Investigations of Fe(II) sorption onto montmorillonite. A wet chemistry and XAS study

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For some important radionuclides (RN) redox processes in high-level waste repositories play an important role in their retention. Virtually all deep underground repository concepts contain large amounts of iron, and reducing conditions will prevail in the long-term. The presence of high ferrous iron (Fe(II)) concentrations in the interstitial porewaters in the near- and far-fields could have a significant influence on the sorption behaviour of certain RNs through sorption competition effects. The best suited approach to investigate the sorption of Fe(II) on clay minerals and the influence of high aqueous Fe(II) concentrations on the RN retention is a multi-disciplinary one, consisting of macroscopic sorption experiments and advanced microscopic techniques, such as X-ray absorption spectroscopy (XAS).

Fe(II) sorption isotherms were measured on native iron containing montmorillonites (SWy with 3.4 wt.% structural Fe and STx with 0.7 wt.% Fe [1]), on a partially reduced SWy (structural Fe(III) reduced by sodium dithionite [2]) and on a synthetic iron-free montmorillonite (IFM) at pH 6.2 in 0.1 M $NaClO_4$ under anoxic conditions ($O_2 < 0.1$ ppm). The iron sorption on a reduced SWy and on IFM is significantly lower than that measured on native SWy and STx montmorillonites and agrees well with a calculated Fe(II) isotherm using the 2 Site Protolysis Non Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) sorption model [3]. The high sorption values on native iron bearing montmorillonites suggest that the sorbed Fe(II) is oxidised at the clay mineral surface to Fe(III).

XAS was employed to determine the oxidation state and the local structural environment of Fe sorbed on IFM. The results indicate that iron is predominantly present as Fe(II). Furthermore, the XAS analysis showed that Fe(II) is forming inner-sphere complexes at the IFM surface.

These findings support the hypothesis that oxidation of sorbed ferrous iron on the clay mineral surface might occur through an electron transfer to the structural ferric iron. 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 interpretation of the Fe(II)-clay interaction at the solid-liquid interface under anoxic conditions.

Reference:

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Identification of Cu-Mo anomalous zones using the Thermo Scientific Niton portable XRF analyzer in the Eaglehead Cu-Mo porphyry deposit, British Columbia, Canada

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Introduction

The Eaglehead Cu-Mo deposit is a classic porphyry style mineralization hosted by a granite-granodiorite intrusion and felsic volcanic wall rocks in northern British Columbia, Canada. The mineralization varies from disseminated to sporadic veins and veinlets of quartz±chalcopyrite±bornite±molybdenite. To identify Cu-Mo anomalous zones and compare assay data from the Thermo Scientific Niton portable XRF analyzer with the lab data, three sets of analyses were carried out on samples from drill hole DDH-106. These assays include direct shot on the core with the analyzer, and analyses of powder samples obtained from portable mill and grinder.

Results and Conclusion

The comparative studies show that Cu correlation (R^2) increases from 0.81 in direct shot assays to 0.84 and 0.86 in powder samples from mill and grinder, respectively (Table 1). Mo correlation increases from 0.87 in direct shot analyses to 0.95 in samples obtained by grinder. Zn correlation also increases by using powder samples from mill and grinder.

Thermo Scientific Niton XRF Analyzer Method	Lab (ICP-MS)		
	Cu	Mo	Zn
Direct Shot	0.81	0.87	0.66
Grinder	0.86	0.95	0.82
Mill	0.84	NA*	0.88
* Mill material contains Mo.			

Table 1: Correlation (R^2) between Thermo Scientific Niton XRF analyzer and lab assays.

In addition, depth-metal diagrams (Figure 1) show that Cu and Mo anomalous zones can be identified by using the Thermo Scientific Niton analyzer in the field.

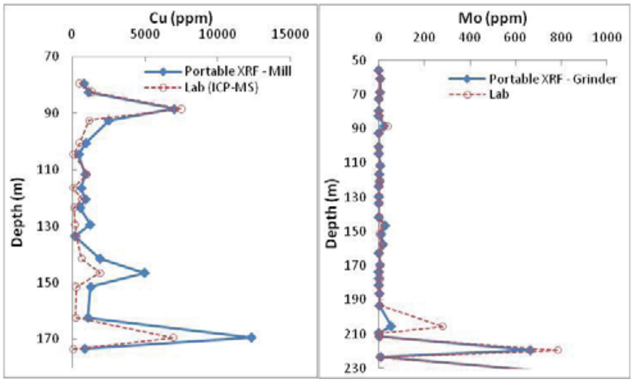

Figure 1: Representtaive depth-metal diagrams for Cu and Mo.