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## Adsorption and retarded diffusion of $\text{Eu}^{III}$ -EDTA -through hard clay rock.

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## Supplementary material for

### Adsorption and retarded diffusion of $\text{Eu}^{\text{III}}$ -EDTA<sup>-</sup> through hard clay rock.

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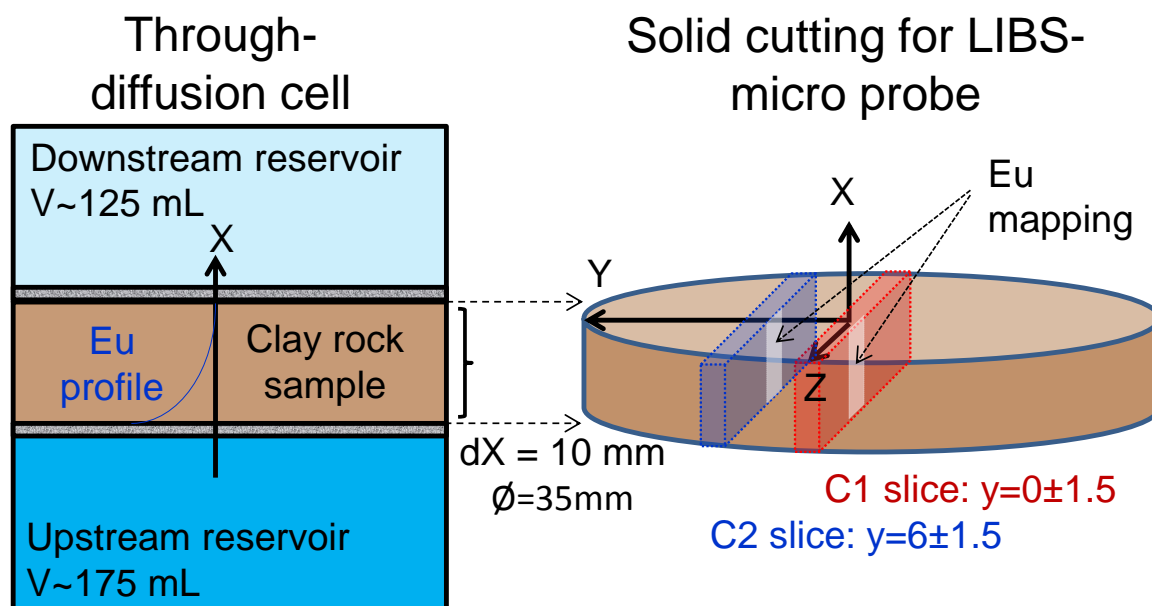
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**Table S1.** Synthetic poral water composition used for this study.

	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Sr <sup>2+</sup>	Cl <sup>-</sup>	ΣCO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	pH
C (10 <sup>-3</sup> moles L <sup>-1</sup> )	35.6	1.48	8.79	7.00	0.13	33.6	2.20	16.9	7.15

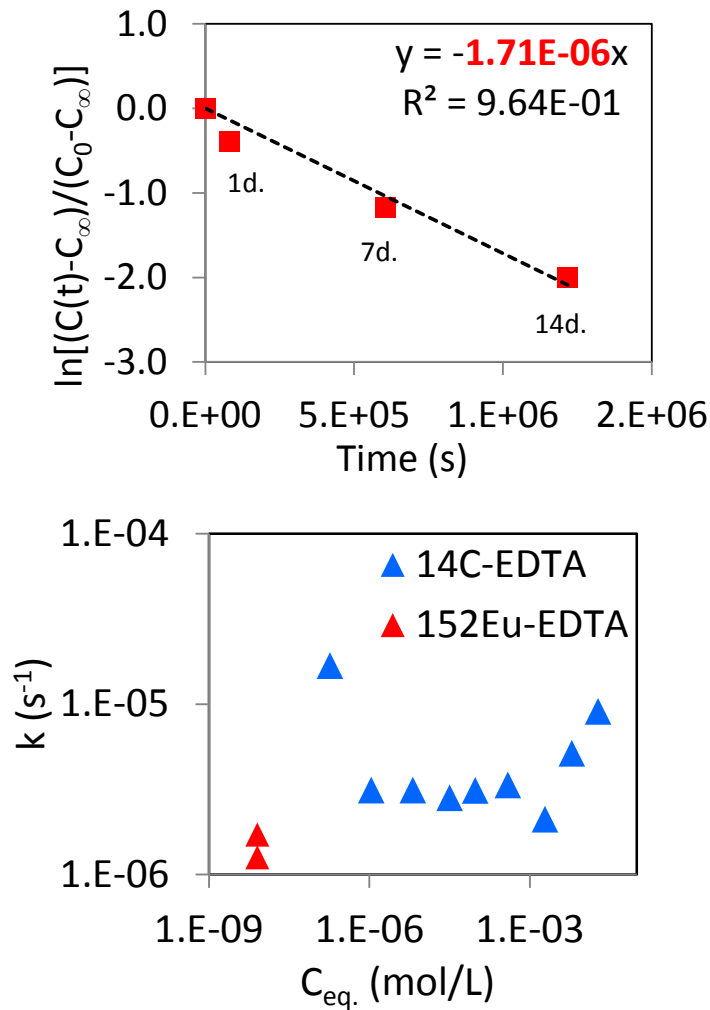


**Figure S1.** Scheme of solid samples sliced for LIBS-micro probe characterization.  
 (Left) Scheme of through-diffusion cell (diffusion gradient along X-axis).  
 (Right) Scheme of C1 and C2 solid samples sliced after diffusion.

A post-mortem characterization of the clay rock was performed after diffusion. To this aim, two rock samples were sliced. Eu mapping was measured by LIBS-micro probe technique. Several mapping were performed on center of C1 and C2 slices. Typical dimensions of mapping were  $dX \times dZ \sim 10 \times 1$  mm<sup>2</sup> as shown in Fig. S1.

### Adsorption kinetics of <sup>152</sup>Eu-EDTA and <sup>14</sup>C-EDTA on COx clay rock

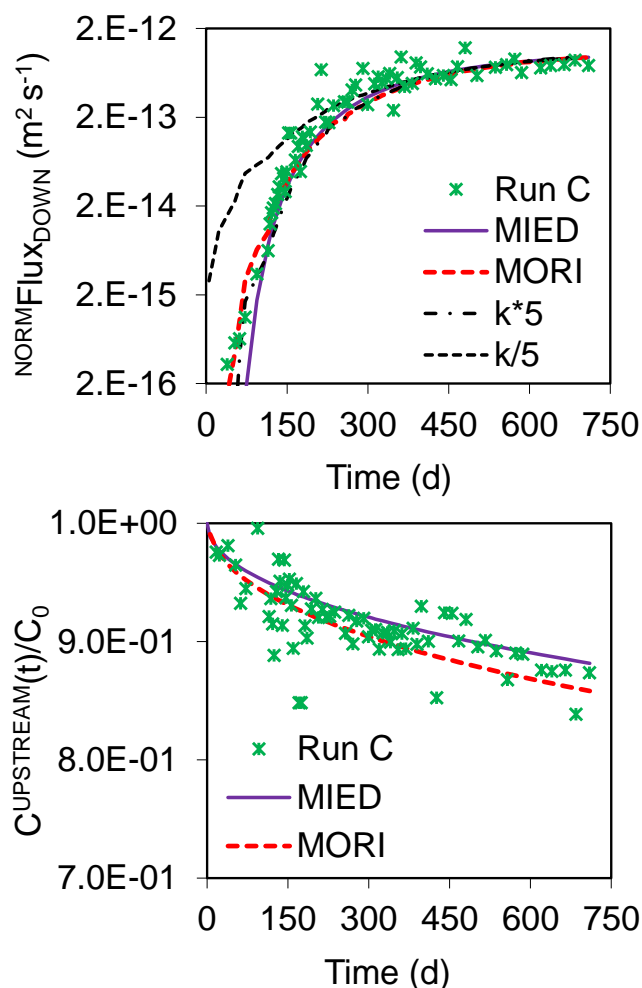
Adsorption kinetics for <sup>152</sup>Eu in presence of EDTA and <sup>14</sup>C-EDTA was measured on COx clay rock up to 14 days. A rough estimation was performed assuming an exponential decay of concentration in solution. The kinetic rate was then extrapolated by linear regression on  $\ln[(C(t)-C_{\infty})/(C_0-C_{\infty})]$  (Figure S2, top). The corresponding rate,  $k^{\text{EXP}} = 1.71 \cdot 10^{-6} \text{ s}^{-1}$ , was used to model run C. All kinetics data are gathered in Figure S2 (bottom) and were in the range  $[10^{-6} - 2 \cdot 10^{-5}] \text{ s}^{-1}$ .



**Figure S2.** Experimental adsorption kinetics of EDTA complexes on COx clay rock.  
 (top) Example of linear regression for  $[Eu]_{eq} = 8 \cdot 10^{-9} \text{ mol L}^{-1}$ .  
 (bottom) Experimental adsorption rates as a function of concentration of adsorbates.

### Effect of kinetics on through-diffusion modelling

The effect of slow reversible adsorption kinetics was modelled using semi-analytical solutions provided for through-diffusion cells by Moridis (1998). The adsorption rate for run C was supposed equal to the value measured by batch experiments:  $k = 1.71 \cdot 10^{-6} \text{ s}^{-1}$ . The best fit was obtained with values  $D_e = 1.74 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  and  $K_d = 2.08 \text{ L} \cdot \text{kg}^{-1}$  is presented in figure S3. This modelling highlights two results. Firstly, an early rise of the downstream flux before 70 days may be explained by slow adsorption. Secondly, such adsorption kinetic fail to explain the main difference between  $R_d$  measured in batch experiments and  $K_d$  adjusted from diffusion experiments.



**Figure S3.** Modelling of downstream flux (top) and upstream concentration (bottom) with two models: MIED and MORI respectively without and with taking into account adsorption kinetics. Adjusted parameters are  $(D_e, K_d) = (1.5 \cdot 10^{-12}, 1.8)$  and  $(1.7 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}, 2.1 \text{ L kg}^{-1})$  for MIED and MORI respectively. Dark curves represent effect of adsorption rates five times higher or five times lower than the experimental value:  $k = 1.71 \cdot 10^{-6} \text{ s}^{-1}$ .

### Bibliography:

Moridis, G.J., 1998. A Set of Semianalytical Solutions for Parameter Estimation In Diffusion Cell Experiments. Sci. New-York.

Wu, S.L., Horrocks, W.D., 1996. General Method for the Determination of Stability Constants of Lanthanide Ion Chelates by Ligand-Ligand Competition: Laser-Excited  $\text{Eu}^{3+}$  Luminescence Excitation Spectroscopy. Anal. Chem. 394–401.