Role of EDTA, citrate and phthalate on Cs, Sr, Eu and U adsorption by smectite and evaluation by geochemical modeling

Tiziana Missana [*], Miguel García-Gutiérrez

CIEMAT, Physical Chemistry of Actinides and Fission Products Unit, Avenida Complutense 40, 28040, Madrid, Spain

ABSTRACT

The presence of organic ligands may exacerbate the mobility of contaminants by stabilizing them in the aqueous phase and reducing their retention on the solid phases, representing an additional environmental hazard.

We investigated the impact of EDTA, citrate and phthalate on the adsorption of four different radionuclides (RN = ^{137}Cs, ^{85}Sr, ^{152}Eu and ^{233}U) by a well-characterized smectite clay and evaluated the capability of sorption modeling to incorporate the impact of these organic ligands.

We analyzed the effect of ligand concentration (from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M) on RN retention at two different pH values (approximately 5 and 9) to contemplate the occurrence of different adsorption mechanisms in clays (cation exchange or surface complexation) as well as the RN and organic speciation.

The results suggested that phthalate had a minimal effect on the retention of the studied RNs, while EDTA and citrate significantly decreased the adsorption of Eu, Sr and U, even making it drop to zero in some cases. The simulation outcomes demonstrated that, in most cases, the variation in the distribution coefficient (K_d) as a function of the organic concentration could be accurately replicated with the available thermodynamic data, but few relevant discrepancies were identified.

The importance of the possible competitive effects of trace ions in the equilibrium water (notably Ca) for the overall assessment of the role of organic matter on RN retention was highlighted.

1. Introduction

Adsorption on mineral surfaces is the main mechanism retarding the migration of toxic elements (such as heavy metals HM or radionuclides RN) from contaminated sites or radioactive waste disposal. In the latter context, clay materials are often used as geochemical or engineered barriers because of their high cation exchange capacity (CEC) and consequent ability to retain contaminants. Bentonite is considered an engineered barrier material in many radioactive waste disposal concepts (Sellin and Leupin, 2014; Pusch, 2006).

All factors affecting contaminant aqueous speciation and solubility—with a special focus on those that may promote their mobility—must be analyzed to provide sound knowledge on contaminant behavior in different scenarios and to assess the safety function of barrier materials.

The presence of organics is an issue of concern because they can cause an enhancement of contaminant mobility. This undesired impact is related to the formation of aqueous stable complexes between HM or RN and the organics, which may increase contaminant aqueous

solubility and/or inhibit the retention on the sorbent mineral surfaces (Santschi et al., 2017) (Hummel et al., 2020). The presence of organic materials is especially concerning in low-intermediate level radioactive waste disposal, as their amount may be higher than that naturally present in a soil or a geological formation and with a large degree of chemical diversity (Abrahamsen et al., 2015) (Serne et al., 1996).

In this study, we focus on three different organic ligands: ethylenediaminetetraacetic acid (EDTA), citrate (CIT) and phthalate (PHT). Chelating agents such as EDTA or citric acid, among others, are used in decontamination processes and can be present in appreciable concentrations in nuclear installations (Rufus et al., 2004) (Byrd et al., 2021) (Seliman et al., 2010). EDTA, was clearly implicated in RN migration at the Oak Ridge National Laboratory, USA, (Killey et al., 1984) and many different studies have shown its capability of strongly chelating tri- and tetravalent actinides (Reinoso-Maset et al., 2012) (May et al., 2012), enhancing their mobility in different environments. Furthermore, EDTA complexes with metals are very stable, persistent, and toxic (Malinen et al., 2022). Apart from having good chelating properties, citric acid is very common in nature, and it is widely used in industry for numerous

applications. The occurrence of phthalic compounds in landfills can be attributed to different sources, including the existence of plasticizers and PVC products (Mersiowsky, 2002). Furthermore, Colombani et al. (2009) (Colombani J et al., 2009) found that phthalates might be released upon PVC degradation due to radiolysis.

The possible adverse consequences of organic ligands on RN migration have been discussed for quite some time; however, accurately modeling and predicting these effects remains a challenging task. The effect of a particular ligand may be completely different for different radionuclides or, for the same element, under different chemical environments, and this highlights the importance of thermodynamic modeling for assessing the role of organics on RN retention (Keith-Roach, 2008).

Thermodynamic sorption models can be a very useful additional tool for the interpretation of experimental sorption data and the evaluation of the retention properties of materials under variable chemical conditions, but indeed, to date, their application for the analysis of RN retention in the presence of organic ligands is very limited (Fralova et al., 2021). Its implementation might also be partly constrained by the availability of comprehensive and accurate thermodynamic data for RN-ligand complexes (Keith-Roach, 2008). For example, despite EDTA being one of the most extensively studied organic ligands, the reported stability constants for actinide-EDTA complexes were reported to vary by orders of magnitude (Cartwright et al., 2007). Hummel et al. (2005) (Hummel et al., 2020) summarized and evaluated the thermodynamic data of different RN (U, Np, Pu, Am, Tc, Se, Ni and Zr) complexes with selected organic ligands (oxalate, citrate, EDTA and isosaccharinate (ISA)) to the best of the experimental data available at that time.

The objective of the present study is to analyze the effects of different organic ligands on the retention of four radionuclides (^{137}Cs, ^{85}Sr, ^{152}Eu and ^{233}U), by a smectite clay (FEBEX bentonite), which has been largely studied in the past, and to evaluate the possibility of modeling their impact as a function of the selected ligand concentration ($1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M), considering the available thermodynamic information.

The selected RNs cover a wide range of physicochemical properties (alkali and earth-alkali metals, lanthanides, and actinides), and their adsorption on the FEBEX clay (in the absence of the organics) was already thoroughly analyzed and modeled, with this information being the basis of the present study. The experimental tests were performed at two different pH values to evaluate the results based on RN and organic speciation and eventually to account for the existence of predominant adsorption mechanisms (cation exchange and/or surface complexation). The significance of trace ions, such as Ca^{2+}, which are frequently present in solutions, even when purified clays are employed, is emphasized.

This systematic approach allowed us to understand the role of the selected ligands on RN retention in a very important barrier material (smectite) and to identify the main uncertainties still related to thermodynamic modeling.

2. Materials and Methods

2.1. Clay

FEBEX bentonite is a Spanish clay that has been studied for a long time in many international projects related to the management of radioactive waste (Fernández et al., 2018). This clay has a high smectite content ($93 \pm 2\%$) with a cation exchange capacity, CEC, of 100 ± 4 meq/100 g and a N_2-BET surface area of 59 m^2 g^{-1} (Missana et al., 2021).

For adsorption studies, the clay was converted into its Na-homoionic form, and the powder was washed three times with 1 M NaClO$_4$. Then, the excess salt was eliminated by washing several times with ultrapure (UP) water until the electrical conductivity of the suspension was lower than 30 μS cm^{-1}. To avoid the loss of the fine fraction, the procedure is carried out using dialysis bags. Then, the solid was dried in an oven at 40 °C, ground in an agate mill and sieved (<64 μm).

2.2. Organics

All the chemicals used were of analytical grade, and the initial solutions of the selected organics were prepared in ultrapure water, dissolving the respective salts: EDTA in the form of disodium salt dihydrated (C$_{10}$H$_{14}$N$_2$Na$_2$O$_8$·2H$_2$O, Merck CAS 6381-92-6) and citric acid (C$_6$H$_8$O$_7$, Sigma Aldrich, CAS 77-92-9). phthalic acid (C$_6$H$_4$(CO$_2$H)$_2$) was obtained upon dissolving phthalic anhydride (C$_8$H$_4$O$_3$, Sigma Aldrich, CAS-85-44-9) in water at 70 °C. Solutions of the organic at different concentrations were prepared for their use in sorption tests (from $1 \cdot 10^{-4}$ to 0.1 M).

2.3. Radionuclides

The isotopes used for these tests were ^{137}Cs, ^{85}Sr, ^{152}Eu and ^{233}U. The initial stock solution are CsCl, SrCl$_2$ EuCl$_3$ in 0.5 M HCl and UO$_2$(NO$_3$)$_2$ in 0.5 M HNO$_3$. The first three isotopes are gamma emitters, and their concentration was measured by γ-counting with a NaI detector (Packard Autogamma COBRA 2) with a 4π geometry. Certified standards are used to determine the counting efficiency for each radionuclide.

Uranium was measured by liquid scintillation counting using a Tri-Carb 4910 TR (PerkinElmer) α/β analyzer and Ultima Gold™ as the scintillation cocktail. The expected quantity of α radiation of ^{229}Th produced by ^{233}U decay is undetectable under the experimental conditions. The concentration of each radionuclide used in sorption tests was $[^{137}Cs] = 1.3 \cdot 10^{-9}$ M; $[^{85}Sr] = 8.9 \cdot 10^{-10}$ M; $[^{152}Eu] = 3.8 \cdot 10^{-10}$ M and $[^{233}U] = 2.7 \cdot 10^{-7}$ M.

2.4. Batch sorption experiments

The degree of RN adsorption was determined by a batch sorption test under aerobic conditions and at room temperature (22 ± 2 °C). The tests were carried out with the Na-exchanged FEBEX clay, suspending 0.01 g of the clay powder in 10 mL of 0.1 M NaClO$_4$ within centrifuge tubes. After solid/electrolyte equilibration, the organic ligand and RN were added. The time between the addition of the ligand (first) and the RN is about 10 min. The concentration of the ligand was varied from approximately $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-3}$ M. Adsorption tests were carried out under both acidic (pH 4.5–5.5) and basic (pH 8–9) conditions, and the pH was adjusted upon RN addition. The mean pH for each test is specified in the figure containing the experimental data and the uncertainty is (± 0.2).

The samples were maintained under stirring for 7 days, and then to separate the solid and the liquid phase, they were centrifuged with a JOUAN MR22i centrifuge (rotor AM 50.14, radius of 97 mm) at the maximum speed (21255·g) during 30 min. This centrifugation ensures the separation of particles with a size higher than 50 nm. The supernatant was analyzed to measure the final activity of RN in the liquid phase at equilibrium; triplicates were used for each sample.

The distribution coefficient, K_d [mL·g^{-1}], represents the ratio between the concentration of RN adsorbed in the solid phase [mol·g^{-1}] and the concentration of RN remaining in the liquid phase [mol·mL^{-1}]. K_d is expressed as:

$$K_d = \frac{[RN]_{in} - [RN]_{fin}}{[RN]_{fin}} \cdot \frac{V}{m}$$

[RN]$_{in}$ represents the RN activity initially added (in *counts per minute per mL*) (cpm·mL^{-1}), [RN]$_{fin}$ is the RN activity measured in the supernatant (cpm·mL^{-1}) upon the separation of the solid and liquid phases, V is the volume of the solution and m is the mass of the solid. To account for the possible variations in this parameter over several orders of magnitude, the experimental data were expressed in logarithmic form (Log(K_d)).

2.5. Modeling

The calculations of RN and organic aqueous speciation and adsorption in the presence of the organics were carried out using the Chess v2.4 code (Van der Lee, 1998). Ionic strength corrections were made with the Davies equation.

Smectite has a permanent structural charge (equivalent to its CEC) and a smaller pH-dependent charge contribution from the amphoteric functional groups (SOH) at the particle edges, where the Si–O–Si or Al–O–Al bonds are broken (silanol and aluminol groups, respectively). These different surface charge contributions imply the existence of two main different adsorption mechanisms on smectite: cation exchange and surface complexation. Radionuclide adsorption processes on the Na-FEBEX clay (in the absence of organics) have been analyzed in the past, and the details of the sorption modeling for each element can be found elsewhere (Cs (Missana et al., 2014); Sr (Missana and García-Gutiérrez, 2007); Eu (Missana et al., 2021) and U (Missana et al., 2009) (Mayordomo, 2017). The same modeling approach for each element (using the same selectivity coefficients and complexation constants already published) was used in the present study, accounting for the presence of the organic ligand and the stability constants reported for the complexes with RNs.

Cesium adsorption by the FEBEX clay is assumed to occur only by cation exchange. In this clay, the existence of low-density but high-affinity exchange sites, such as the frayed edge sites, FES, was demonstrated. These FES-like sites are only accessible for alkali metals such as Cs^+ and K^+, and their cation exchange capacity (CEC_{FES}) is much smaller than the CEC of the clay. Considering this premise, the adsorption behavior of Cs on the FEBEX clay was modeled considering a two-site exchange model (Missana et al., 2014). In this work, the constants reported in (Missana et al., 2014) for the Na-FEBEX are used.

The sorption model for Sr, Eu and U by the FEBEX clay included both cation exchange and surface complexation reactions. The complexation model considers the existence of two SOH-type sites (weak, S_wOH, and strong, S_sOH). The main properties of the clay needed for sorption modeling are summarized in Table 1.

The thermodynamic database (TDB) used for calculation is ThermoChimie (TC-TDB), (Grivé et al., 2015) developed by the consortium Andra-RWM-Ondraf (the radioactive waste management agencies of France, UK and Belgium, respectively). This is mainly based on the books of the Nuclear Energy Agency of the Organization for Economic Co-operation and Development (OECD-NEA), which periodically publishes the updates of thermodynamic data for many radionuclides. The list of the data available for EDTA, CIT and PHT that were used for calculations are summarized in Table 2. Apart from the data related to the studied RN, the data relative to Ca -ORG complexes are also reported because the effect of Ca^{2+} will be included in the discussion. As previously reported, trace cations (Ca, Mg, Al, K) can be present in aqueous solutions in contact with the FEBEX clay, even after homoionization (Missana et al., 2014, 2021). For example, the range reported for Ca in the contact aqueous phase with Na-FEBEX is $5 \cdot 10^{-6}$ - $1 \cdot 10^{-4}$ (Missana

et al., 2021). The possible formation of aqueous complexes between these trace ions and the organic ligand must be evaluated because it can significantly modify the overall behavior of the considered RN (Keith-Roach, 2008).

As can be observed in Tables 2 and in the TC-TDB, some values needed for the modeling are missing: i.e., data for the Cs-PHT, Sr-PHT, Eu-CIT and Eu-EDTA systems. Therefore, for the Sr-PHT system, the Ca-PHT reactions and values were used, and for Eu, the data were available for the Cm/Am-CIT and Cm/Am-EDTA systems. The chemical analogy between Cm(III), Am(III) and Eu(III) is often assumed (Fralova et al., 2021).

The organic speciation ($1 \cdot 10^{-4}$ M) was calculated with TC-TDB (Fig. S1, of the Supplementary Material). The main species under the acidic/alkaline range for EDTA are: H₂(EDTA)[2-]/H(EDTA)[3-] (Fig. S1a). For citrate, the main species are H₂(CIT)[-] or H(CIT)[2-]/(CIT)[3-] under acidic/alkaline pH, and finally, for phthalate, H (PHT)[-]/(PHT)[2-].

The speciation of each RN (at the same concentration used in sorption tests) as a function of pH in 0.1 M NaClO₄ and in the presence of the ligands ($1 \cdot 10^{-4}$ M) was calculated with the data summarized in Table 2. As the sorption tests were carried out under atmospheric conditions, calculations also included the presence of carbonates. The results are provided in the Supplementary Material (Fig. 2S-5S).

3. Results and discussion

3.1. Cesium

Cesium adsorption on smectite occurs mainly by cation exchange and therefore is almost independent of pH. Cs adsorption in the Na-FEBEX clay has been observed to be nonlinear due to the existence of high affinity (FES-like) sorption sites, and therefore, K_d values depend on the Cs concentration. At a low RN concentration, such as that used in this study ($1.3 \cdot 10^{-9}$ M), Cs adsorption is dominated by FES. In the absence of organics and at an ionic strength of 0.1 M, the logarithm of the distribution coefficient ($LogK_d$) for Cs in the clay is approximately 4 (Missana et al., 2014). The $Log(K_d)$ values corresponding to [ORG] = 0 has been plotted on the y axis as a reference (blue points for pH~5 and red points for pH~9).

The distribution coefficients (K_d) for Cs in the clay, in the presence of increasing concentrations of organic ligands, are shown in Fig. 1. Fig. 1a, b and 1c shows the adsorption data in the presence of EDTA, CIT and PHT, respectively, and each figure includes the results obtained under both acidic and alkaline conditions.

No variations in K_d values can be seen within the experimental error, indicating that the presence of EDTA, CIT or PHT does not modify Cs retention. Only at pH = 9.4 and the highest PHT concentration is a decrease (of approximately half an order of magnitude) in $Log(K_d)$ observed. These results are in agreement with previous studies on Cs retention in natural materials which reported small to null effects of the presence of organic ligands (Byrd et al., 2021) (Montgomery et al., 2017) (Reinoso-Maset et al., 2013).

The variation in K_d as a function of the different ligand concentrations was calculated by sorption modeling (Section 2.5), and the continuous lines superimposed on the experimental points in Figs. 1–4 represent the results of the modeling calculations.

For Cs, even in the presence of organic ligands, the predominant species in solution is always Cs^+ and although Cs(EDTA)[3-] and Cs(CIT) [2-] species can be formed (Fig. S2), their concentration is negligible and does not alter Cs retention by the clay. The simulations performed agree with the experimental data (Fig. 1a and b).

No thermodynamic data were available for Cs-PHT, so the (small) decrease in adsorption experimentally observed at pH = 9.4 (Fig. 1c), in the presence of the highest concentration of PHT, could not be evaluated by modelling. As the presence of organic ligands shows no influence on the Cs uptake by the smectite clay, competitive Ca-ORG complexes were

Table 1
Surface properties of the clay needed to perform sorption modeling.

CEC	16.95 μeq·m²
CEC_{FES}	$7 \cdot 10^{-4}$ μeq·m²
S_wOH density	1.02 μeq·m²
S_sOH density	0.03 μeq·m²

Protonation and deprotonation reactions of SOH sites and surface species with respective LogK, as expressed in the geochemical CHESS code.

Equation	Surface species	Composition	LogK
$SsOH \Leftrightarrow SsO^- + H^+$	S_sO^-	1 S_sOH, −1 H^+	−9.9
$SsOH_2^+ \Leftrightarrow SsOH + H^+$	$S_sOH_2^+$	1 S_sOH, 1 H^+	4.8
$SwOH \Leftrightarrow SwO^- + H^+$	S_wO^-	1 S_wOH, −1 H^+	−8.4
$SwOH_2^+ \Leftrightarrow SwOH + H^+$	$S_wOH_2^+$	1 S_wOH, −1 H^+	5.3

Table 2

Thermodynamic data used for adsorption modeling in the presence of organic ligands (from ThermoChimie TDB).

	RN-ORG	Species	Composition	LogK
Cs(I)	**Cs-EDTA**	Cs(EDTA)[3-]	1 Cs [+], 1 EDTA[4-]	1.3
	Cs-CIT	Cs(CIT)[2-]	1 Cs [+], 1 CIT [3-]	0.98
	Cs-PHT	*No information included in TDB*		
Sr(II)	**Sr-CIT**	Sr(CIT)[-]	1 Sr [2+], 1 CIT [3-]	4.24
		Sr(CIT)$_2$(OH)[5-]	1 Sr [2+], 2 CIT [3-], −1 H^{+}, 1 H2O	−1.78
		Sr(CIT)$_2$ [4-]	1 Sr [2+], 2 CIT [3-]	4.84
		Sr(H$_2$CIT)[+]	1 Sr [2+], 1 CIT [3-], 2 H^{+},	12.46
		Sr(HCIT)	1 Sr [2+], 1 CIT [3-], 1 H^{+},	9.0
	Sr-EDTA	Sr(EDTA)[2-]	1 Sr [2+], 1 EDTA [4-]	10.3
		Sr(HEDTA)[-]	1 Sr [2+], 1 EDTA [4-], H^{+}	14.7
	Sr-PHT	*No information included in TDB. Values given for Ca-PHT*		
Eu(III)	**Eu-EDTA**	*No information included in TDB. Values given for Am/Cm-EDTA*		
	Am-EDTA	Am(EDTA)[-]	1 Am[3+], 1 EDTA[4-]	19.670
		Am(HEDTA)	1 H^{+}, 1Am[3+], 1 EDTA [4-]	21.84
	Eu-CIT	*No information included in TDB. Values given for Am/Cm-CIT*		
	Am-CIT	Am(HCIT)$_2$[-]	2 H^{+}, 1 Am[3+], 2 CIT[3-]	23.52
		Am(HCIT)[+]	1 H^{+}, 1Am[3+], 1 CIT [3-]	12.860
		Am(CIT)	1 Am[3+], 1 CIT[3-]	8.550
		Am(CIT)$_2$[3-]	1 Am[3+], 2 CIT[3-]	13.90
	Eu-PHT	Eu(PHT)[+]	1 Eu^{3+}, 1 PHT [2-]	4.96
		Eu(PHT)$_2$[-]	1 Eu^{3+}, 2 PHT [2-]	7.34
U(VI)	**U-EDTA**	(UO$_2$)$_2$(EDTA)	2 UO$_2$[2+], 1 EDTA[4-]	20.6
		UO$_2$(EDTA)[2-]	1 UO$_2$ [2+], 1 EDTA[4-]	13.7
		UO$_2$(HEDTA)[-]	1 UO$_2$ [2+], 1 H^{+}, 1 EDTA[4-]	19.61
	U-CIT	UO$_2$(HCIT)	1 UO$_2$ [2+], 1 H^{+}, 1 CIT[3-]	11.36
		UO$_2$(CIT)[-]	1 UO$_2$ [2+], 1 CIT[3-]	8.96
		UO$_2$(CIT)$_2$[2-]	2 UO$_2$ [2+], 2 CIT[3-]	21.3
	U-PHT	UO$_2$(PHT)	1 UO$_2$ [2+], 1 PHT[2-],	5.56
Ca(II)	**Ca-EDTA**	Ca(EDTA[2-]	1 Ca^{2+}, 1 EDTA [4-]	12.69
		Ca(HEDTA)[-]	1 Ca^{2+}, 1 H^{+}, 1 EDTA [4-]	16.23
	Ca-CIT	Ca(CIT)[-]	1 Ca^{2+}. 1 CIT[3-]	4.8
		Ca(H$_2$CIT)[+]	1 Ca^{2+}, 2 H^{+}, 1 CIT [3-]	12.67
		Ca(HCIT)	1 Ca^{2+}, 1 H^{+}, 1 CIT [3-]	9.28
	Ca-PHT	Ca(HPHT)[+]	1 Ca^{2+}, 1 H^{+}, 1PHT[2-]	6.420
		Ca(PHT)	1 Ca^{2+}, 1PHT [2-]	2.49

not considered in the modeling.

3.2. Strontium

Strontium adsorption on FEBEX clay occurs mainly by cation exchange, and under acidic/neutral conditions, it is independent of pH. A small contribution of surface complexation is observed at pH > 8, leading to a slight increase in K_d values. At an ionic strength of 0.1 M, the measured Log(K_d) is approximately 2.2 at pH 5 and 2.3 at pH 9 (Missana and García-Gutiérrez, 2007).

The variation in the K_d values for Sr as a function of the organic concentration is shown in Fig. 2. Fig. 2a, b and 2c show the adsorption data in the presence of EDTA, CIT and PHT, respectively, under both acidic and alkaline conditions are reported.

Fig. 2a shows that at pH 5.1, the effect of EDTA on Sr adsorption is negligible, whereas at pH 8.7, when the EDTA concentration exceeds $1 \cdot 10^{-5}$ M, the measured K_d values drop below 1 mL g^{-1} (null adsorption, these points cannot be included in the graph). Similarly, Fig. 2b shows that the presence of CIT does not affect Sr adsorption at pH 5.1, but a clear decrease in sorption is observed at pH = 8.6, although the effect is observed only at the highest CIT concentration ($1 \cdot 10^{-3}$ M).

Fig. 2c shows that the effect of the presence of PHT on Sr adsorption is negligible under both acidic and alkaline conditions.

A full consensus on the role of organic ligands in Sr retention/migration behavior does not exist, and a lack of understanding still exists (Reinoso-Maset et al., 2013). Apart from the differences related to the chemical environment, the uncertainties are attributed to different causes, such as the instability and dissociation of Sr-ligand complexes (Pace et al., 2007) or the possible formation of ternary complexes (RN-ligand-sorbent) (Seliman et al., 2010).

The speciation of Sr is significantly different in the presence of the different ligands. In the EDTA-Sr system, the predominant species under acidic conditions is Sr^{2+}, whereas under alkaline conditions, the predominant species is the Sr(EDTA)[2-] complex. Accordingly, a minor effect of the ligand is expected under acidic conditions; modeling calculations of Sr adsorption at pH 5.1 agree very well with the experimental data, which are, in effect, minimally affected by EDTA (Fig. 2a).

However, under alkaline pH, model calculations predict a much stronger impact of EDTA on Sr retention than the experimentally observed (continuous red line). Nevertheless, If we assume the existence of $1 \cdot 10^{-5}$ M Ca (a value in the range of that experimentally measured Ca in solution), the simulation of the Log(K_d) for Sr retention at pH 8.7 and in the presence of EDTA fits much better the experimental data (red dashed line in Fig. 2a). Thus, the presence of Ca mitigates the effect of this organic on Sr retention. This shows that it is important to account for the formation of Ca-EDTA complexes competing with Sr-EDTA complexes, and this can also be true for other strong ligands. Thus, small changes in aqueous chemistry may lead to very different consequences in relation to RN migration in the presence of organics and their interpretation. Hereafter, in all further calculations, the effect of Ca was checked. The inclusion of Ca ($1 \cdot 10^{-5}$ – $1 \cdot 10^{-4}$ M) in the modelling at pH ∼ 5 did not modify the simulation.

In the Sr-CIT system, the predominant species in the pH range from 3 to 9 is Sr^{2+} (Fig. S3b). At pH 5.1, no Sr-CIT complexes are present, but the concentrations of Sr(CIT)[-] and Sr(CIT)$_2$(OH)[5-] are not negligible at pH 8.6. The variation in the Log(K_d) of Sr as a function of the CIT concentration under both acidic and alkaline conditions could be satisfactorily reproduced by calculations. The inclusion of Ca-ORG complexes did not change the simulations.

No thermodynamic data are available in the TC-TDB for Sr-PHT; therefore, in substitution, the stability constant reported for Ca has been used for modeling. Calculations showed that the presence of the Sr (HPHTHALAT)[+] complex is predicted at very low concentrations, so its effect on Sr adsorption is expected to be negligible, as shown by the
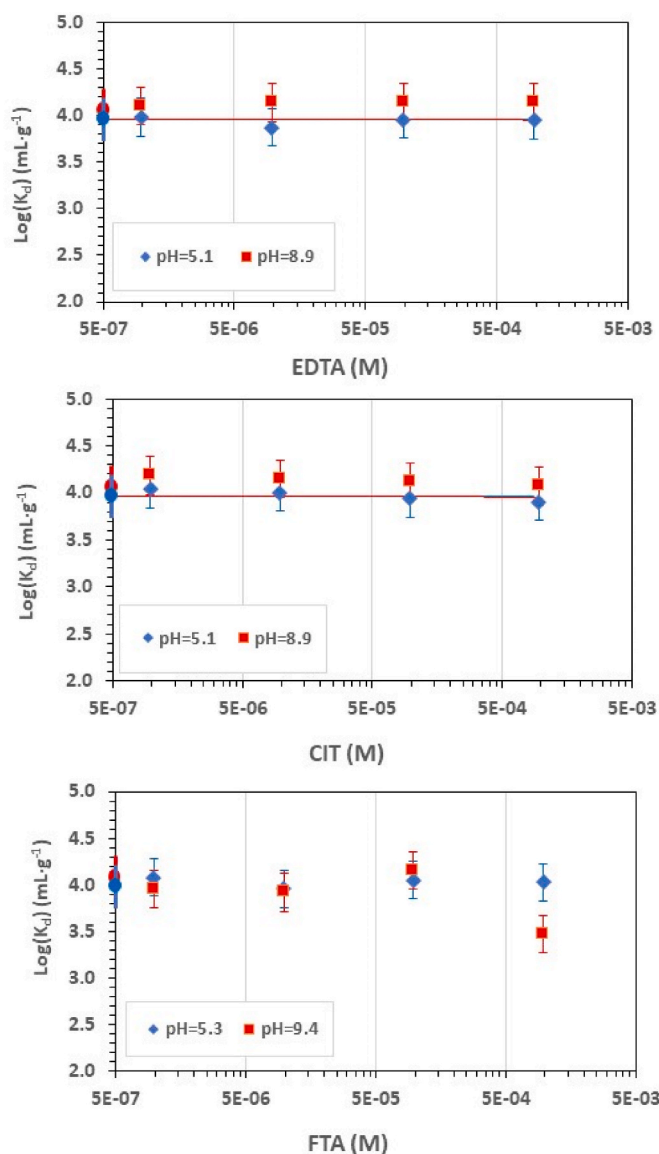
Fig. 1. Adsorption of Cs in clay in 0.1 M NaClO$_4$ in the presence of organics [ORG]: a) EDTA; b) CIT and c) PHT. (●) corresponds to data in the acid range of pH and (■) to the alkaline range. Continuous lines correspond to modeling calculations.

Fig. 2. Adsorption of Sr in the clay in 0.1 M NaClO$_4$ in the presence of organics [ORG]: a) EDTA; b) CIT and c) PHT. (●) corresponds to data in the acid range of pH and (■) to the alkaline range. Continuous lines correspond to modeling calculations. The dashed line represents the modeling including [Ca] = $1·10^{-5}$ M.
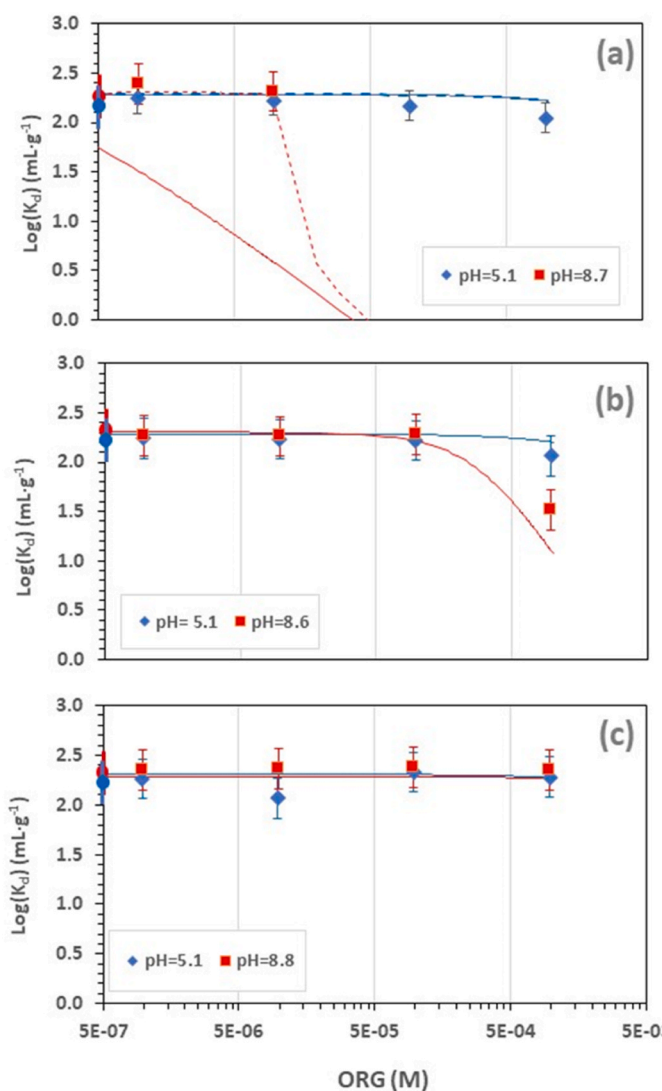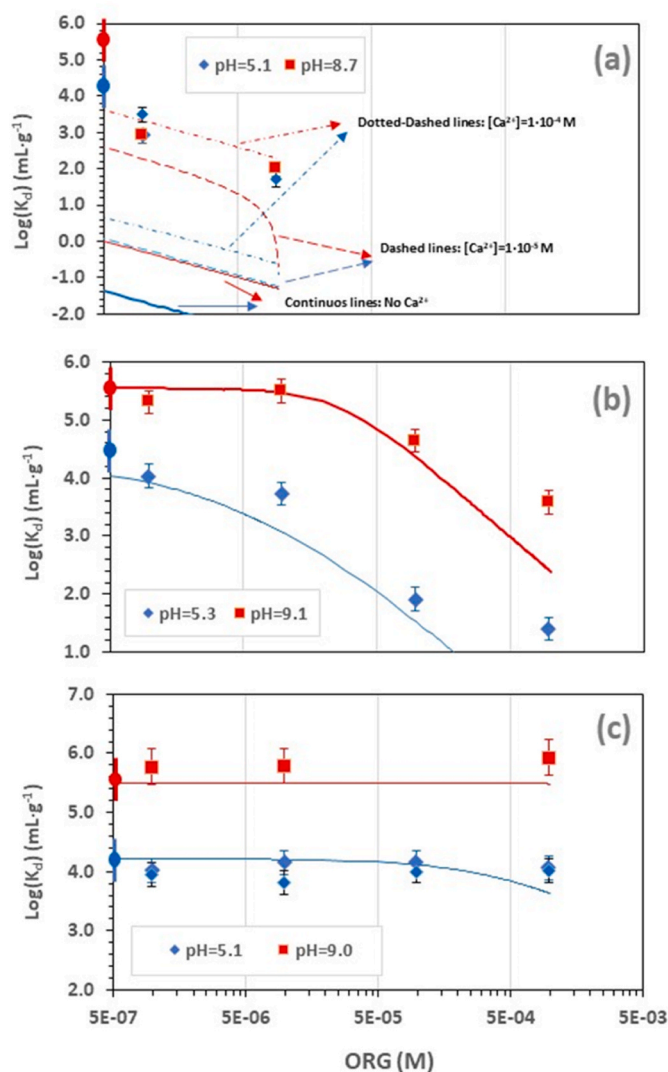
modeling calculations (continuous lines in Fig. 2c) and in agreement with the experimental data. No difference in the simulations were observed when including Ca.

3.3. Europium

Europium adsorption in FEBEX clay has a clear component due to ionic exchange at pH < 5, where adsorption is observed to be strongly dependent on the ionic strength and independent of pH (Missana et al., 2021). At higher pH, according to the predominance of inner sphere surface complexation, the dependence on the pH increases, and the dependence on the ionic strength becomes limited. At a NaClO$_4$ concentration of 0.1 M, at pH 5–5.5, the log(K_d) was ~3.6–4 and higher at pH 8–9, Log(K_d) ~ 5–6) (Missana et al., 2021).

The Log(K_d) for Eu in the presence of increasing concentrations of organics are shown in Fig. 3. Fig. 3a, b and 3c shows the adsorption data in the presence of EDTA, CIT and PHT, respectively.

As shown in Fig. 3a, at pH = 8.7, a very limited concentration of EDTA ($1·10^{-6}$ M) decreases the K_d by more than 2 orders of magnitude

with respect to the value reported in the absence of organics. Under both acidic and alkaline conditions, when the EDTA concentration exceeds $1·10^{-5}$ M, sorption becomes null (<1 mL g^{-1}). The lack of data points for high EDTA concentration is due to zero sorption (which cannot be expressed in logarithmic form).

Similarly, Fig. 3b shows that the presence of CIT (>$1·10^{-5}$ M) clearly affects Eu adsorption, even if to a lesser extent than EDTA, under both acidic and alkaline conditions. The observed decrease in K_d is approximately 2–3 orders of magnitude, more accentuated under acidic conditions.

Fig. 3c shows that the effect of PHT on Eu adsorption is negligible both at pH 5.1 and at pH 9, where Eu adsorption is still almost quantitative even in the presence of the ligand. As reported in the literature, the mobility of trivalent elements is generally impacted by the presence of EDTA and CIT, even if the degree strongly depends on the environmental conditions (Seliman et al., 2010) (Verma et al., 2014).

For Eu, as indicated in Table 2, no thermodynamic data are available for the Eu-EDTA or Eu-CIT systems. Calculations were carried out with the data available in the TC-TDB for the Am/Cm-EDTA and Am/Cm-CIT complexes. For the Eu-EDTA system, according to the speciation graph
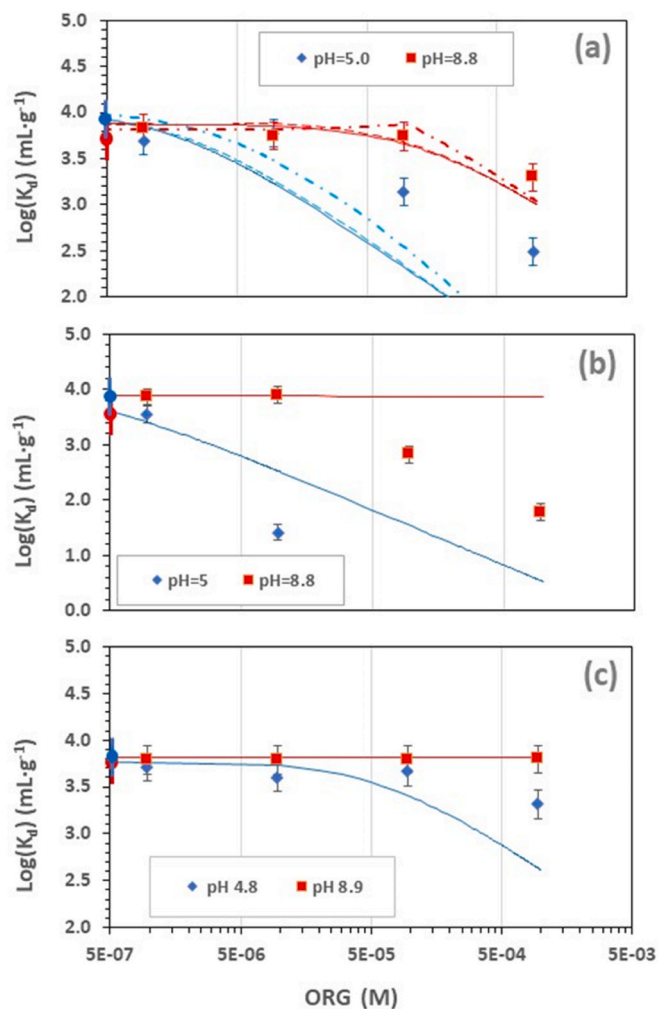
Fig. 3. Adsorption of Eu in the clay in 0.1 M NaClO$_4$ in the presence of organics [ORG]: a) EDTA; b) CIT and c) PHT. (●) corresponds to data in the acid range of pH and (■) to the alkaline range. Continuous lines correspond to modeling calculations. Dashed and dotted-dashed lines represent the modeling including [Ca] = 1·10^{-5} M or [Ca] = 1·10^{-4} M, respectively.

Fig. 4. Adsorption of U in the clay in 0.1 M NaClO$_4$ in the presence of organics [ORG]: a) EDTA; b) CIT and c) PHT. (●) corresponds to data in the acid range of pH and (■) to the alkaline range. Continuous lines correspond to modeling calculations. Dashed and dotted-dashed lines represent the modeling including [Ca] = 1·10^{-5} M or [Ca] = 1·10^{-4} M, respectively.

(Fig. S4a), the Eu(EDTA)[-] complex would dominate in the entire pH range; thus, a strong effect of EDTA on Eu adsorption is expected under both acidic and alkaline conditions, as experimentally observed (Fig. 3a). The simulations of data for the Eu-EDTA system, using the data of Table 2 (continuous lines), strongly underpredict the adsorption of Eu at both pH 5.1 and 8.7. Considering the presence of Ca in the system, over the possible range of concentration expected ([Ca] = 1·10^{-5} M, dashed lines and [Ca] = 1·10^{-4} M, dotted-dashed lines), the simulation improves for the data in the alkaline range, but it is still unsatisfactory for the data at pH 5.1, significantly underpredicting the model the experimental data.

The discrepancies observed in Fig. 3a between the data and the modelling can be attributed to either higher presence of divalent ion in solution competing with Eu for the formation of EDTA-metal complexes, or the possible formation of ternary Clay-Eu-EDTA, which will be discussed later.

In the Eu-CIT system, the major species at both pH 5 and 9 is Eu(CIT)$_2$[3-] (Fig. S4). The simulation of Log(K_d) of Eu as a function of CIT concentration is acceptable at both pHs but underpredicts adsorption at the highest ligand concentrations (Fig. 3b). In this case, considering the

presence of Ca does not improve the model.

In the Eu-PHT system, according to speciation calculations shown in Fig. S3c, Eu^{3+} is the major species under acidic conditions, but Eu(PHT)[+] also appears in nonnegligible concentrations. No relevant Eu-PHT complexes appear under alkaline conditions. In all cases, the effect of PHT on Eu adsorption on FEBEX clay was negligible. The predictions of Eu adsorption behavior in the presence of PHT are acceptable for both pH 5.1 and pH 9.0. The inclusion of Ca does not improve the model.

3.4. Uranium

Uranium adsorption in FEBEX clay is produced by the combination of cation exchange and surface complexation processes. Ionic exchange predominates at pH < 4, whereas at higher pH, surface complexation is the main adsorption mechanism. Missana et al. (2009) reported U sorption at an ionic strength of 0.1 M, log K_d values of 3.7–4.2 at pH 5–5.5 and of 3.5–4 at pH 8.5–9 (Missana et al., 2009).

The Log(K_d) for U on the clay in the presence of increasing concentrations of organics are shown in Fig. 4. Fig. 4a, b and 4c shows the adsorption data in the presence of EDTA, CIT and PHT, respectively, and each figure includes the results obtained under acidic and alkaline conditions.

Fig. 4a shows that the presence of EDTA decreases the Log(K_d) of

uranium under both acidic and alkaline conditions (approximately one order of magnitude), with a more pronounced effect at pH = 5 than at pH = 8.8.

Fig. 4b shows that the effect of CIT on U adsorption is even stronger. At pH = 8.8, the Log(K_d) decreases by more than two orders of magnitude, and at pH 5, for CIT concentrations higher than $1 \cdot 10^{-5}$ M, the measured K_d values drop below the detection limit ($K_d = 0$ cannot be included in the logarithmic scale).

Fig. 4c shows the U sorption behavior in the presence of PHT. No effects are observed at pH 8.9, whereas a small decrease in K_d values is noticed under acidic pH at the highest PHT concentrations.

In the literature, a decrease in U retention (or increase in U solubility) is reported in the presence of EDTA or CIT (Van der Lee, 1998) (Barger and Koretsky, 2011) (Felipe-Sotelo et al., 2015) (Lozano et al., 2011), even though it is recognized that due to complex U speciation under natural conditions, it is not often easy to fully interpret the underlying reaction mechanisms (Fralova et al., 2021) (Reinoso-Maset et al., 2013) (Kornilovich et al., 2006).

For U, the speciation diagram for U-EDTA (Fig. S5a) shows that UO$_2$(HEDTA)[-] dominates at pH 5, whereas at pH 8.8, the complex UO$_2$(EDTA)[2-] exists, but carbonate and hydrolyzed species are also relevant. Sorption modeling calculations reproduce the data quite well at pH 8.8, whereas less adsorption than experimentally observed is predicted at pH = 5. The inclusion of Ca ([Ca] = $1 \cdot 10^{-5}$ M, dashed lines and [Ca] = $1 \cdot 10^{-4}$ M, dotted-dashed lines) does not significantly change the model of data at pH 8.8 and only slightly improves the modeling of data at pH 5.

Speciation calculations in the U-CIT system indicate that UO$_2$(CIT)[-] is dominant over a wide range of pH values (3.5–7.5), but no U-CIT species appear at pH > 8 (Fig. S5b). Modeling calculations do not reproduce well the experimental data neither at pH 5 or pH 8.8. What is most concerning is that, at pH 8.8, the model notably underestimates the impact of CIT, as it lacks a relevant U-CIT complex in its database within the alkaline pH range.

Finally, the U-PHT complex was predicted under acidic conditions (Fig. S5c). The simulations of U adsorption in the presence of phthalate are quite satisfactory, with a slight underestimation of adsorption at pH 5.

Considering the RN speciation in the presence of the different organic ligands and the results of the modelling, it seems clear that the ORG-RN complexation in the liquid phase is the main mechanism affecting RN retention in the clay. Nevertheless, other possible mechanisms affecting the overall system behavior may exist. For example, the adsorption of the organic ligand on the clay or the formation of a solid-ligand-RN ternary complex has the potential to decrease the concentration of the ligand-RN complex in the liquid phase (Barger and Koretsky, 2011) (Kornilovich et al., 2006).

Previous studies on the retention of organic ligands in clayrock indicated no negligible adsorption (1–50 mL g^{-1}) for EDTA, CIT and PHT under neutral conditions (Rasamimanana et al., 2017) (Dagnelie et al., 2014). Complementary sorption tests were carried out to evaluate the extent of organic sorption in the Na-FEBEX clay. For all the three organics, the adsorption in the clay was null o very low (<5–8 %) and higher sorption values were always measured under acidic conditions. This is logical considering that the clay has a permanent negative charge, and surface interactions with negatively charged ligands (Fig. S1) are expected to occur only in the positively charged SOH sites.

Nevertheless, the formation of a ternary complex can be also promoted by the adsorption of charged aqueous ORG-RN species; this cannot be ruled out and would also reduce the effect of the presence of ligands.

As a summary of the experimental results, Table 3 includes the reduction observed for K_d values at the highest concentration of ligand investigated ($1 \cdot 10^{-3}$ M) with respect to the value obtained without the organic under the same experimental conditions. The presence of organic ligands in the system may become concerning when the K_d value

Table 3

Summary of the effects on K_d observed at the highest organic concentration ($1 \cdot 10^{-3}$ M) (OM = order of magnitude).

RN	EDTA		CIT		PHT	
	Acid	alkaline	acid	alkaline	acid	alkaline
Cs	*Negligible*	*Negligible*	*Negligible*	*Negligible*	*Negligible*	~0.5 OM
Sr	*Negligible*	$K_d = 0$	*Negligible*	~1 OM	*Negligible*	*Negligible*
Eu	$K_d = 0$	$K_d = 0$	~3 OM	~2 OM	*Negligible*	*Negligible*
U	~1.0 OM	~0.5 OM	$K_d = 0$	~2 OM	*Negligible*	*Negligible*

decreases by more than one order of magnitude and is critical when sorption is completely suppressed ($K_d = 0$).

Based on the experimental results, it appears that PHT has the least impact on the retention of the studied radionuclides, and Cs is the radionuclide least influenced by the presence of ligands.

Sr retention is decreased by EDTA and CIT (to a lesser extent) but only under alkaline conditions; Eu retention is drastically decreased by EDTA and CIT (to a lesser extent) both under acidic and alkaline conditions; U retention is also reduced by EDTA and CIT (more under acidic than alkaline conditions), but in this case, CIT has a stronger effect than EDTA. In general, thermodynamic modelling could reproduce the experimental behavior and helped understanding the most important factors which can affect RN mobility in the presence of organics in a clayey system.

4. Conclusions

The adsorption behavior of four radionuclides (^{137}Cs, [85]Sr, [152]Eu and [233]U) by Na-smectite clay in the presence of organic ligands (EDTA, citrate and phthalate) has been experimentally studied, and the results have been analyzed by sorption modeling.

Considering the RN speciation in the presence of the organic and the results of the modelling, it results that the ORG-RN complexation in the liquid phase is the main mechanism affecting RN retention in the clay.

The results show that the presence of phthalate has a negligible effect on the adsorption of all the studied RNs and that the adsorption of Cs is not affected by the presence of any ligand. EDTA and CIT significantly affect the adsorption of Eu and U and even, in some cases, completely suppress their retention in clay; Sr adsorption is only reduced under alkaline conditions.

Simulations of the dependence of K_d as a function of the ligand concentrations were acceptable in most cases. The presence of trace cations in the aqueous phase (such as Ca) may be very relevant to the overall RN behavior; thus, it is extremely important to analyze the water chemistry in detail. The effect of Ca is particularly important as competitive ion in the case of EDTA and its presence significantly mitigates the effects of this ligand on RN retention.

The simulations of Eu-EDTA and U-EDTA sorption data at pH 5 underestimated the experimental adsorption, which might be attributed to the possible interaction of the organic ligand with the clay under acidic conditions and/or the formation of clay-RN-ORG ternary complexes.

Finally, it is noteworthy that in the U-CIT system, the predictions significantly underestimated the detrimental role of CIT on U retention by the clay, especially under alkaline conditions.

Based on these findings, it is evident that accurate predictions regarding RN behavior in the presence of ligands necessitate strong support from thermodynamic modeling, which, in turn, calls for updated databases. Furthermore, a comprehensive understanding of the prevailing geochemical conditions is indispensable for an accurate interpretation of the results.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2023.105811.

References

Abrahamsen, L., Arnold, T., Brinkmann, H., Leys, N., Merroun, M., Mijnendonckx, K., Moll, H., Polvika, P., Sevcu, J., Small, J., Vikman, M., Wouters, K., 2015. A Review of Anthropogenic Organic Wastes and Their Degradation Behaviour. MIND Proj, p. 97. http://www.mind15.eu/wp-content/uploads/2015/11/MIND-Deliverable-1.1-Review-of-anthropogenic-organic-wastes.pdf.

Barger, M., Koretsky, C.M., 2011. The influence of citric acid, EDTA, and fulvic acid on U (VI) sorption onto kaolinite. Appl. Geochem. 26 https://doi.org/10.1016/j.apgeochem.2011.03.092. S158–S161.

Byrd, N., Lloyd, J.R., Small, J.S., Taylor, F., Bagshaw, H., Boothman, C., Morris, K., 2021. Microbial degradation of citric acid in low level radioactive waste disposal: impact on biomineralization reactions. Front. Microbiol. 12, 1–14. https://doi.org/10.3389/fmicb.2021.565855.

Cartwright, A.J., May, C.C., Worsfold, P.J., Keith-Roach, M.J., 2007. Characterisation of thorium-ethylenediaminetetraacetic acid and thorium-nitrilotriacetic acid species by electrospray ionisation-mass spectrometry. Anal. Chim. Acta 590, 125–131. https://doi.org/10.1016/j.aca.2007.03.010.

Colombani J, G.T., Herbette, G., Rossi, C., Joussot-Dubien, C., Labed, V., 2009. Leaching of plasticized PVC: effect of irradiation. J. OfAppliedPolymer Sci. 112, 1372–1377.

Dagnelie, R.V.H., Descostes, M., Pointeau, I., Klein, J., Grenut, B., Radwan, J., Lebeau, D., Georgin, D., Giffaut, E., 2014. Sorption and diffusion of organic acids through clayrock: comparison with inorganic anions. J. Hydrol. 511, 619–627. https://doi.org/10.1016/j.jhydrol.2014.02.002.

Felipe-Sotelo, M., Edgar, M., Beattie, T., Warwick, P., Evans, N.D.M., Read, D., 2015. Effect of anthropogenic organic complexants on the solubility of Ni, Th, U(IV) and U (VI). J. Hazard Mater. 300, 553–560. https://doi.org/10.1016/j.jhazmat.2015.07.060.

Fernández, A.M., Kaufhold, S., Sánchez-Ledesma, D.M., Rey, J.J., Melón, A., Robredo, L. M., Fernández, S., Labajo, M.A., Clavero, M.A., 2018. Evolution of the THC conditions in the FEBEX in situ test after 18 years of experiment: smectite crystallochemical modifications after interactions of the bentonite with a C-steel heater at 100 °C. Appl. Geochem. 98, 152–171. https://doi.org/10.1016/j.apgeochem.2018.09.008.

Fralova, L., Lefèvre, G., Madé, B., Marsac, R., Thory, E., Dagnelie, R.V.H., 2021. Effect of organic compounds on the retention of radionuclides in clay rocks: mechanisms and specifiCITies of Eu(III), Th(IV), and U(VI). Appl. Geochem. 127 https://doi.org/10.1016/j.apgeochem.2020.104859.

Grivé, M., Duro, L., Colàs, E., Giffaut, E., 2015. Thermodynamic data selection applied to radionuclides and chemotoxic elements: an overview of the ThermoChimie-TDB. Appl. Geochem. 55, 85–94. https://doi.org/10.1016/j.apgeochem.2014.12.017.

Hummel, W., Anderegg, G., Rao, L., Puigdomènech, I., Tochiyama, O., 2020. Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands. OECD Publishing. http://books.google.com/books?id=n1wPm-TeK_4C.

Keith-Roach, M.J., 2008. The speciation, stability, solubility and biodegradation of organic co-contaminant radionuclide complexes: a review. Sci. Total Environ. 396, 1–11. https://doi.org/10.1016/j.sCITotenv.2008.02.030.

Killey, R.W.D., McHugh, J.O., Champ, D.R., Cooper, E.L., Young, J.L., 1984. Subsurface cobalt-60 migration from a low-level waste disposal site. Environ. Sci. Technol. 18, 148–157. https://doi.org/10.1021/es00121a004.

Kornilovich, B.Y., Pshinko, G.N., Bogolepov, A.A., 2006. Effects of EDTA and NTA on sorption of U(VI) on the clay fraction of soil. Radiochemistry 48, 584–588. https://doi.org/10.1134/S1066362206060087.

Lozano, J.C., Blanco Rodríguez, P., Vera Tomé, F., Calvo, C.P., 2011. Enhancing uranium solubilization in soils by CITrate, EDTA, and EDDS chelating amendments. J. Hazard Mater. 198, 224–231. https://doi.org/10.1016/j.jhazmat.2011.10.026.

Malinen, L., Repo, E., Harjula, R., Huittinen, N., 2022. The effect of UV-C irradiation and EDTA on the uptake of Co2+ by antimony oxide in the presence and absence of competing cations Ca2+ and Ni2+. Nucl. Eng. Technol. 54, 627–636. https://doi.org/10.1016/j.net.2021.08.002.

May, C.C., Young, L., Worsfold, P.J., Heath, S., Bryan, N.D., Keith-Roach, M.J., 2012. The effect of EDTA on the groundwater transport of thorium through sand. Water Res. 46, 4870–4882. https://doi.org/10.1016/j.watres.2012.06.012.

Mayordomo, N., 2017. Experimental and theoretical studies of mixed smectite and Al2O3 nanoparticles to improve pollutant retention in geochemical barriers. Dr. Thesis. http://escuela-doctorado.uah.es/tesis/tesis.asp?CdPlan=D348&expe=4&proy=1&idioma=ingles.

Mersiowsky, I., 2002. Mersiowsky 2002- Long-term fate PVC in landfills.pdf. Prog. Polym. Sci. 27, 2227–2277.

Missana, T., García-Gutiérrez, M., 2007. Adsorption of bivalent ions (Ca(II), Sr(II) and Co (II)) onto FEBEX bentonite. Phys. Chem. Earth 32, 559–567. https://doi.org/10.1016/j.pce.2006.02.052.

Missana, T.L., Alonso, U., García-Gutierrez, M., Albarran, N., 2009. Experimental study and modeling of uranium (VI) sorption onto a Spanish smectite. Mater. Res. Soc. Symp. Proc. 1124, 5–10.

Missana, T., Benedicto, A., García-Gutiérrez, M., Alonso, U., 2014. Modeling cesium retention onto Na-, K- and Ca-smectite: effects of ionic strength, exchange and competing cations on the determination of selectivity coefficients. Geochem. Cosmochim. Acta 128, 266–277. https://doi.org/10.1016/j.gca.2013.10.007.

Missana, T., Alonso, U., García-Gutiérrez, M., 2021. Evaluation of component additive modelling approach for europium adsorption on 2:1 clays: experimental, thermodynamic databases, and models. Chemosphere 272. https://doi.org/10.1016/j.chemosphere.2021.129877.

Montgomery, D., Barber, K., Edayilam, N., Oqujiuba, K., Young, S., Biotidara, T., Gathers, A., Danjaji, M., Tharayil, N., Martinez, N., Powell, B., 2017. The influence of CITrate and oxalate on 99TcVII, Cs, NpV and UVI sorption to a Savannah River Site soil. J. Environ. Radioact. 172, 130–142. https://doi.org/10.1016/j.jenvrad.2017.03.017.

Pace, M.N., Mayes, M.A., Jardine, P.M., McKay, L.D., Yin, X.L., Mehlhorn, T.L., Liu, Q., Gürleyük, H., 2007. Transport of Sr2+ and SrEDTA2- in partially-saturated and heterogeneous sediments. J. Contam. Hydrol. 91, 267–287. https://doi.org/10.1016/j.jconhyd.2006.11.006.

Pusch, R., 2006. Chapter 11.4 clays and nuclear waste management. Dev. Clay Sci. 1, 703–716. https://doi.org/10.1016/S1572-4352(05)01023-8.

Rasamimanana, S., Lefèvre, G., Dagnelie, R.V.H., 2017. Adsorption of polar organic molecules on sediments: case-study on Callovian-Oxfordian claystone. Chemosphere 181, 296–303. https://doi.org/10.1016/j.chemosphere.2017.04.086.

Reinoso-Maset, E., Worsfold, P.J., Keith-Roach, M.J., 2012. The effect of EDTA, NTA and picolinic acid on Th(IV) mobility in a ternary system with natural sand. Environ. Pollut. 162, 399–405. https://doi.org/10.1016/j.envpol.2011.11.038.

Reinoso-Maset, E., Worsfold, P.J., Keith-Roach, M.J., 2013. Effect of organic complexing agents on the interactions of Cs+, Sr2+ and UO22+ with silica and natural sand. Chemosphere 91, 948–954. https://doi.org/10.1016/j.chemosphere.2013.01.105.

Rufus, A.L., Velmurugan, S., Sathyaseelan, V.S., Narasimhan, S.V., 2004. Comparative study of Nitrilo Triacetic Acid (NTA) and EDTA as formulation constituents for the chemical decontamination of primary coolant systems of nuclear power plants. Prog. Nucl. Energy 44, 13–31. https://doi.org/10.1016/S0149-1970(04)90005-4.

Santschi, P.H., Xu, C., Zhang, S., Schwehr, K.A., Lin, P., Yeager, C.M., Kaplan, D.I., 2017. Recent advances in the detection of specific natural organic compounds as carriers for radionuclides in soil and water environments, with examples of radioiodine and plutonium. J. Environ. Radioact. 171, 226–233. https://doi.org/10.1016/j.jenvrad.2017.02.023.

Seliman, A.F., Borai, E.H., Lasheen, Y.F., Abo-Aly, M.M., Devol, T.A., Powell, B.A., 2010. Mobility of radionuclides in soil/groundwater system: comparing the influence of EDTA and four of its degradation products. Environ. Pollut. 158, 3077–3084. https://doi.org/10.1016/j.envpol.2010.06.035.

Sellin, P., Leupin, O.X., 2014. The use of clay as an engineered barrier in radioactive-waste management - a review. Clay Clay Miner. 61, 477–498. https://doi.org/10.1346/CCMN.2013.0610601.

Serne, R., Felmy, A.R., Cantrell, K.J., 1996. Characterization of radionuclide-chelating agent complexes found in low-level radioactive decontamination waste. Lit. Rev. Prep. U.S. Nucl. Regul. Comm. NUREG/CR-6124 PNL-8856. http://www.iaea.org/inis/collection/nclcollectionstore/_public/27/063/27063466.pdf.

Van der Lee, J., 1998. Thermodynamical and Mathematical Concepts of CHESS.

Verma, P.K., Pathak, P., Mohapatra, P.K., 2014. Sorption of metal cations on suspended bentonite: effects of pH, ionic strength and complexing anions. Radiochim. Acta 102, 401–409. https://doi.org/10.1515/ract-2014-2160.