefore, the usual approach consists to investigate environmentally-relevant pure clay minerals. This is supported by the fact that in most systems clay minerals are the predominant sorbing phase. Consequently, a fundamental understanding of the surface reactivity and metal uptake mechanisms of clay particles is of key importance to maintain environmental quality and to assess the long-term stability of radioactive waste repositories. Several uptake mechanisms have been proposed on clay particles: Sorption on edge sites, cation exchange in interlayer sites and formation of lamellar nucleation phases, such as neoformed layer silicates and mixed layered double hydroxides.

In this study, powder EXAFS and polarized EXAFS (P-EXAFS) were used to investigate the predominant uptake modes of Ni(II) on the ubiquitous dioctahedral smectitic clay mineral, montmorillonite (STx-1 and SWy-1). Samples were prepared at different surface loading (4-150 µmol/g), pH (5-8) and reaction time (1-360 days). The reversibility of Ni sorption was examined over the course of one year.

At near neutral pH and low Ni concentration, P-EXAFS measurements indicated the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets. This complex was found to be stable over one year under these chemical conditions. Ni diffusion into the montmorillonite structure could be excluded. The structural order about Ni atoms increased with time, and this molecular-scale observation provides a rationale to explain the reduction of Ni desorption measured on aged products. In conclusion, metal attachment through edge-sharing surface complex may reduce durably metal bioavailability and mobility in soil and water environments.

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Specific sorption of Fe(II) on synthetic montmorillonite in anoxic conditions

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Previous studies on natural montmorillonite (MX80 <2µm fraction) showed that broken clay edges sorbed Fe(II) with a great efficiency in anoxic conditions [1]. This high affinity of Fe(II) for clay surfaces was explained by a two-steps mechanism in which Fe(II) was specifically sorbed prior to oxidation by clay structural Fe(III) [2].

The present study aimed to confirm the clay high affinity for Fe(II) specific sorption in absence of structural oxidant. A synthetic montmorillonite, free of iron (structural formula: $Ca_{0.3}$ $(Al_{1.4}Mg_{0.6})$ (Si_4) $O_{10}(OH)_2$), was used. ^{57}Fe(II) sorption experiments were conducted in strict anoxic conditions (N_2 atmosphere gloves-box, O_2 content < 1 ppm). Solid samples were collected and analyzed by Mössbauer spectroscopy.

Mössbauer spectra show that most of sorbed Fe(II) is oxidized despite of the absence of oxidant in the suspension. Comparisons with ferrous hydroxide, synthesized in the same redox conditions at higher pH, show that this oxidation can not be due to remaining O_2 in the suspension. Fe(III) Mössbauer contribution are present as paramagnetic doublets. Then, iron did not polymerize prior to sorption. These results confirm that a two-steps (sorption + oxidation) takes place at the clay-water interface. The nature of the oxidant seems to be water but H_2 release measurements are needed to assess this hypothesis.

References

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