Effects of ionic strength and multivalent cations on humic substances

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ANDRA is currently directing a research program aiming at providing the necessary data for assessing the feasibility of a deep reversible geological storage for High-Level and Long Lived (HLLL) nuclear waste at a depth of 500 m in the eastern of the Paris basin. It has been proved that the exposition of the host rock to concrete generates fulvic and humic acids [1]. The size and the charge of humic substances are key parameters to access their transport properties and their potential ability of complexation of radionuclides in the soil

We have already shown that an original method - high precision conductimetry coupled to a suitable transport theory [2] - give access, at various pH, to the size and the effective charge of reference humic substances and their analogues [3]. The results were confirmed by two independent techniques : atomic force microscopy (AFM), dynamic light scattering (DLS).

We now present the results obtained by conductimetry at different ionic strengths and in the presence of multivalent cations: (i) present in the host rock poral water (Ca^{2+}, Mg^{2+}), (ii) models for fission products (Cs^{+}) and actinides (Eu^{3+}) [4]. The mobility of the eventually formed complex is analyzed and the first results of this study are presented.

Sizes and effective charges of reference humic substances measured in these various conditions of ionic strength will be discussed together with AFM, DLS and also zetametry measurements.

[1] Claret *et al.* (2003) *Sci. Tot. Env.* **317** 189. [2] G.M. Roger *et al.* (2009) *J. Phys.Chem. B* **113** 8670. [3] G.M. Roger *et al.*, (2010) *Colloid Surf. A,* in press (doi:10.1016/j.colsurfa.2009.12.029) [4] ANDRA (2005) Dossier 2005 : Évaluation de la faisabilité du stockage géologique en formation argileuse, Châtenay Malabry

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Cr$^{(VI)}$ removal from alkaline COPR leachate using Green Rust

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Green rust materials have the potential to decontaminate Cr $^{(VI)}$ waste liquor especially at elevated pH, where other materials are ineffective. Chromium ore processing residue (COPR) produces highly alkaline leachate contaminated with chromate. Often a remediation strategy involves permeable reactive barrier (PRB) technology with zero valent iron (ZVI) as the reactive material. However ZVI does not immobilise Cr $^{(VI)}$ solutions of pH 12, typical of COPR leachate.

Laboratory based batch experiments were used to evaluate the effectiveness of ZVI and several different green rust formulations in removing Cr $^{(VI)}$ from anoxic chromate solutions over a range of alkaline pH values. Figure1 demonstrates the fast (10^3 s) removal of Cr $^{(VI)}$ from chromate solutions when reacted with carbonate green rust at pH 12. This behaviour is contrasted with the lack of Cr $^{(VI)}$ removal in the experiments with ZVI at the same pH over a timescale of 10^6 s.

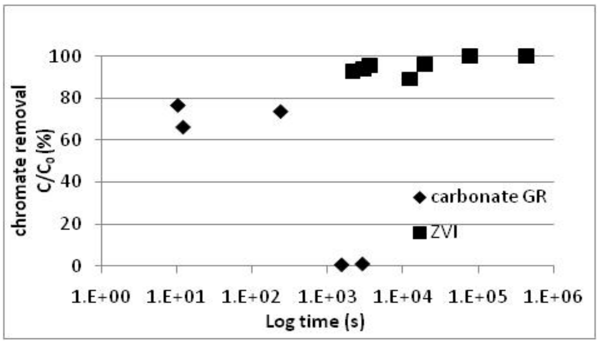

Figure 1: Rate of chromate removal at pH 12

The removal mechanism is presumed to be via reduction to Cr $^{(III)}$. Insoluble Cr $^{(III)}$ products precipitate onto the reactive material and can be removed. Therefore Green Rusts are ideal candidates for immobilising Cr $^{(VI)}$ from leachate at alkaline pH levels. They may also have an application in 'remediation by reduction' of other brownfield and radioactive contaminants such as U, Se, Tc and even recalcitrant organic contaminants such as tetrachloroethene.