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Retention behavior of As, Cr, B, Hg, and Cd on Teguline Clay samples

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Several low-level radioactive wastes (LLW) are characterized by their content in toxic elements (e.g. As, Cr, B, Hg, and Cd) in addition to radionuclides. Surficial aquitards are currently investigated for the containment of such radioactive and toxic waste, including Albian teguline Clay in the eastern part of the Paris Basin Lerouge et al. (2015). Teguline Clay is dominated by clay fraction: chlorite, kaolinite, illite-smectite mixed layer minerals, illite and /or muscovite and glauconite (35-65 %) associated with quartz-feldspar silty fraction (18-58 %). The carbonate fraction varies a lot in quantity but is essentially represented by calcite with minor dolomite (0-30 %). Ankerite and siderite are detected as well in the formation. Furthermore, accessory minerals like pyrite, celestite, gypsum, phosphates, and iron oxi-hydroxides are present (Lerouge et al. (2015)).

This work aimed at quantifying the retention of As, Cr, B, Hg and Cd in the teguline Clay. Preliminary bulk chemistry measurements revealed significant B ($106 \pm 10 \mu\text{g g}^{-1}$) and Cr ($115 \pm 2 \mu\text{g g}^{-1}$) unperturbed geochemical background, and lower As ($17 \pm 4 \mu\text{g g}^{-1}$), Cd ($3 \pm 0.2 \mu\text{g g}^{-1}$) and Hg ($4 \pm 2 \text{ng g}^{-1}$) content.

The natural release and the retention of As, Cr, B, Hg and Cd were investigated on a sample representative of the formation at 21.20 - 21.35 meter depth from the ground (AUB00307; reduced conditions) and on a sample near the surface at 8.25-8.41 meter depth from the ground (AUB00976; oxidizing conditions). All the experiments were carried out in a glove-box under anoxic conditions (concentration of O₂ in the glove-box atmosphere < 5 ppmv) in order to prevent the oxidation of redox sensitive solids and targeted elements (As, Cr, Hg). The solid samples was initially in contact with a solution with a composition close to the pore water composition determined for the Teguline Clays by Lerouge et al. (2015). The kinetics of As, Cr, B, Hg, and Cd release from the solids was followed during a 30 days equilibration period. In addition, batch retention tests were made with solid to liquid ratio of 10 g.L⁻¹ and with equilibration times up to 4 days.

The natural release tests revealed that both oxidized and reduced sample did not release Hg in solution, released only sporadically Cd (up to $2 \cdot 10^{-10} \text{mol L}^{-1}$) and Cr (up to $2 \cdot 10^{-9} \text{mol L}^{-1}$), and released significantly As ($4 \cdot 10^{-9} \text{mol L}^{-1}$) and B ($6 \cdot 10^{-6} \text{mol L}^{-1}$). Despite similar natural abundance in the solid, Cr and B had completely opposite behavior. This result was mainly due to the presence of Cr in the Cr(III) redox form, which is known to be poorly soluble. On the contrary, the high B release influenced the retention tests and its natural abundance had to be taken into account to determine its retention coefficients (R_D). Furthermore, B concentration was greatly influenced by the solid over liquid ratio (R_{SL}) ratio, increasing with R_{SL} . Its release was slightly higher for the reduced sample (AUB00307) than for the oxidized one. It is noteworthy that B could not only come from calcite as the B release by this mineral was one order of magnitude lower than the B measured for the clay samples. The limited release of the other elements had no influence on the retention coefficient calculations.

The retention tests enabled to classify the behaviour of these five toxic elements in three groups: (1) the redox sensitive elements whose retention was influenced by their redox state (Hg and Cr), (2) the

redox sensitive elements whose sorption was not influenced by their redox state (As), and (3) the elements not sensitive to redox (B and Cd). Cr was initially introduced in its hexavalent form and was quickly reduced by the samples and then immobilized. This reduction was more efficient in the case of AUB00307 than for AUB00976. Hg was injected in its Hg^{2+} form; a reduction in Hg^0 occurred in the sample AUB00307 and was not observed in AUB00976. This reduction led to the volatilization of part of the total Hg inventory and influenced the calculation of its retention coefficient. Unlike Cr and Hg, As retention was independent on whether arsenite or arsenate was injected and so the extent of As retention was not controlled by As redox state in our conditions. Cd was not impacted by the redox of the samples but co-precipitation products appeared at high concentration and influenced the calculation of the R_D values. At last, B retention was similar on the two samples and did not depend on the reducing capacity of the rock. However, if its natural abundance was not considered, the R_D was underestimated by 2 to 3 orders of magnitude.

Our experiments evinced that the redox potential of the sample and the elemental natural abundance were the two main parameters influencing the retention behavior of toxic elements.

References

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