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

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Supplementary material for

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Content:

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

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	Cl^-	ΣCO_2	SO_4^{2-}	pH
C (10^{-3} moles L^{-1})	35.6	1.48	8.79	7.00	0.13	33.6	2.20	16.9	7.15

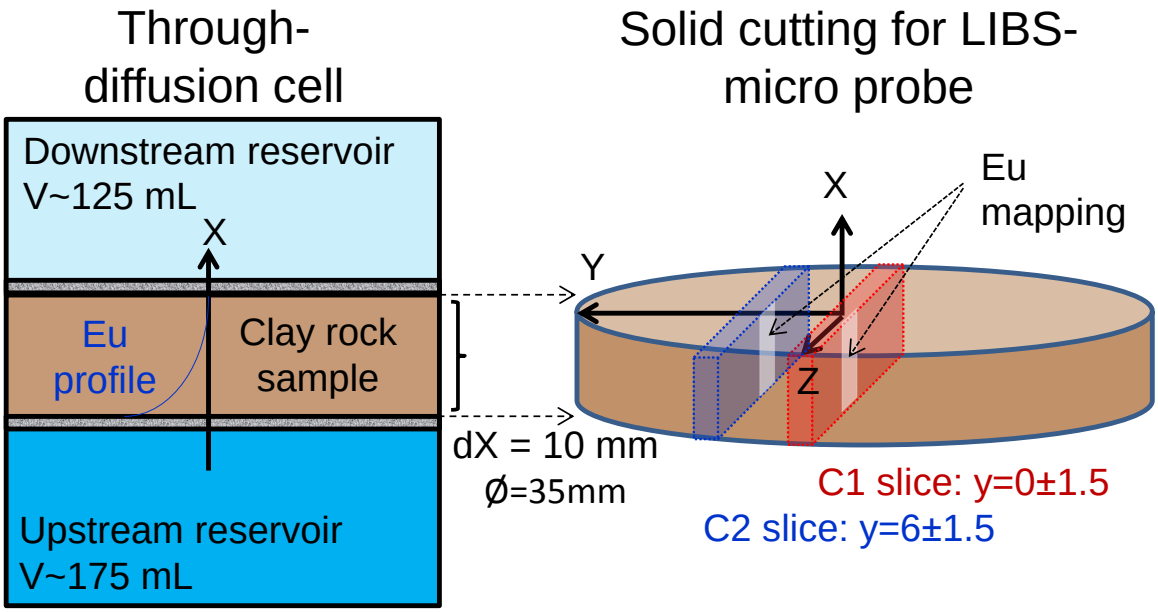

Figure S1. Scheme of solid samples sliced for LIBS-micro probe characterization.
(Left) Scheme of through-diffusion cell (diffusion gradient along X-axis).
(Right) Scheme of C1 and C2 solid samples sliced after diffusion.

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×dZ~10×1 mm^2 as shown in Fig. S1.

Adsorption kinetics of ^{152}Eu-EDTA and ^{14}C-EDTA on COx clay rock

Adsorption kinetics for ^{152}Eu in presence of EDTA and ^{14}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, $k^{EXP} = 1.71\ 10^{-6}\ s^{-1}$, was used to model run C. All kinetics data are gathered in Figure S2 (bottom) and were in the range $[10^{-6} - 2\ 10^{-5}]\ s^{-1}$.

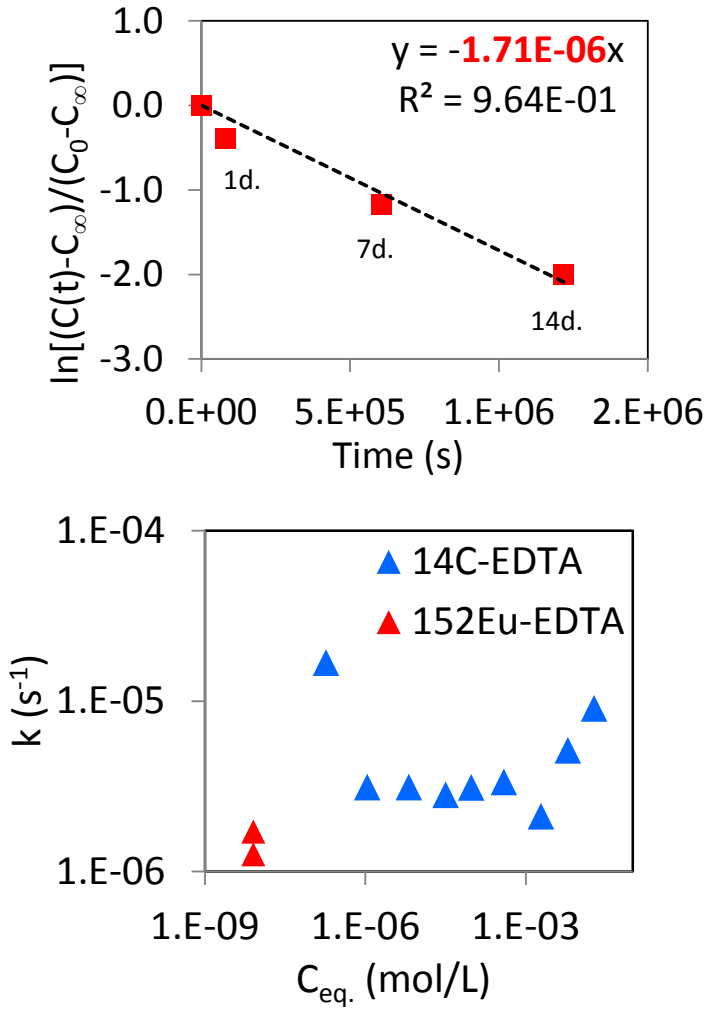

Figure S2. Experimental adsorption kinetics of EDTA complexes on COx clay rock.
(top) Example of linear regression for $[Eu]_{eq.} = 8\ 10^{-9}$ mol L^{-1}.
(bottom) Experimental adsorption rates as a function of concentration of adsorbates.

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: $k = 1.71\ 10^{-6}\ s^{-1}$. The best fit was obtained with values $D_e = 1.74\ 10^{-12}\ m^2.s^{-1}$ and $K_d = 2.08\ L.kg^{-1}$ 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.

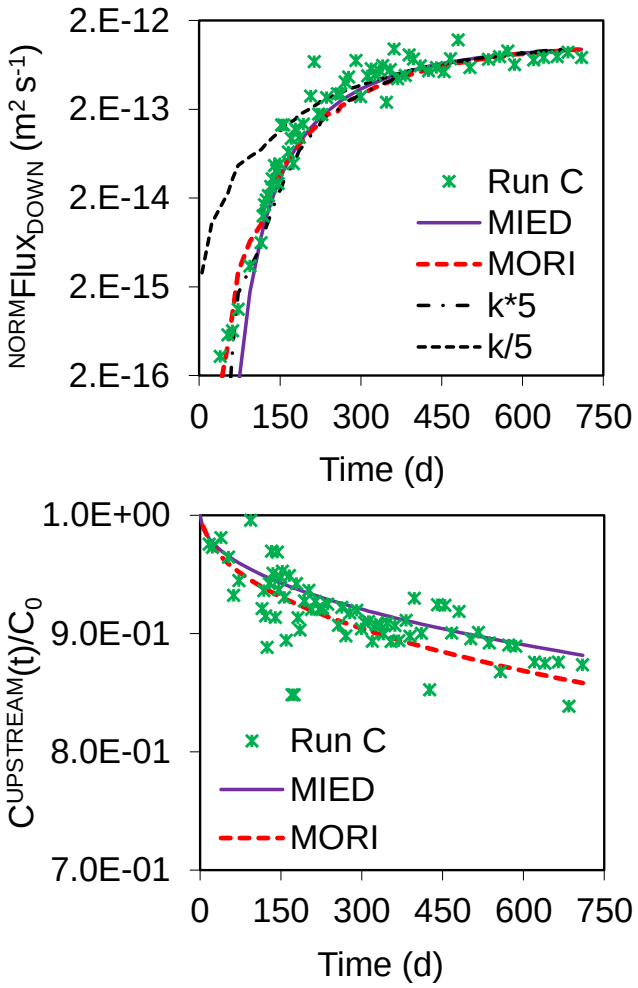

Figure S3. Modelling of downstream flux (top) and upstream concentration (bottom) with two models: MIED and MORI respectively without and with taking into account adsorption kinetics. Adjusted parameters are (D_e, K_d) = (1.5 10^{-12}, 1.8) and (1.7 10^{-12} m^2 s^{-1}, 2.1 L kg^{-1}) for MIED and MORI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

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