

Fe(II) uptake mechanisms on montmorillonite clay minerals: A multidisciplinary approach

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Virtually all radioactive waste repository designs contain large amounts of iron (steel canisters) and reducing conditions will prevail in the long-term. Due to the corrosion of steel canisters, high ferrous iron (Fe²⁺) concentrations in the interstitial porewaters in the near- and far-fields might be expected, which could have a significant influence on the sorption behaviour of other radionuclides through sorption competition effects. The best suited approach investigating the sorption of Fe²⁺ on clay minerals and the influence of high aqueous Fe²⁺ concentrations on the radionuclide retention by clay minerals is a multi-disciplinary one, consisting of macroscopic sorption experiments, geochemical modelling and advanced spectroscopic techniques, such as X-ray absorption spectroscopy (XAS). Fe²⁺ uptake on an iron-free synthetic montmorillonite in the absence of any competing metal was measured by batch sorption experiments under anoxic conditions (O₂ <0.1 ppm). A two-site protolysis nonelectrostatic surface complexation and cation exchange sorption model¹ was used to quantitatively describe the uptake of Fe²⁺ on montmorillonite. Two types of clay surface binding sites, so-called strong ($\equiv\text{S}^{\text{S}}\text{OH}$) and weak ($\equiv\text{S}^{\text{W}}\text{OH}$) edge sites, were required to model the Fe²⁺ sorption isotherms. XAS data showed spectroscopic differences between Fe sorbed at low and medium concentrations, which were chosen to be characteristic for uptake on strong and weak sites, respectively. The XAS data analysis indicated that Fe is located in the continuity of the octahedral sheet.²

Sorption competition experiments of divalent metals Fe and Zn were carried out to further elucidate the uptake processes at the clay mineral-water interface. The competition experiments were performed for the combinations of Zn(II)/Fe(II) and Fe(II)/Zn(II), where the former represents the trace index metal and the latter the blocking metal at high concentration. The results of the wet chemistry and XAS measurements indicate that Fe(II) is competing with Zn(II) if the Fe(II) is present in excess (blocking metal). However, no competition effects between Fe(II) and Zn(II) were observed if Zn(II) is the blocking metal. These results can be explained by a selective uptake of trace Fe on montmorillonite due to Fe(II)/Fe(III) redox processes taking place at the clay surface.² The outcome of this study contributes to an improved molecular understanding of the Fe-clay interaction under anoxic conditions in the absence and presence of other divalent metals.

[1] Bradbury&Baeyens. *J. Contam. Hydrol.*, 1997, **27**(3-4), 223-248. [2] Soltermann *et al. Environ. Sci. Technol.*, 2012, doi: 10.1021/es304270c.

Application of portable XRF analyzers in Au and PGE exploration: An example from the Bushveld Complex, South Africa

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Field portable X-ray fluorescence (FPXRF) analyzers are used worldwide in exploration and mining of various types of metallic and non-metallic deposits from base metals to REEs, precious metals and even hydrocarbons. FPXRF application in base metal and REE exploration and mining is relatively easy and straight forward due to their high economic threshold combined with low detection limit of these metals by FPXRF. Application in precious metal projects needs good understanding of the limitations of the technique; however, FPXRF can still be utilized in such cases using pathfinder elements. This paper summarizes one of these cases in Au-PGE exploration in the Bushveld Complex, South Africa.

In this study, the pathfinder elements were defined using lab assays of 63 samples that were collected along a stratigraphic section. Elements with highest correlation with the target metals (Au, Pt and Pd) were classified as pathfinder elements. These elements were Ni and Cu in this case study (Figure 1). Analyzes of the samples (both direct shot and pulp samples) by FPXRF indicate that all anomalous zones of Au, Pt and Pd can be easily identified by locating anomalies of Ni and Cu on prepared (pulp) and even un-prepared samples. Such anomalous samples have target elements lower than detection limit of FPXRF and should be analyzed by laboratory techniques.

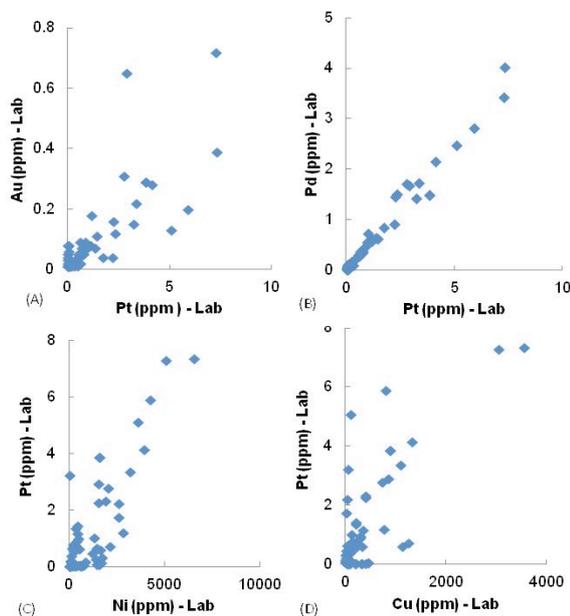


Figure 1: A and B) Correlation between target elements. C and D) Correlation between Pt and pathfinder elements (Ni and Cu).