

Effect of competitive ions on radiocaesium retention in clay mineral phases from *raña* deposits (NE Portugal)

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The *raña* deposits studied, forming thick but spatially confined sequences at NE Portugal mainland, are continental detrital sediments whose fine matrix comprises abundant clay minerals (smectite 15 Å, kaolinite, and illite) and quartz, besides minor amounts of iron hydroxides. The grain size fraction <63 µm was examined for radiocaesium (¹³⁷Cs) adsorption/desorption in order to test its use as liner/backfill/buffer for low and intermediate level waste (LILW) repositories. The ¹³⁷Cs adsorption was studied as a function of the initial Cs⁺ concentration (10⁻⁴ to 5x10⁻³M) in presence of K⁺ (poorly hydrated ion) and Mg²⁺ (strongly hydrated ion) competitive ions using a batch method. The ionic strength of the potassium and magnesium solutions was adjusted to concentrations similar to those found in surface natural waters streaming in the region where the *rañas* were sampled. The simulation of in situ conditions for ¹³⁷Cs desorption in case of an incident/accident scenario considered two different procedures: static and dynamic. In the static procedure the initial solution is kept in contact with the *raña* during all the experiment while in the dynamic pro-

cedure, at each contact time, the initial solution is replaced by a new one. The solutions pH value was controlled during the adsorption/desorption procedures. The ¹³⁷Cs adsorption is quite rapid, attaining the maximum saturation value after two weeks of contact time. The adsorption percentage values obtained in presence of Mg²⁺ are around 20% for the highest Cs concentration (5 x10⁻³M), ranging from 35% to 40% for lower Cs concentrations. The results obtained suggest also that the Regular Exchange Sites (RES) of clay mineral phases may become saturated at higher Cs concentrations, resulting in lower Cs adsorption at the Frayed Edge Sites (FES). Desorption studies reveal that the solid/liquid equilibrium was more quickly attained in the static system (1-2 days) than in the dynamic system (around two weeks). In addition, the ¹³⁷Cs retention in presence of Mg²⁺ ranges between 60% and 70% in the static system, being just around 30% in the dynamic system. As expected, cation exchange between Cs and competitive ions is more efficient in the dynamic system. In both systems, the strongly hydrated ion Mg²⁺, may lead to a wedge-effect in the FES pool,

allowing a Cs penetration into the clayed-matrix and a consequent decrease in ^{137}Cs desorption levels. In the static system, the Mg and Cs concentrations in solution reach a dynamic equilibrium; consequently, no further ^{137}Cs is released without renewal of the solutions. Contrarily, in the dynamic system the renewal of Mg-solution leads to an equilibrium breakdown, leading to an increase of ^{137}Cs release. The results obtained for K^+ as well as for a

bi-ionic scenario $\text{K}^+-\text{Mg}^{2+}$ in the liquid phase, indicate similar trends. According to these experimental results, the clay fraction of raña deposits can be faced as a potential liner/backfill/buffer component to be used in LILW repositories.

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