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Highlights

- Fe(II)-Al(III)-Cl LDH removes > 90% of aqueous Tc at pH > 6
- Tc retention is primarily due to Tc(VII) reduction to Tc(IV)
- Tc(IV) forms inner-sphere complexes and incorporates in secondary formed hematite

Abstract

Layered double hydroxides (LDH) play a decisive role in regulating the mobility of contaminants in natural and engineered environments. In this work, the retention of an Fe(II)-Al(III)-Cl LDH towards pertechnetate (TcO_4^-), which is the most stable and highly mobile form of Tc under aerobic conditions, is investigated comprehensively as a function of pH, Tc concentration and ionic strength. For a technetium initial concentration of 5 µM, its retention yield is higher than 80% from pH 3.5 to pH 10.5, especially at NaCl concentration below 0.1 M.

1

A combination of vibrational and X-ray absorption spectroscopy provides structural information on the retention mechanism on a molecular scale. X-ray absorption near edge spectroscopy (XANES) confirms that most of the Tc uptake is due to an initial Tc(VII) reduction to Tc(IV), and consecutive Tc(IV) interaction with the solid. The analysis of the extended X-ray absorption fine structure (EXAFS) reveals two different mechanisms of Tc(IV) interaction with hematite (sub-product of the LDH oxidation and confirmed by Raman microscopy). At low pH, sorption of Tc(IV) dimers via inner-sphere monodentate complexation on hematite dominates. In contrast, under alkaline conditions, Tc(IV) is incorporated into the structure of hematite. Additionally, *in situ* attenuated total reflection Fourier-transform infrared spectroscopy (ATR FT-IR) evidences a small contribution of the total uptake corresponding to Tc(VII) anion exchange.

The derived molecular structures increase confidence in predictive modelling of Tc migration patterns in subsurface environments, e.g. in the vicinity of a radioactive waste repository and treatment sites or in polluted areas due to other anthropogenic Tc sources.

1 Introduction

Technetium (Tc) is a transition metal placed in group 7 of the periodic table and is the lightest element whose isotopes are all radioactive [1]. Among them, ^{99}Tc is of highest environmental concern. It is a β-emitter with a long half-life ($2.1 \cdot 10^5$ years) that is produced in high yield (6%) during the fission of ^{235}U and ^{239}Pu and it is mainly spread in the environment by anthropogenic sources such as nuclear fuel cycle, nuclear weapon detonations and medical diagnostics [2] utilizing ^{99m}Tc mainly for skeleton scintigraphy and myocardial perfusion imaging.

Significant emissions of ^{99}Tc into the biosphere can cause damages to living organism after long-term exposure, in particular via accumulation in the food chain. [3]. Tc uptake has been reported in, e.g., crabs and lobsters after the discharge of waste waters from the British Nuclear Fuels Ltd reprocessing plant in Sellafield, GB [4,5]. In humans, ^{99}Tc accumulates in the thyroid

gland and gastrointestinal tract but it is excreted constantly [6], creating a secondary contamination source. Therefore, the U.S. Environmental Protection Agency (EPA) has established a maximum permitted concentration of 900 $pCi \cdot L^{-1}$ (33 $Bq \cdot L^{-1}$ or 0.54 nM) in drinking water [7].

The mobility and hazards of the Tc are predominantly determined by its oxidation state [2] ranging from +VII to –I, among them +VII and +IV are considered relevant in the environment under oxidizing and reducing conditions, respectively. In aqueous media Tc(VII) prevails as pertechnetate anion, $Tc(VII)O_4^-$ that is considered as chemically inert, i.e. it hardly interacts with mineral surfaces and hence, easily migrates within the groundwater [8]. On the contrary, the main species of Tc(IV), TcO_2, is a low soluble solid [9] whose formation leads to the removal of Tc from solution.

For a safe management of nuclear waste from electricity production or diagnostics avoiding the emission of radionuclides to the environment, several repository concepts are considered. All of them consist of a multibarrier system to prevent radionuclides leakage [10]. In this regard, scientists have investigated the Tc retention capabilities of potentially engineered and natural occurring materials in the near- and far-field of a nuclear waste repository [11,12]. Among them, layered double hydroxides (LDHs) are promising candidates for Tc scavenging [13].

The LDH phases, also referred to as cationic clays, are mixed solid hydroxides of divalent and trivalent metals [14]. They exhibit low solubility [15] and are formed *in situ* in nature [16] when divalent cations interact with either trivalent metal oxides, e.g. Al_2O_3 [17], or aluminum silicates [18,19]. Their structure consists of layers of MO_6 octahedra with divalent cations −M(II)− in which partial substitution by trivalent cations −M´(III)− leads to a permanent positive charge that is balanced by counter anions in solution. Such ions are susceptible to anion exchange by other anionic pollutants in solution e.g. chromate, bromate, arsenate, selenite and

selenate [20]. Pertechnetate is also likely to be retained by this mechanism. Daniels et al. have investigated the interaction of Tc(VII) with Mg(II)-M´(III) LDH (M´(III) = Fe, Al) [21]. The results evidence that the uptake of Tc(VII) from the solution follows the restoring of a LDH structure via anion exchange. These studies showed that Tc(VII) was present after interaction with LDH [21,22]. A scoping sorption study about Tc removal using M(II)-Al(III) LDH with variable M (M = Cd, Co, Cu, Fe, Mg, Ni and Zn) [23] was published but the experiments were limited to pH 8.5 and no molecular information about Tc interaction with the LDH was reported.

In this work, we evaluate the Tc scavenger properties of Fe(II)-Al(III)-Cl LDH. Recently, we reported the formation of this phase in the context of Tc immobilization by γ-Al$_2$O$_3$ nanoparticles coated with Fe^{2+} [24]. Its Tc retention capabilities need further attention, in particular to understand the impact of pH, ionic strength and Tc concentration as well as the retention mechanism at a molecular level. We hypothesize that Fe(II)-Al(III)-Cl LDH provides optimal aqueous Tc uptake because of the combination of high anion sorption capability of the LDH structure and the capability of structural Fe(II) to reduce Tc(VII).

In the past, interactions of anions with LDH were only investigated at neutral or alkaline pH conditions. However, for a comprehensive description of the Tc retention in the environment, a broader range of conditions such as lower pH values, different ionic strengths and Tc concentrations have to be considered too. In this study, we work in the pH range 3.5-10.5, at ionic strength ranging from 0.1 M NaCl to Milli-Q water and at Tc concentrations from 10^{-11} to 10^{-3} M, as well as under ambient and inert gas (N$_2$) atmosphere. This approach is accompanied by a detailed characterization of the molecular environment of Fe(II)-Al(III)-Cl LDH, by advanced molecular spectroscopy, namely XANES, EXAFS, *in situ* IR spectroscopy, as well as Raman microscopy.

2 Materials and methods

2.1 General information about materials and experimental conditions

All experiments were carried out in laboratories where the work with radioactive material is regulated. Most of the preparations and experiments were performed inside a glove box with N_2 atmosphere (GS Glovebox-System GS050912, $O_2 < 0.5$ ppm). Details on measurements of pH and Eh, as well as on suspension preparation have already been reported elsewhere [24].

2.2 Synthesis and characterization of Fe(II)-Al(III)-Cl LDH

The synthesis was carried in a glove box ($O_2 < 2$ ppm). Briefly, a $FeCl_2$ aqueous solution was mixed with an $AlCl_3$ aqueous solution, the pH of the resulting solution was fixed to 9.5 and co-precipitation occurred. The obtained suspension was heated up to 65 °C and ultrasound were applied for 30 min. Finally, the suspension was washed with water three times and dried with a lyophilizator. More details about this synthesis can be found in the supporting information of a previous paper [24].To ensure that only Fe(II) and Al(III) were present in the LDH structure, we analyzed the Fe(II) solution, as explained below in this section. The Fe(II)-Al(III)-Cl LDH used in this work was already synthesized and characterized by XRD, Raman and SEM microscopies [24].

The general formula of a LDH is given in [25] and represents the following composition:

$$M(II)_a M'(III)_b X^-_{2b} (OH)_{(2a+2b)} \cdot nH_2O \tag{1}$$

where *M(II)* is a divalent cation present in *a* molar fraction, *M´(III)* is a trivalent cation found in a *b* molar fraction and X^- represents a counter anion. In this work, $M =$ Fe, $M´=$ Al and $X^- =$ Cl⁻.

The molar fractions *a* and *b* were calculated using the equations:

$$a = \frac{([Fe(II)]_0 - [Fe(II)]_f)}{\left(([Fe(II)]_0 - [Fe(II)]_f) + [Al(III)]_0 - [Al(III)]_f\right)} \tag{2}$$

$$b = \frac{([Al(III)]_0 - [Al(III)]_f)}{\left(([Fe(II)]_0 - [Fe(II)]_f) + [Al(III)]_0 - [Al(III)]_f\right)} = 1 - a \tag{3}$$

where $[Fe(II)]_0$ and $[Al(III)]_0$ represent the initial molar concentration of the respective cations in the mixing solution and $[Fe(II)]_f$ and $[Al(III)]_f$ are the final measured concentrations of Fe(II) and Al(III) in solution subsequent to co-precipitation of the LDH has occurred.

All concentrations of Fe(II) and Al(III) were measured by inductively coupled plasma mass spectrometry (ICP-MS) (NexION 350x, Perkin Elmer). It was verified that the initial Fe solution contained exclusively Fe^{2+} by comparing the Fe concentration values obtained by ICP-MS and by UV-vis spectroscopy (Tidas 100 J and M analytic AG. TIDAS DQ). The photometrical determination of Fe^{2+} by UV-vis was carried out with the ferrozine assay [26], using the experimental conditions described elsewhere [24].

In addition, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to analyze the water content of the solid. Inside a N_2 glove box, 26 mg of solid were weighted in Al_2O_3 crucibles and then measured (STA 499 F5 Jupiter 215, Netzsch). Under inert conditions, the sample was heated up from 21°C to 1000°C and reverse in steps of 15°C·min^{-1}. The results show that 1.3 water molecules are present in the solid structure (see supplementary material S1).

The LDH composition was determined to be $Fe(II)_{0.52}Al(III)_{0.48}Cl_{0.95}(OH)_2$ $1.3H_2O$. For the sake of brevity, LDH is used as short version for the Fe(II)-Al(III)-Cl LDH utilized in this work. The characterization of the solid by powder X-ray diffraction, scanning electron microscopy and Raman spectroscopy was reported previously [24]. The specific surface area (N_2 BET value by multipoint surface analyzer SA 3100, Beckman Coulter) was determined to be 84.3 ± 1.9

$m^2 \cdot g^{-1}$. Hydrodynamic diameter and zeta potential measurements (Zetasizer NanoS, Malvern) were carried out using a $0.05\ g \cdot L^{-1}$ LDH suspension in 0.1 M NaCl (> 99.5 %, Carl Roth) with pH values between 3.5 and 10.5. The experimental conditions and detailed results are given in supplementary material S2. Briefly, the hydrodynamic diameter of the Fe(II)-Al(III)-Cl LDH particles in suspension is higher than 450 nm and in most cases it exceeds the colloidal size range (> 1 μm). The isoelectric point was determined at pH_{IEP} 8.

2.3 Batch contact experiments

The retention of ^{99}Tc (added as $K^{99}TcO_4$) by LDH was studied as a function of time, pH and Tc concentration at N_2 and ambient atmosphere. An overview of the experimental conditions and parameters is given in Table 1. All experiments were carried out in duplicates.

Generally, the LDH was weighted in a 15 mL polypropylene tube. Subsequently, degassed deionized Milli-Q water (resistivity = 18.2 MΩ cm, Water Purified®) or the background electrolyte solution (0.01 M or 0.1 M NaCl) was added and the required amount of ^{99}Tc was injected. The total volume of the suspensions was 10 mL. The pH was adjusted by addition of HCl or NaOH (0.02 to 0.2 M). The Tc-containing suspensions were shaken in a horizontal shaker for the required experimental time. Throughout the experiment, the pH of the suspension was monitored and readjusted if necessary. After a certain contact time, the tubes were centrifuged (600×g for 60 min, Hettich). The supernatant was analyzed with regard to pH, Eh and Tc concentration in solution (explained in 2.3.1).

Additional batch contact experiments used for XAS and Raman measurements were carried out at slightly different conditions due to the requirement of high Tc loads for Tc K-edge XAS experiments. The experimental information and data are shown in the supplementary information S3 and Table S3.1.

2.3.1 Determination of Tc concentration in solution

The amount of ^{99}Tc in solution was quantified by liquid scintillation counting (Wallac 1414, Perkin Elmer). For this, 0.25 mL of the supernatant were mixed with 5 mL of scintillation cocktail (Ultima Gold™, Perkin Elmer).

The fraction of Tc (in %) removed from solution by interaction with the LDH and the resulting distribution coefficient (K_D) were calculated according to:

$$\%Tc_{removed} = \frac{([Tc]_0 - [Tc]_t)}{[Tc]_0} \times 100 \tag{4}$$

$$K_D = \frac{([Tc]_0 - [Tc]_t)}{[Tc]_t} \times \frac{V}{m} \tag{5}$$

where $[Tc]_0$ is the initial Tc concentration in solution (in Bq·mL^{-1}), $[Tc]_t$ is the concentration of Tc in solution (in Bq·mL^{-1}) after contact time t, V is the volume of suspension (in mL) and m is the mass of LDH (in g).

2.4 Raman microscopy

Raman microscopy (Aramis, Horiba) was used to identify secondary phases formed after Tc interaction with the LDH. To ensure inert conditions during the Raman measurements, the 20 µL aliquot samples were deposited in an air-tight cell (described elsewhere [24]) containing two CaF$_2$ windows inside a glove box with N$_2$ atmosphere. Spectra were collected using a Raman microscope (λ_{exc} = 532 nm) with a 10-fold objective with no filter and a hole of 300 µm and a slit-width of 300 µm. Each spectrum was averaged from three independent scans of 10 s. The conditions of the samples measured by the Raman microscope are shown in Table S3.1.

2.5   *In situ* Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) spectroscopy

The experiments were carried out using an FT-IR spectrometer (Bruker Vertex 80/v) equipped with a horizontal ATR diamond crystal (DURA SamplIR II, Smiths Inc., 9 reflections, 45° angle of incidence) and a Mercury Cadmium Telluride detector with a low frequency cutoff at 580 cm^{-1}. Each spectrum was averaged over 256 scans with a spectral resolution of 4 cm^{-1}. The experimental procedure is described elsewhere in detail [27,28]. Here, a solution containing ^{99}Tc (500 µM $KTcO_4$ in 0.01 M NaCl at pH 4.5) and a respective blank solution (0.01 M NaCl at pH 4.5) were used. A spectrum of an aqueous solution of 500 µM $KTcO_4$ in 0.1 M NaCl (pH 4.0) was recorded serving as a reference.

2.6   X-ray absorption spectroscopy (XAS)

The Tc K-edge (21,044 eV) XAS spectra were collected in fluorescence mode with a 13-element, solid state Ge detector (Canberra) equipped with a digital spectrometer (XIA XMAP) at the Karlsruhe Research Accelerator synchrotron (KARA), Germany [29]. During the measurements, the samples were cooled with a He-Ne cryostat at 15 K. For the rejection of higher harmonics and the monochromatization of the incident X-rays, two Rh-coated mirrors and a double Si(111) crystal monochromator were used. The latter was calibrated with a Mo-K edge (20,000 eV). The program EXAFSPAK [30] was used for the dead time correction, the statistical weighting and averaging of the detector channel signals, the energy calibration and averaging of the multiple sample scans, the isolation of the EXAFS signal and for the shell fit. The Tc K-edge ionization potential was arbitrary defined as 21,060 eV.

The calculation of the theoretical scattering phase and amplitude functions were performed with the *ab initio* real space multiple scattering code FEFF8.20 [31] by using a model structure containing two Tc and Fe atoms (Figure S6.1).

The EXAFS spectra were analyzed by using iterative transformation factor analysis (ITFA) [32], a combination between target factor analysis (TFA) [33] and FEFF calculations, and Monte Carlo target transformation factor analysis (MCTFA) [34–36].

Briefly, ITFA is a well-established numerical method to decompose spectra into the single contributing components (n) to determine their respective fractions [32,37,38]. However, for a successful decomposition of the spectral mixtures by ITFA at least $n-1$ components, n fractions must be known or their single component spectra must be available. Unfortunately, this is not the case, therefore, we used a combination of FEFF [31] calculations and target factor analysis (TFA) [33,39,40] (supplementary material S5).

The TFA allows the identification of possible component spectra by testing spectra (target spectra) on their ability to reproduce the spectral mixtures by linear combination. The target spectra are usually supplied by a spectral database. As an alternative, these target spectra can be derived from FEFF calculations, which precisely determine the EXAFS spectra based on structural models. Once the best matching structural models are identified by TFA, the structures are further refined by MCTFA and their fractions are calculated by ITFA. The application and the results of our proposed multi-method approach is described in detail in the supplementary information (S6).

Table S3.1 summarizes the chemical composition of the Tc-containing LDH samples that were measured as wet pastes. The samples were prepared under either N_2 or ambient atmosphere. To inhibit further reactions, the samples were frozen in liquid nitrogen and stored at 77 K until measurement.

3   Results and discussion

3.1   Tc retention by LDH

The removal of Tc(VII) by LDH as a function of time, technetium concentration, pH and ionic strength is shown in Figure 1. The Tc uptake increases with time from 30 % (log K_D = 2.3) after 15 min of contact to 99.7 % (log K_D = 5.3 - 6.1) after one day of contact (Figure 1a). The increase of Tc removal fits to a mono-exponential growth curve (r^2 = 0.989), which is indicative of first order reaction kinetics. The results show that the Tc scavenging rate from solution by LDH is faster compared with other reported systems, where in most of the cases days up to months are required to reach quantitative Tc reduction [12].

Figure 1b shows that the sorption of Tc per gram of LDH is promoted with the increase of Tc concentration in solution. At the lowest investigated Tc concentration, the Tc removal yield is higher than at 72 % (log K_D = 3.7) at pH 4.5 and increases to 99.9 % (log K_D = 6.1) and 99.6 % (log K_D = 4.6 – 5.7) at pH 6.5 and pH 9.5, respectively. The removal yield for the highest investigated Tc concentration is 27 % (log K_D = 2.8) at pH 4.5, 35 % (log K_D = 3.0) at pH 6.5 and up to 99.6 % at pH 9.5. In general, the sorption isotherms suggest the amount of surface reactive groups involved in the sorption [41]. In Figure 1b, the linearity of the Tc sorption isotherm plots indicates that only one surface reactive group sorbs Tc under the given conditions. In contrast to pH 9.5, a decrease of Tc uptake by LDH for the highest Tc concentration at pH 4.5 and 6.5 is observed, indicating that different Tc uptake mechanisms are likely depending on pH. The decrease of pollutant removal at high initial pollutant concentration is generally observed in isotherm experiments and it is due to the saturation of surface reactive sites [41], which explains the trend observed at pH 4.5 and 6.5.

The impact of ionic strength is prominent only at pH < 6 under the given experimental conditions (Figure 1c) with Tc retention (at [Tc]$_0$ = 5 µM) increasing with decreasing ionic

11

strength. On the contrary, at pH > 6 Tc uptake ranges from 99.6 to 99.9 % (log K_D = 5.7 – 6.1) regardless of the ionic strength value. The measured redox potentials (Eh) (Figure 1d) at pH > 6 lie in the stability region of Tc(IV), while for the experiments at pH < 6, in the region of Tc(VII) (using the equation provided in [42]). Combining these results (Figure 1c and 1d), two different Tc retention mechanisms are suggested: at pH < 6 anion exchange for Tc(VII)O_4^- and at pH > 6 reductive immobilization. However, this hypothesis needs verification, e.g. by a combined spectroscopic approach, of X-ray absorption and vibrational spectroscopy, as described in the next sections.

Additional batch experiments were performed in absence and presence of oxygen (atmospheric conditions) at different pH and Tc loadings (Table S3.1). Technetium removal from solution under nitrogen atmosphere ranges from 90.3 to 99.6 %, regardless of the pH or Tc loading. In contrast, the Tc retention by LDH in presence of oxygen varies from 68 to 95 %. The Tc removal from solution decreases with increasing pH and decreasing initial load of Tc. Additional information about these experiments can be found in the supplementary material S3 and in Table S3.1.

For Tc concentrations in the lower micromolar range (5 µM), LDH showed to be an effective Tc scavenger, with > 90 % ($K_D \approx 2 \cdot 10^5$ mL·g^{-1}) Tc removal from solution at pH > 6 (Figure 1c). These results contrast with those obtained by Wang *et al.* reporting a Tc distribution coefficient in Fe(II)-Al(III)-CO$_3$ LDH of K_D = 3 mL·g^{-1} at pH 8.5 [23]. However, their experimental conditions differ significantly (Tc concentration and Fe/Al ratio) from our work, and other parameters (e.g. specific surface area) were unfortunately not specified. Thus, both works cannot be compared.

3.2 Raman microscopic identification of the LDH phase subsequent to Tc retention

Figure 2 shows the Raman spectra obtained from different (microscopic) regions of the LDH being in contact with Tc at pH 4.5, 6.5, and 9.5. The resulting spectra are different depending on the region that was examined (Figure 2), which implies that the samples were highly heterogeneous.

Apart from the band at 321 cm^{-1}, which is due to the CaF_2 window of the Raman cell, several features are common in all the spectra. The bands around 370, 510 and 710 cm^{-1} are related to ferrihydrite [43–45]. The peaks at 235, 412, 611, 1321 and 2630 cm^{-1} are associated to hematite [43], at 1629 cm^{-1} to maghemite [43] and at around 3350 cm^{-1} to the LDH [24]. However, the assignment of the bands at 150 and 200 cm^{-1} to distinct phases remains difficult. These results evidence a change of the mineralogical composition of LDH due to the oxidation of the structural Fe(II) to Fe(III). This is corroborated by the color change of the suspension observed by naked eye during the batch experiments, where the dark green suspension turns to red at pH < 6.

3.3 Tc interaction with LDH analyzed by *in situ* infrared spectroscopy

In situ ATR FT-IR spectroscopy allows the monitoring of molecular surface processes on a solid phase with dissolved heavy metal species, such as the TcO_4^- anion. From the evolution of the spectra with time and the pattern of the bands observed, the formation of inner- or outer-sphere complexes and the local symmetry of the tetraoxoanion, that is the coordination mode (denticity) of the adsorbate on the solid phase can be potentially derived [28,46,47].

The spectra of the aqueous TcO_4^- anion recorded at pH 4.5, serving as a reference, and of the Tc(VII) interacting with the LDH phase are shown in Figure 3.

The fully hydrated pertechnetate ion in aqueous solution adopts a tetrahedral (T_d) symmetry, exhibiting a triply degenerated Tc-O asymmetric stretching mode $\nu_3(TcO_4)$ [48]. In accordance to [49], the band of this mode is observed at 906 cm^{-1} in the spectrum of 500 µM Tc(VII) reference solution (Figure 3a). This band is also observed in the spectra recorded during sorption and desorption experiments of Tc(VII) on the LDH at pH 4.5 (Figure 3b and c). The maximum is slightly shifted to 901 cm^{-1}, reflecting the interaction with the solid phase. Regarding the unaltered band shape, a significant change of the T_d symmetry occurring upon coordination to the solid phase can be ruled out. The band intensity barely increases with exposure time representing the accumulation of the Tc on the LDH phase (Figure 3b). Subsequent flushing of the LDH phase with blank solution reveals the release of Tc species by negative bands observed at the same frequency with similar band intensities (Figure 3c).

The small frequency shift of the band in comparison with the Tc(VII) reference spectrum and the high reversibility of the sorption reaction implies outer-sphere complexation of Tc(VII) [28,50], suggesting that Tc(VII) interacts with the LDH mainly by anion exchange. The low amplitudes of the sorption spectra suggest rather weak interaction between Tc(VII) and LDH. This might be due to the fact that Cl$^-$ is one of the most structural stabilizing counter anions of LDHs [25] and, hence, the anion exchange process might be limited.

3.4   X-ray absorption spectroscopy (XAS)

The XANES and the EXAFS spectra are shown in S4 (Figure S4.1 and Table S4.1) and Figure 4, respectively. The XANES spectra of all the measured samples are very alike showing a characteristic broad peak with two maxima at 21,067 eV and 21,074 eV (Figure S4.1b), regardless of the pH, Tc load or atmosphere conditions. Both features in combination with the absence of the typical pre-edge adsorption band of the electronic transition 1s→4f of Tc(VII)

at ~21,050 eV (dotted line in Figure S4.1a) [51] indicate that Tc(IV) was the main oxidation state in all the samples, whereas Tc(VII) presence is expected below 10% (Table S4.1).

The experimental k^3-weighted EXAFS spectra and their corresponding Fourier transform (FT) are shown as black lines in Figure 4. Especially in the region between k = 6-8 Å^{-1} and for k > 10 Å^{-1} the spectra show different shapes (Figure 4a). In the FT (Figure 4b), an intense peak at R + ΔR = 1.5 Å is observed in all spectra and represents O atoms in the first shell of the Tc(IV). The peaks at higher radial distances (R + ΔR = 2.23 Å and 2.68 Å) are likely to originate from polynuclear Tc species and/or surface atoms like Fe. Hence, it is assumed that several structurally different Tc species coexist. These species obviously vary in their relative fractions, since the EXAFS spectra change depending on the physicochemical conditions of the samples (pH, Tc concentration and presence/absence of O_2).

The ITFA analysis of the spectra reveals that the EXAFS oscillations can be described by a linear combination of two components (red lines in Figure 4). Furthermore, only the first two ITFA calculated eigenvectors, which measure the influence of a component on the spectral variations, show EXAFS-like oscillations (Figure S6.2). Hence, two spectral components represent Tc(IV) in two structurally different environments occurring in the sample series.

Deciphering the atomic environment of Tc(IV) for the two components is challenging as Raman measurements demonstrate that the LDH phase contains fractions of ferrihydrite, hematite and other accessory Fe-containing minerals, such as maghemite. Thus, several structures have been tested within the multi-method approach (S5 and S6). From all tested structural arrangements for component 1, the best match with the experiment is achieved by Tc(IV) dimers, that are two edge sharing TcO_8-octahedra, bound via inner-sphere coordination and corner sharing to an FeO_6-octahedra of hematite (Figure 5c). The Tc(IV) atoms are located in an octahedral coordination sphere of oxygen atoms, whose distances (Table 2) are in agreement with those

15

previously reported in the literature for Tc(IV)-O distances [52–55], Tc-Tc distances [55–58] and Tc-Fe interaction in the second shell (from 3.48 Å to 3.54 Å) [55,57–63].

For component 2, the best match with the experimental data is achieved for Tc(IV) substituting a six-fold coordinated Fe atom of hematite. Thus, a Tc atom is coordinated by six O atoms, which, in turn, connect four different FeO_6 octahedra (Figure 5c). This corresponds to an incorporation of Tc(IV) into hematite, which is obviously due to the favorite six-fold coordination number and the same ionic radii (0.785 Å) of both, Fe^{3+} and Tc^{4+} [64]. In this structure, the Tc-O distance is 2 Å, while TcO_6-octahedra is face-sharing with one FeO_6 octahedra and edge-sharing with three FeO_6 octahedra resulting in Tc-Fe distances of 2.62 Å and 3.08 Å, respectively (Table 2).

The distance of 2.62 Å is similar to the Tc-Fe distance found for Tc(IV) surface complexation with goethite, hematite and ferrihydrite (values range between 2.57 Å and 2.59 Å) [57,58]. Furthermore, an additional scattering contribution at 3.08 Å was assigned to a Tc-Fe distance, which is however, significantly shorter than that for component 1 (3.56 Å). In the case of structural incorporation of Tc(IV) in magnetite, the two Tc-Fe distances range from 2.98 Å to 3.09 Å and from 3.48 Å to 3.49 Å [55,59,61,62]. The simultaneous occurrence of a short and a long Tc-Fe distance have been reported for other iron oxides, like goethite [60] and hematite [65]. The Tc-Fe distances reported in this work are the shortest ones reported up to date for Tc(IV) incorporation into a Fe(III) mineral.

For both components, the MCTFA simulates target spectra and the corresponding predicted spectra, i.e. the isolated component spectra, are in excellent agreement (Figure 5a). Moreover, the multiple scattering (MS) events stemming from the nearly linearly six-fold degenerated 3- and 4-legged Tc-O-O´-Tc and Tc-O-Tc-O´-Tc MS paths, which are visible in the experimental EXAFS spectra in the k-space at 3 $Å^{-1}$ (Figure 4), are well reproduced (Figure 5a and b). In the

final step of our multi-method approach, we have used the MCTFA predicted spectra to calculate the fractions of the two components by IFTA (S6). The contribution of component 1 to the spectra decreases with increasing pH of the samples while component 2 increases instead (Figure S6.7).

Lukens and Saslow studied the Tc(IV) incorporation in the hematite structure and they revealed that 2.7 wt.% of the Tc is incorporated in the hematite structure [65]. The same value was previously predicted by a theoretical simulation where the charge mismatch caused by Tc(IV) incorporation was balanced by the pair Fe^{2+}/Tc^{4+} substitution of two Fe^{3+} atoms [66]. In our case, it represents as maximum 0.044 wt.%, which is far below the theoretical value calculated (2.6 wt.%) for an energetically feasible Tc(IV) incorporation into hematite [66].

Tc incorporation in hematite as suggested by Lukens and Saslow, shows Tc-Fe distances of 3.05 Å and 3.49 Å, and a Tc-Tc distance of 2.56 Å [65]. As these values differ from those found in this paper, we assume that the chemical reaction by which hematite is formed – here by oxidation of LDH and in [65] by direct oxidation of Fe(0) – has implications on the Tc(IV) incorporation geometry.

Likewise, we observe that LDH oxidation triggers the formation of different Fe(III) phases depending on pH or Tc concentration. This observation supports the lack of a specific trend in the distribution of components 1 and 2 at different Tc loads (Figure S6.7). In addition, the XAS of a sample (prepared at pH 4.5, 400 ppm load, in N_2 atmosphere) has neither contributions from component 1 nor component 2, but its experimental data are purely described by a single, completely different component. Despite this topic needs further evaluation to clarify the mechanism triggering the formation of that species, this is beyond the scope of this work, which is describing the main components contributing to the interaction of Tc(VII) with LDH. This behavior clearly shows the enormous heterogeneity present in the Tc(VII) - LDH system.

The results under ambient atmosphere (from 70 to 95 % of Tc removal) indicate that the Tc(VII) reduction is quantitative (Table S3.1). The re-oxidation of Tc(IV) to Tc(VII) might be hindered due to the formation of stable Tc(IV)-hematite interactions, either by inner-sphere surface complexation or by incorporation (Figure S6.7). It is known that the mobilization of Tc is prevented when Tc(IV) is incorporated in a solid structure and associates with the internal domains of the precipitate [58] because Tc is shielded against interactions with oxygen. In this case, it seems that both Tc environments prevent re-oxidation of Tc and a subsequent re-dissolution of Tc(VII).

4   Conclusions

The Fe(II)-Al(III)-Cl LDH phase is an effective Tc(VII) scavenger in the pH range from 3.5 to 10.5, especially under low ionic strength conditions and at Tc concentrations in the µM range. At pH values below 6, the removal of Tc increases with decreasing the ionic strength, reaching a maximum removal of 95% in deionized water. At higher pH, the removal of Tc is quantitative.

According to our results, the present LDH can be used as Tc sorbent under both inert and atmospheric conditions. However, as a side effect LDH transforms into several Fe(III) mineral. To optimize the use of LDH for Tc uptake applications, the integrity of the LDH needs to be preserved before its use as Tc scavenger. This can be ensured by storing the solid under inert conditions, which will prevent the formation of those Fe(III) minerals.

It is shown that Tc(VII) is retained by two different reactions. Initially, the retention of Tc(VII)O_4^- occurs by anion exchange with Cl$^-$ as it was pointed out by in situ IR spectroscopy. Subsequently, the reductive immobilization as Tc(IV) is dominant due to results obtained from batch samples investigated by XAS.

As previously stated by Boglaienko and Levitskaia [12] or Lukens and Saslow [65], it is still a challenge to unambiguously describe the molecular interactions of Tc after reductive

immobilization by an iron phase. The highly similar molecular environment of the iron-containing solids hampers a straightforward interpretation of the EXAFS data. This implies that varying parameters, such as interatomic distances, can be obtained for similar considered structures. A solution to this problem might be a combined approach of techniques providing the identification of iron phases formed, such as XRD, and/or Raman and Mössbauer spectroscopies. A subsequent analysis of the Tc interactions with the solid phase by XAS might reveal reliable structures of the Tc related atomic environment. However, acquiring further fundamental understanding of Tc molecular interactions with iron-containing solids should include alternative techniques (for instance solid state NMR). This will then allow unanimous identification of the Tc fate in the environment. Other prerequisites to determine the reactions and the thermodynamic constants related with the formation of these Tc(VII) and Tc(IV) species are more precise information on Fe(II) mineral redox potentials, the Al(III) species formed after LDH decomposed, and the mechanism driving the formation of Fe(III) secondary phases.

So far, EXAFS analysis identifies two different Tc(IV) species: a dimeric monodentate inner-sphere complex on hematite and another one incorporated into the hematite structure. These species are found in both, N_2 and ambient atmospheres. The inner-sphere complex prevails under acidic conditions. The formed structures prevent re-oxidation of Tc(IV) to Tc(VII).

The overall results confirm that LDH significantly decreases Tc mobility and reveal the molecular interaction of Tc with LDH (or formed secondary phases). The information provided increases confidence in predictive modelling of Tc migration patterns. This in turn supports the safe management of Tc waste in the contexts of a nuclear waste repository or environmental pollutions due to other anthropogenic Tc sources.

Abbreviation

ATR FT-IR, attenuated total reflection Fourier transform infrared. DSC, differential scanning calorimetry. EXAFS, extended X-ray absorption fine structure. ITFA, iterative transformation factor analysis. KARA, Karlsruhe Research Accelerator Synchrotron. LDH, layered double hydroxide. MCTFA, Monte Carlo simulations target transformation factor analysis. MS, multiple scattering. TFA, transformation factor analysis. TGA, thermogravimetric analysis. XANES, X-ray absorption near edge structure. XAS, X-ray absorption spectroscopy.

Acknowledgments

5   Bibliography

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