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Sorption of Am(III) on clays and clay minerals: A review

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Abstract
The problem connected to the long-term storage of high-level nuclear waste has initiated an extensive search for suitable host rock formations and backfill materials to guarantee an isolation of hazardous nuclear elements from the biosphere for thousands of years. Besides other alternatives, clays and clayey materials have been in the focus of various sorption studies. With respect to long-term predictions of migration processes, the transuranium elements and fission products are of particular interest. The present review gives a detailed summary of sorption studies conducted during the past decades describing the impact of various geochemical parameters on the immobilization of Am(III) by different clays and clay minerals.

Keywords Americium · Sorption · Clay minerals · Nuclear waste disposal

Introduction

The search for suitable host rock formations for the final disposal of high-level nuclear waste has lead to strong scientific effort worldwide with the aim of weighing the advantages and disadvantages of different potential host rocks. Besides rock salt and crystalline formations (e.g. granite), clay rocks are considered and investigated in various countries (e.g. Belgium [1], China [2], France [3], Germany [4], and Switzerland [5]). Furthermore, the potential backfill material bentonite, which is considered in various nuclear waste repository scenarios, is mainly constituted of clay (typically 60–80% montmorillonite) as well.

Positive characteristics of clays include a high sorption capacity for heavy metals and the self-healing of cracks due to swelling. Therefore, a strong retardation of radionuclides, when released from their primary containment during storage, is assumed. With respect to long-term predictions and any safety assessment, the long-lived radionuclides, which will determine the long-term radiotoxicity of the waste material, are of particular interest. These include the transuranium elements Np, Pu and Am, whose geochemistry and migration behavior is thus of high importance.

The relevant geochemical processes include sorption onto and diffusion in the clay, complexation reactions with potential ligands in the deep waters, and dissolution/precipitation reactions. All of these processes are strongly dependent on the characteristic geochemical conditions of the potential storage site. Important parameters include pH, redox potential, ionic strength, temperature and inorganic (especially carbonate) or organic ligands (e.g. humic substances) which are ubiquitous found in natural waters.

Due to the strongly reducing conditions expected in the near-field of a nuclear waste repository, resulting from the corrosion of the steel containments, +3 (Pu, Am) and +4 (Np) will be the predominant oxidation states of the transuranium elements [6]. Therefore, various studies during the past decades have focused on the interaction between trivalent actinides with clays. Compared to Pu(III), Am(III) offers a strong advantage through its redox stability, which simplifies the chemical handling.

Different modeling approaches to describe the uptake mechanisms of actinides by various sorbents, including clays, have been the topic of a very extensive review by Geckeis et al. [7]. The present work is a continuation of the

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detailed literature survey that has already been conducted for neptunium [8].

The focus of the present review lies on sorption studies that have been performed during the last decades and provides a detailed description of trends and the effects of various system parameters on the extent of americium uptake by various clay materials ranging from well characterized source clays to highly heterogeneous natural sorbents.

General remarks

When discussing geochemical interactions of actinides in the ternary system actinide-clay-aquifer, it has to be focused on two main aspects: The aqueous speciation in the natural waters and the subsequent interaction with the clay surface. This chapter will give a brief overview about the essential geochemical characteristics of Am(III) and general differences between different sorts of clay regarding their structure and sorption properties.

Aqueous geochemistry of americium

With + 3 being the only stable oxidation state of americium under environmentally relevant conditions, redox reactions are rather unimportant in americium geochemistry. However, the aqueous speciation of Am(III), which is determined by hydrolysis and complexation reactions with organic and inorganic ligands, is diverse and has to be considered carefully. The most important system parameter influencing these processes is the pH value. Other factors include the ionic strength, the partial pressure of CO_2 (defining the carbonate concentration in the system) and the concentration of other potential complexing agents in solution (e.g. natural organic matter ranging from small carboxylic ligands to macromolecular humic substances).

Most natural waters exhibit near-neutral pH ranges between 5 and 9, the presence of cement in a nuclear waste repository (e.g. technical barrier or waste form) can lead to significantly higher pH values. Whereas the solubility of Am(III) is rather high at acidic pH, it decreases continuously with increasing pH to levels $\leq 10^{-9}$ mol/L at pH > 8 [9]. The most important interaction processes of Am(III) in aqueous solution are hydrolysis and carbonate complexation. Figure 1 shows the Am(III) speciation as a function of the pH value in the presence (top) and absence (bottom) of ambient CO_2 ($10^{-3.42}$ atm). The calculations were carried out for an equilibrium concentration of 10^{-6} mol/L using the software package Visual MINTEQ 3.0 [10] with the thermodynamic constants given in Table 1. Note that Am(III) might precipitate at high pH due to the formation of hydroxide, carbonate or mixed hydroxide-carbonate species; the species distribution in solution, however, will not change visibly. In both cases, the pure Am^{3+} ion dominates the speciation up to pH = 5. With increasing pH, the formation of $AmOH^{2+}$ sets in, reaching a maximum at pH = 7. Whereas $Am(OH)_2^+$ becomes the dominating species at pH ≥ 8 in the absence of CO_2, it plays only a minor role under ambient conditions with $Am(CO_3)_n^{3-2n}$ ($n = 1, 2, 3$) being subsequently formed

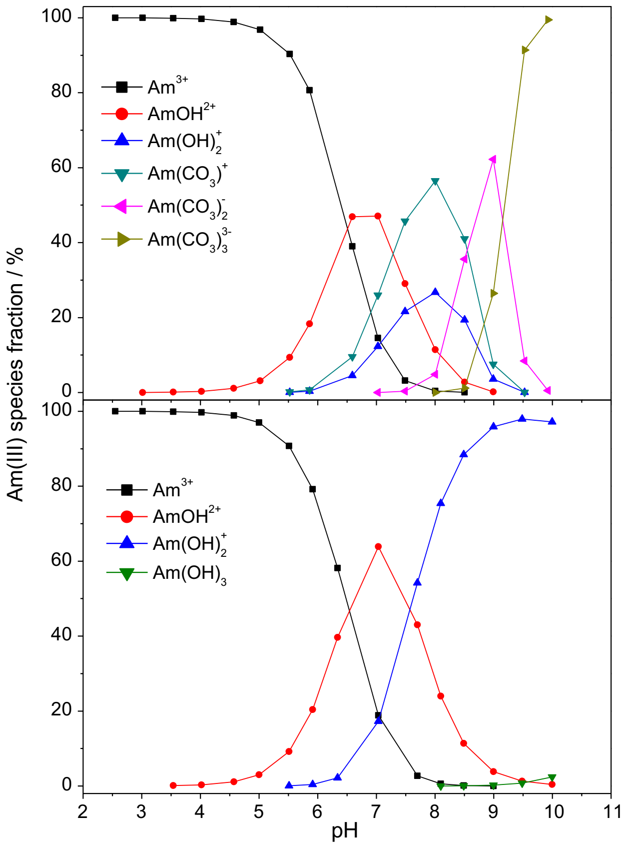

Fig. 1 Aqueous speciation of Am(III) as a function of the pH value in presence (top) and absence (bottom) of ambient CO_2 ($10^{-3.42}$ atm)

Table 1 Thermodynamic data used for the calculation of Am(III) speciation shown in Fig. 1

Reaction	Log K^0	References
$H_2O \rightleftharpoons H^+ + OH^-$	− 13.997	[16]
$H^+ + CO_3{}^{2-} \rightleftharpoons HCO_3{}^-$	10.329	[17]
$2\ H^+ + CO_3{}^{2-} \rightleftharpoons H_2CO_3$ (aq)	16.681	[17]
$Am^{3+} + H_2O \rightleftharpoons AmOH^{2+} + H^+$	− 6.497	[16]
$Am^{3+} + 2\ H_2O \rightleftharpoons AmOH_2{}^+ + 2\ H^+$	− 14.094	[16]
$Am^{3+} + 3\ H_2O \rightleftharpoons AmOH_3$ (aq) + $3\ H^+$	− 25.691	[16]
$Am^{3+} + CO_3{}^{2-} \rightleftharpoons AmCO_3{}^+$	7.8	[16]
$Am^{3+} + 2\ CO_3{}^{2-} \rightleftharpoons Am(CO_3)_2^-$	12.3	[16]
$Am^{3+} + 3\ CO_3{}^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$	15.2	[18]

at pH > 6. At pH = 10, $Am(CO_3)_3^{3-}$ is present quantitatively. It has also to be noted, that hydrolysis species of Am(III) are known to form colloidal species which also might influence the sorption behavior significantly [9, 11]. Compared to carbonate, the complexation properties of other inorganic ligands occurring in natural water (e.g. Cl^-, F^-, HPO_4^{2-}, SO_4^{2-}) are significantly weaker and play only a minor role. Besides their low stability constants of the respective complexes with trivalent actinides, they are often also less abundant compared to CO_3^{2-}. A detailed summary of thermodynamic parameters describing these processes has been published by the Nuclear Energy Agency (NEA) [12, 13]. Besides inorganic ligands, organic compounds can also be found in natural water. Whereas small organic ligands (e.g. formate, acetate, propionate, etc.) provide small stability constants regarding their complexation with trivalent heavy metals and are normally present at relatively low concentrations (e.g. in pore waters of natural clays [14, 15]), macromolecular ligands are much stronger complexation agents. As a result, complexation with a variety of humic substances (e.g. humic and fulvic acids) has been a broad topic in the context of nuclear waste disposal and actinide geochemistry for a long time.

Clays and clay minerals

Clays can be divided into three main types; in the case of 1:1 clay minerals (e.g. kaolinite) the 1:1 layers are composed of one tetrahedral (SiO_4) and one octahedral [$Al(O,OH)_6$] sheet. These TO layers do not reveal a significant charge and are therefore held together only by weak attractive forces (hydrogen bonds, dipole–dipole- and van der Waals interactions). In contrast to this, 2:1 minerals (e.g. smectite, illite) are composed of TOT layers which are negatively charged as a result of substitution of tetrahedral or octahedral cations by cations of lower charge. The adjacent negatively TOT layers are held together by the introduction of cations into the interlayers. The last group of clays, the 2:1:1 minerals (chlorite group minerals), consists of layers composed of two tetrahedral and two octahedral sheets. However, 2:1:1 minerals are generally only present as minor components in most natural clays considered for nuclear waste disposal. Similar to 1:1 minerals, the layers are uncharged. Detailed information on the structure [19, 20] and uptake mechanisms for heavy metals [7] of different sorts of clays and clay minerals can be found in the literature.

Review of literature data

Kaolinite

A number of studies has been conducted to characterize the interaction between Am(III) and kaolinite. Buda et al. [21] examined the sorption of 8×10^{-9} mol/L Am(III) on 4 g/L kaolinite (KGa-1b, Georgia, USA) in 0.1 mol/L $NaClO_4$ solution as a function of the pH value (1–11) under aerobic and anaerobic conditions. The presence of atmospheric CO_2 had no visible effect, suggesting that the formation of Am(III)-carbonate species is unimportant with respect to the extent of sorption under the chosen experimental conditions. In both cases Am(III) sorption increases continuously with increasing pH. The sorption edge is located at pH = 5.5, at pH ≥ 9 Am(III) sorption is almost quantitative.

Sorption of Am(III) on the same sort of kaolinite has also been investigated by other research groups. Křepelová et al. [23] chose a higher initial Am(III) concentration (10^{-6} mol/L) compared to Buda et al. studying the effects of pH (3–10), solid-to-liquid ratio (1 and 4 g/L), and humic acid (0 and 10 mg/L M42 HA [22]). All experiments were carried out under ambient air conditions in 0.01 mol/L $NaClO_4$ solution. For a sorbent concentration of 4 g/L no significant difference was observed regarding the results in presence or absence of HA. Am(III) sorption equals 98–100% in the entire pH range and addition of HA affects the amount of sorption only by ≤ 1%. The reduction of the solid-to-liquid ratio to 1 g/L has a strong effect on the run of the sorption curves; in the absence of HA sorption increases from about 50% at pH 3 to about 100% at pH 6. At pH > 9 sorption decreases down to < 60% at pH 10 due to the formation of Am(III) carbonate species. The position of the sorption edge (pH 6) is similar to the findings of Buda et al. Addition of 10 mg/L HA leads to an increase of sorption by 10–15% at pH < 4.5. At pH ≥ 4.5 sorption is visibly decreased in the presence of HA. Minimum sorption is observed at pH 6–6.5 (40%), at pH ≥ 9.5 the effect of HA is much less pronounced. The first effect is explained by the strong sorption of HA at low pH which creates a higher number of binding sites. This is also reflected by the sorption behavior of HA itself on kaolinite which continuously decreases with increasing pH. In the near neutral to basic pH range sorption of Am(III) decreases due to the formation of soluble Am(III)-humate species. At pH ≥ 9.5 carbonate has the dominating impact on Am(III) sorption which explains the minor effect on Am(III) uptake when adding HA which also demonstrates that ternary Am(III)-humate-carbonate species (if existent) have no influence on Am(III) sorption at the chosen experimental conditions. The strong difference to the results at a solid-to-liquid ratio of 4 g/L is most probably attached to a high excess of potential sorption sites on the kaolinite surface leading to a quantitative sorption of Am(III) in the entire pH range. Kinetic effects are ruled out as the investigation of the effect of equilibration time showed that the sorption of 10^{-6} mol/L Am(III) on 4 g/L kaolinite at pH 5 is already complete after 30 min.

The last study on the sorption characteristics of the kaolinite KGa-1b with respect to Am(III) has been conducted by Lee et al. [24]. They also investigated the effects of pH and purified Aldrich HA on Am(III) sorption on 1.3 g/L kaolinite under ambient air conditions. Furthermore, they varied the initial Am(III) concentration (10^{-5} and 10^{-4} mol/L), the ionic strength (0.01 and 0.1 mol/L $NaClO_4$ solution) and checked the difference between results obtained after equilibrating Am(III) with kaolinite and then adding HA or equilibrating Am(III) with HA and adding kaolinite afterwards (the equilibration time was 1 day in both cases). Lastly, original Aldrich HA was divided into size fractions of 10–30, 30–100, and 100–300 kDa to investigate the influence of HA on Am(III) depending on the size of the organic molecules. Similar to the findings summarized above, sorption of HA itself on 4 g/L kaolinite decreases with increasing pH, the increase of the initial HA concentration from 5 to 50 g/L also leads to a significant decrease of HA sorption probably due to a saturation of sorption sites. The increase of ionic strength from 0.01 to 0.1 M also increases the HA uptake by kaolinite by 5–20%. Sorption of 10^{-4} mol/L Am(III) on 4 g/L kaolinite in the absence of HA (0.01 mol/L $NaClO_4$ solution) increases continuously with increasing pH (3–10) from about 60 to almost 100%. A decrease of the initial Am(III) concentration to 10^{-5} mol/L slightly increases the sorption by $\leq 5\%$ due to higher excess of sorption sites on the clay surface. No decrease of sorption due to formation of Am(III)-carbonate species at high pH was observed. However, it remains unclear whether the authors added $NaHCO_3$ or Na_2CO_3 to the sample solutions to accelerate the equilibration with the atmospheric CO_2 as Buda et al. and Křepelová et al. performed it. This is very important, as the equilibration by just exposing the sample solution to the atmosphere is very slow and thus not sufficient. This was shown by Turner et al. [25] who obtained comparable results for the sorption of Np(V) on montmorillonite when performing the experiments either in a CO_2-free glove box or simply capping the sample solutions immediately after addition of all constituents and pH adjustment. The effect of 50 mg/L HA as a function of the pH value (3–10) on Am(III) sorption on 4 g/L kaolinite was investigated at an ionic strength of 0.01 mol/L and an initial Am(III) concentration of 10^{-5} mol/L. As also shown by Křepelová et al. Am(III) sorption increases in the presence of HA at acidic pH and decreases at $pH > 6$. Interestingly, this effect is much more pronounced when equilibrating Am(III) with HA for 1 day before adding the sorbent pointing out the either irreversible or kinetically inhibited formation of soluble Am(III)-humate species. The strongest change is observed at pH 10 where Am(III) sorption decreases by 50% compared to the experiment in absence of HA. Furthermore, it was shown that the size of HA plays an important role. At low pH, the large HA fraction (100–300 kDa) has the strongest immobilizing effect whereas the small HA fraction (10–30 kDa) leads to a stronger decrease of Am(III) sorption in the near neutral to basic pH range. These effects can be attributed to stronger complexation properties of the small HA molecules towards Am(III) and the larger increase of sorption sites when sorbing large macromolecules onto the clay surface rather than small humics.

Am(III) sorption on another batch of kaolinite (Iwamoto Mineral Co., Japan) was studied by Samadfam et al. [26] in the absence of CO_2 using 0.1 mol/L $NaClO_4$ solution as background electrolyte. The initial Am(III) concentration and the solid-to-liquid ratio were held constant at 10^{-7} mol/L and 1 g/L, respectively. The pH was varied between 3.5 and 10. Furthermore, the influence of purified Aldrich HA (0, 5, 10, and 20 mg/L) on Am(III) sorption was investigated. The general trends are similar to the previously discussed studies. The sorption of HA itself on kaolinite decreases with increasing pH and HA concentration. In the absence of HA, Am(III) sorption increases continuously with increasing pH, the related distribution coefficients range between 5×10^2 and 10^6 L/kg. In the presence of HA, Am(III) sorption is enhanced at low pH whereas less Am(III) is sorbed at $pH > 5.5$. With increasing HA concentration, these effects are more pronounced. The maximum effect is observed at $pH = 8$ and $[HA] = 20$ mg/L decreasing the K_d-value of Am(III) by almost three orders of magnitude compared to the results in absence of HA.

The effect of 30 mg/L HA (extracted from paddy soil Tochigi Prefecture, Japan) on Am(III) uptake by 2 g/L of another commercial kaolinite (Wako Pure Chemical Ind. Ltd) in 0.02 mol/L $NaClO_4$ solution was investigated by Takahashi et al. [27]. The pH was varied between 1 and 13. Am(III) sorption increases with increasing pH in the absence of HA. When adding HA to the sample solutions, Am(III) sorption is increased at $pH < 4$ whereas less Am(III) uptake is observed at $pH > 4$. A detailed comparison with data summarized above is not possible as no Am(III) concentration is stated in this work.

The latest batch sorption study was conducted recently by Ma et al. [28] who investigated the sorption of 6×10^{-10} mol/L Am(III) onto Maoming kaolinite (Maoming FengHua kaolinite Co., Guangdong province, China) which, besides 82.4% kaolinite, contained also visible amounts of quartz (12.5%) and illite (4.9%). By variation of the solid-to-liquid ratio between 0 and 10 g/L (pH = 5.6, 0.1 M NaCl solution) a rather constant distribution coefficient ranging between 5×10^3 and 1×10^4 L/kg was derived. The variation of the pH between 3 and 10 (*s*/*l* ratio = 1 g/L, 0.1 M NaCl solution) leads to a strong increase of Am(III) sorption between pH 4.5 and 6.5. The sorption edge is located around pH 5, at pH > 6 sorption is almost quantitative. Lastly, the effect of ionic strength was investigated varying the NaCl concentration between 0 and 0.3 mol/L at pH 4 and 6.6. Whereas only a minor effect was observed at pH 6.6, Am(III) sorption at pH 4 decreases with increasing ionic strength from 80 to < 10%. The authors attributed this effect, which differs to the work of Lee et al. [24], to the lower Am(III) concentration. However, another possible explanation might be the illite content of about 5%, which generally shows a significant ionic strength dependency at low pH, where cation exchange is the dominating uptake process.

A single study is found in the literature focusing on the spectroscopical characterization of Am(III) sorption species on kaolinite. Stumpf et al. [29] investigated two sorption samples of Am(III) on kaolinite from St. Austell (UK) using EXAFS spectroscopy. The initial Am(III) concentration equaled 10^{-3} mol/L, the solid-to-liquid ratio was 2.5 g/L using 0.025 mol/L $NaClO_4$ solution as background electrolyte. The samples were prepared at pH 6 and 8 under anaerobic conditions (N_2 glovebox). Due to the absence of Am–Si/Al or Am–Am contributions it is not possible to distinguish between inner- and outer-sphere complexation. With increasing pH, however, a decrease of the coordination number with respect to oxygen in the first coordination sphere from 9–10 to 6–7 was observed. As this coordination number is not expected to change according to laser-spectroscopic investigations of respective Cm(III) samples, the authors suggested that this apparent decrease might by related to an increased asymmetry of the Am-O shell and, thus, a dampening of the EXAFS amplitude for example due to the formation of a ternary OH^-/Am/clay surface species. This would also explain the increase of the related Debye–Waller factor (σ^2).

In general, sorption of Am(III) on kaolinite increases continuously with increasing pH in the absence of CO_2. Under ambient air conditions, the presence of carbonate generally decreases Am(III) uptake by kaolinite at high pH-values due to the formation of negatively charged Am(III)-carbonate species. According to the above mentioned studies, this effect strongly depends on the initial Am(III) concentration and becomes less important at very low Am(III) concentrations probably due to the high excess of sorption sites on the clay surface. The presence of humic substances leads to an increased Am(III) sorption at acidic pH resulting from strong sorption of HA on the clay which increases the amount of potential sorption sites. At near-neutral to basic pH, sorption of Am(III) decreases in the presence of HA which is attributed to the formation of soluble Am(III)-humate species.

Smectite/montmorillonite

Besides kaolinite, montmorillonite, as a representative smectite clay, is the most extensively studied reference clay, regarding its sorption behavior towards Am(III). In contrast to kaolinite, the interlayers of smectite clays exhibit the possibility of cation exchange, determining the Am(III) uptake especially in the acidic pH range. Furthermore, montmorillonite is the main constituent of bentonite, an important potential backfill material, which will be discussed separately (see below).

Ticknor et al. [30] studied the influence of 0.5–5.0 mg/L fulvic acid (FA) on the sorption of 1.4–1.8×10^{-10} mol/L Am(III) on montmorillonite (SWy-1, Wyoming, USA) at pH:7.6 under aerobic conditions. Generally, Am(III) sorption decreases with incresing FA concentration. Due to the detection limit of 0.09 Bq/mL for ^{241}Am, a distinct distribution coefficient could only be determined for the highest FA concentration (5.0 mg/L), the K_d-value equaled 890 ± 330 L/kg. At lower FA concentrations, the K_d was stated according to the detection limit, ranging between ≥ 1800 and ≥ 2200.

The sorption characteristics of this Wyoming montmorillonite have been the topic of several studies. Bradbury and Baeyens investigated the sorption on SWy-1 Na-montmorillonite at trace concentrations of Am(III) (1.4×10^{-13} mol/L) in the presence and absence of Eu(III) as a blocking metal (5×10^{-6} or 1×10^{-4} mol/L) at pH 6.7 in 0.1 mol/L $NaClO_4$ solution at a solid-to-liquid ratio of 0.51 g/L in controlled N_2 atmosphere [31]. The log (R_d/L/kg) were found to decrease from 5.0 ± 0.2 in the absence to 3.3 ± 0.1 (1×10^{-4} mol/L Eu(III)) or 3.9 ± 0.1 (5×10^{-6} mol/L Eu(III)) in the presence of the blocking metal. The same authors studied the sorption of 1.5×10^{-10} mol/L Am(III) on 0.62 g/L SWy-1 montmorillonite in 0.1 mol/L $NaClO_4$ and 6.2×10^{-8} mol/L Am(III) on 0.86–2.0 g/L in 0.066 mol/L $CaCl_2$ as a function of the pH value (2.5–11.0) under inert atmosphere conditions [32]. Whereas maximum sorption was found to be very similar in both systems (log (R_d/L/kg) = 5.5–6 at pH > 8), stronger differences were observed in the acidic pH range, which is dominated by cation exchange. In the $CaCl_2$ system, log R_d is lower by more than one order of magnitude compared to the $NaClO_4$ system.

The effect of ionic strength (0.1 and 1.0 mol/L $NaClO_4$) on the sorption of 3×10^{-8} mol/L Am(III) on 4 g/L

Na-smectite in the pH range 2–11 was studied by Gorgeon [33] (cited in [34]). As in the work of Bradbury and Baeyens [32], maximum sorption was observed at pH > 8 for both ionic strengths with log (K_d/L/kg) ranging between 5.0 and 5.6. However, at low pH (2–5) the log K_d differs by more than two orders of magnitude pointing out the strong effect on the uptake of Am(III) by montmorillonite which decreases massively with increasing ionic strength.

The sorption of Am(III) on montmorillonite colloids (< 1 µm, origin not stated) was investigated by Degueldre et al. [35]. At pH = 8 ([CO_3^{2-}] = 0.01 mol/L), the log (K_d/L/kg) for the sorption of 8.5×10^{-10} mol/L decreases slightly from ≈ 5.0 to ≈ 4.2 with increasing colloid concentration. The effect of carbonate was studied further at pH = 8; by increasing [CO_3^{2-}] from 10^{-4} mol/L to 0.1 mol/L, log (K_d/L/kg) with respect to Am(III) sorption on 83 ppm montmorillonite decreased from ≈ 5.5 to ≈ 3.5 which is attributed to the formation of aqueous Am(III) carbonate species.

Stumpf et al. [29] used a combination of TRLFS (Cm(III)) and bulk-EXAFS spectroscopy (Am(III)) at varying pH (4–8) to identify and characterize the surface species formed during sorption on smectite. The initial Am(III) concentration equaled 10^{-3} mol/L, the solid-to-liquid ratio was 2.5 g/L using 0.025 mol/L $NaClO_4$ solution as background electrolyte. Structural data of the Am(III)-aquo ion was determined using EXAFS under nitrogen atmosphere. An Am–O distance of 2.47–2.49 Å was found and a coordination number of 8–9 oxygen atoms is observed for the Am(III) and its first coordination sphere. The coordination number of Am(III) sorbed onto smectite at pH = 8 differs from pH = 4 and 6. The comparison between TRLFS-Cm(III) and EXAFS-Am(III) data points out that An(III)/smectite outer sphere complexes are formed at pH 4. With increasing pH, inner-sphere sorption onto smectite occurs. The coordination number of sorbed Am(III) at pH 8 exhibits an apparent decrease, which might be affected by the formation of ternary OH^-/Am/clay mineral surface species. Therefore, the results exhibit that two types of surface complexes are formed.

Nagasaki et al. [36] investigated the ion-exchange stoichiometry and sorption ratio of 1×10^{-5} mol/L Am(III) and Ln(III) (Nd, Eu, Gd) onto montmorillonite (from Tsuukinuno, Japan) colloidal particles (< 45 µm) in NaCl (0.04–0.64 mol/L) solutions at pH = 4 under the aerobic conditions. The dependence of K_d on the Na^+ concentration is apparently composed of two distinct regions: A first region at low Na^+ concentration (Log[NaCl] < − 0.5) where log K_d decreases linearly with increasing log[Na^+] and a second region of high Na^+ concentration (Log[NaCl] > − 0.5) where the sorption ratio was found to be constant. The K_d values are similar but specific for Am(III) and each Ln(III) increasing in the following order: Gd(III) < Eu(III) < Am(III) < Nd(III). This is in the reverse order of hydration free energy.

The effects of pH, ionic strength and presence of different cations (Ca^{2+}, Na^+) and anions (Cl^-, NO_3^-, SO_4^{-2}) on the sorption of Am(III) on a smectite-rich natural clay in granitic ground water from Western India have been investigated by Kumar et al. [37]. Under N_2 atmosphere, the sorption of 6×10^{-9} mol/L Am(III) on 0.5 g/L Na-equilibrated natural clay at varying ionic strength (0.01–0.1 M NaCl) increases continuously with increasing pH (2.5–8), reaching a constant value at pH ≥ 8. When increasing the ionic strength from 0.01 to 0.1, the respective log (K_d/L/kg) decreases visibly by up to 1.5 orders of magnitude in the acidic to near neutral pH range (2.5–6). This indicates the main role of ion exchange reactions at low pH. In the presence of Ca^{2+} (0.0335 mol/L $CaCl_2$ solution), Am(III) sorption increases continuously with increasing pH (pH 10: log (K_d/L/kg) > 6). At pH 7.1, the effect of increasing Ca^{2+} concentration was examined but did not show any effect. The effect of different anions at pH 2–10 was investigated by comparison of sorption curves using NaCl, $NaNO_3$ and Na_2SO_4 (I = 0.1 mol/L) as background electrolytes. The presence of SO_4^{2-} shows a small decrease of Am(III) sorption at low pH, however the effects are minor in all cases pointing out the low effect of different anions which are known to have low complexation properties towards actinides (compare general remarks).

Bentonite

Bentonite generally contains between 60 and 80% of montmorillonite, thus implying a similar sorption behavior compared to pure montmorillonite which is discussed above. However, the minor constituents including quartz, calcite, pyrite, feldspare, etc. might visibly influence the uptake process. As bentonite has been the topic to various studies, we decided to discuss its sorption properties separately.

Two sorption studies were carried out by Nagasakit et al. [38, 39] using the bentonite Kinigel V1 (Kunimine Industries Co. Ltd., Japan). At a pH of 8.2, Am(III) (initial concentrations 10^{-9} or 10^{-10} mol/L) was found to form colloids in carbonate solution (equal to a partial pressure of CO_2 of $10^{-4.5}$ atm). When equilibrating the solution with bentonite, colloid formation was enhanced. As the distribution coefficient increases with decreasing S/L ratio, the authors concluded a strong correlation between colloid formation and the sorption process. Maximum K_d values determined after ultrafiltration are > 10^4 L/kg [38]. The effect of redox potential on the uptake of 10^{-9} mol/L Am(III) was studied at pH 9 in 0.1 mol/L $NaClO_4$ solution under anaerobic conditions. Under these conditions, Am(III) sorption on bentonite is insensitive to the redox potential (from − 100 to 200 mV) and the K_d-value remains constant at 6.5×10^3 L/kg.

Also other working groups studied the sorption characteristics of commercial bentonites originating from the same company. Kozai et al. [40] investigated the sorption of 5×10^{-10} mol/L Am(III) on Kunigel V1 bentonite as a function of the pH value in 0.01 mol/L $NaClO_4$ solution under CO_2-free conditions. Over the entire pH range (final pH 2–8) Am(III) sorption is almost quantitative. Comparison to montmorillonite experiments in the same study suggest that sorbed Am is mostly attached to the montmorillonite fraction of the bentonite. Only in the pH range of 6.5–8 minor mineral phases, probably including pyrite, impact the sorption behavior of Am(III), as the amount of unexchangeable sorption (which refers to Am(III) that could be desorbed with 1 mol/L HCl but not with 1 mol/L KCl solution) increases to an extent that can not be explained with Am(III) speciation at pH > 6.

Iijima et al. studied the sorption of Am(III) on Kunipia F bentonite (Kunimine Industry Co. Ltd., Japan) as a function of various parameters (initial Am(III) concentration: 5×10^{-10}, 5×10^{-9}, 5×10^{-8} mol/L; pH: 8, 10; S/L ratio: 0–0.05 g/L) in 0.001 mol/L $Na_2S_2O_4$ solution under anaerobic conditions [41]. The determined K_d values range from 4×10^6 to 9×10^7 L/kg at pH 8 and 5×10^7 to 2×10^8 L/kg at pH 10. The fact, that these values are much higher compared to literature data was attributed to the low carbonate concentration in solution and/or the high reactive site capacity of the colloids.

Lastly Konishi et al. [42] studied a commercial bentonite (exact name not stated) also purchased from Kunimine Kogyo Co. Ltd. (Japan). Applying column experiments, the K_d-values of 10^{-9} mol/L Am(III) were determined at pH = 2 in deionized water (6800 L/kg) and synthetic ground water (3800 L/kg) and at pH = 6 in deionized water only (23,000 L/kg).

Am(III) sorption on a natural bentonite from Kutch (India) was studied by Murali et al. using borehole water from a granite formation as liquid phase. K_d values were reported for 10^{-9} mol/L Am(III) on 2.5 g/L bentonite as a function of pH and increase continuously from 1.9×10^3 L/kg at pH 3.2 to 4.5×10^3 L/kg at pH 7.5 [43].

Lastly, the sorption characteristics of a chinese bentonite (Gaomiaozi bentonite, Inner Mongolia of China) towards 3.6×10^{-9} mol/L Am(III) have been the topic of a study by Yu et al., who investigated the effects of various experimental parameters (contact time, temperature, presence/concentration of humic acid, pH, and ionic strength) [44]. The sorption process was found to be completed after a very short time span of 4 h. Sorption on 0.1 g/L increases strongly with increasing pH (2–12) from 0 to 100%. As expected for a sorbent mainly constituted of montmorillonite, ionic strength has a strong effect in the acidic pH range and Am(III) sorption decreases with increasing ionic strength (0.01–0.1 mol/L NaCl solution). Introduction of 5 and 10 mg/L humic acid (origin or type not stated) leads to a slight enhancement of Am(III) uptake at low pH and a strong reduction of Am(III) sorption at pH > 6. As discussed before, these effects are attached to strong sorption of HA on the clay at low pH and the formation of aqueous humate complexes at neutral to basic conditions. The effect of temperature (25, 45, 65 °C) was studied at pH = 3. An increase of Am(III) uptake from about 55% at room temperature to almost 80% at 65 °C clearly indicates an endothermic sorption behavior. The respective K_d-values equal 14,370 (25 °C), 21,160 (45 °C), and 23,410 L/kg (65 °C).

Illite

Among the pure clay minerals, illite has been investigated as a sorbent for Am(III) to a much lower extent compared to kaolinite or smectite.

Bradbury and Bayens [45] studied the sorption of 4×10^{-11} mol/L Am(III) on 0.58 g/L Na-illite (du Puy) in 0.1 mol/L $NaClO_4$ solution in the pH range 2.5–11 under anaerobic conditions. Sorption of Am(III) increases continuously with increasing pH reaching a plateau at pH ≈ 6. The respective log (K_d/L/kg) values range between 3 and 6. This study also cites results of Gorgeon [33] who investigated the effect of ionic strength (0.1 and 1.0 mol/L $NaClO_4$ solution) on the sorption of Am(III) on illite at pH 2.5–10. In 0.1 M $NaClO_4$ solution, the log (K_d/L/kg) values lie in the same range (≈ 2.7–5.7). The increase of ionic strength leads to a significant deacrease of log (K_d/L/kg) at pH < 6. In this pH region the Am(III) uptake is dominated by cation exchange which is impacted strongly by Na^+ in solution. At pH > 6 both sorption curves are almost identical.

Maes et al. [46] investigated the sorption behavior of 1.5×10^{-8} mol/L Am(III) on 0.5 g/L illite from Silver Hill (Montana, USA) in 0.01 mol/L NaCl solution as a function of the pH (2.5–10) under ambient air conditions. Am(III) sorption increases with increasing pH reaching a plateau at pH ≈ 4; at pH > 8.5 sorption decreases. The respective log (K_d/L/kg) values range between 3.5 and 5.9.

Lastly, Degueldre et al. [35] studied the uptake of 8.5×10^{-10} mol/L Am(III) by illite colloids (particles < 1 µm, origin not stated) as a function of the solid-to-liquid ratio at pH = 8 and the carbonate concentration at pH = 8 or 10. 0.5 mol/L $NaClO_4$ solution was used as background electrolyte in all cases. The variation of the solid-to-liquid ratio between 0.001 and 0.3 g/L leads to a slight decrease of Am(III) uptake (log (K_d/L/kg) = 4.5 – 6.0) at pH = 8 and a total carbonate concentration of 0.01 mol/L. The variation of the carbonate concentration between 10^{-4} and 10^{-1} mol/L has also a minor effect on the Am(III) sorption at both pH values (8 and 10). The respective log (K_d/L/kg) range between 4.5–5.5 and 5.0–6.0, respectively. By tendency log (K_d/L/kg) decreases with increasing carbonate concentration due to the formation of Am(III)-carbonate species.

Literature data for Am(III) sorption on illite clearly reflect the impact of the pH value and the importance of different uptake mechanisms; i.e. cation exchange and surface complexation. Compared to studies on the sorption onto kaolinite, a lot more distribution coefficients (log (K_d/L/kg)) are reported in the case of illite. The determined maximum log (K_d/L/kg) values agree very well throughout the literature ranging between 5.5 and 6.0.

Natural clays and heterogeneous sorbents containing clay

Whereas bentonite is mainly composed of montmorillonite, a number of even more heterogeneous sorbents has been investigated with regard to their sorption properties towards Am(III).

In an early study, Erickson investigated the uptake of 3.6×10^{-6} mol/L Am(III) by an abyssal red clay in 0.69 mol/L NaCl solution at two different pH values [47]. Whereas log (K_d/L/kg) values in the range of 5–6 were obtained at pH = 6.9, significantly lower values (log (K_d/L/kg) ≈ 1–2) were observed at acidic pH (2.7).

Konishi et al. [42] investigated sorption of 2×10^{-9} mol/L Am(III) on two loams of different origin (Takadate and Hachinohe; both located in the Tohoku district) and composition (Takadate: 40% clay and 60% silt; Hachinohe: 10% clay and 90% silt) in deionized water at pH 6–7. Whereas the loam, containing a higher amount of clay, provided a K_d-value of 11,000 L/kg, a significantly lower distribution coefficient of 1300 L/kg was obtained for the loam rich in silt. The results clearly point out the stronger sorption affinity of clay minerals towards Am(III) compared to silt.

Am(III) sorption onto another clayous material of non-stated origin has been studied by Stammose et al. [48, 49]. The purified solid contained 7% kaolinite and 93% mixed layers (composed of 53% kaolinite and 47% smectite). Sorption of 10^{-8} mol/L Am(III) on this material was found to be reversible and to consist of a rapid and a slow interaction mechanism; the first process was interpreted as a sorption onto the clay surface, whereas the slower process was explained with a diffusion into the first hydrated layers of the solid. When varying the pH and the ionic strength between 3–6 and 0.01–3.0 mol/L ($NaClO_4$ solutions), respectively, Am(III) sorption generally increases with increasing pH. At pH > 6, Am(III) sorption increases with increasing ionic strength. Ambient CO_2 was not excluded from the experiments; however, as no carbonate was added to the sample solutions, it is not assured that samples at the highest pH values were in equilibrium with atmospheric CO_2. Log (K_d/L/kg) varies between 1 and 6 under the chosen experimental conditions. However, the authors point out that a part of uncertainty remains in the magnitude of the K_d variations considering the very high values of K_d in some cases.

Maes et al. [46] studied the uptake of Am(III) by Boom clay (Mol, Belgium) which is considered as a potential host rock for nuclear waste disposal in Belgium. The Am(III) concentration ranged between 10^{-7} and 10^{-10} mol/L and the experiments were carried out under anaerobic conditions with a CO_2 concentration of 0.4%. In a first experiment the effect of solid-to-liquid ratio was investigated. The log (K_d/L/kg) values before and after ultrafiltration equal 2.86 and 3.69 for a solid-to-liquid ratio of 5 g/L and 2.1 and 3.4 for an solid-to-liquid ratio of 370 g/L. The differences were attributed to the natural organic matter contained in the real Boom Clay water (RBCW). Thus at a lower solid-to-liquid ratio, the formation of Am-NOM complexes/colloids is less pronounced. The log K_d increases with ultrafiltration due to the removal of colloids from the supernatant solution. To further investigate this effect, the authors compared results obtained in RBCW (pH = 8.20–8.65, with NOM) and synthetic Boom Clay water (SBCW, pH = 7.95–8.35, without NOM). Log (K_d/L/kg) values without and with ultrafiltration equal 2.86 and 3.69 (RBCW) and 3.89 and 5.19 (SBCW). The decrease of log K_d with ultrafiltration in SBCW lead the authors to the conclusion, that colloids (inorganic or eigencolloids) are also formed in the absence of NOM.

Another natural clay rock that is considered as a host rock in Switzerland (Opalinus Clay) has been investigated by Amayri et al. [50] with respect to the sorption behavior towards different actinides. The sorption of 8.6×10^{-9} mol/L Am(III) was studied as a function of the solid-to-liquid ratio (2–20 g/L) under aerobic conditions using synthetic Opalinus clay pore water as background electrolyte (pH = 7.6). The respective average K_d value equals 29,800 ± 1800 L/kg.

A series of studies by Lujaniene et al. [51–55] focused on the sorption characteristics of a Triassic clay from the Šaltiškiai quarry (North Lithuania) towards Am(III). This sorbent mainly consists of smectite, illite, and chlorite. The K_d-value for the sorption of 3.2×10^{-11} mol/L Am(III) was determined to range between 15,000 and 80,000 L/kg. Up to 40% of the Am(III) were found in exchangeable and carbonate bound fractions. However, the exact experimental conditions of this experiment are not clear from the description [51, 52].

The effect of ionic strength on the sorption of 1×10^{-10} mol/L Am(III) on 1 g/L of the Triassic clay under Ar atmosphere was studied in the pH range of 3.5–8.5 using 0.01 and 0.1 mol/L $NaNO_3$ solution as background electrolyte. For the lower ionic strength, Am(III) sorption ranges between 90 and 100%; when increasing the ionic strength to 0.1 mol/L, Am(III) sorption decreases to 75–95%. This effect is explained by an increasing influence of NO_3^- on the aqueous Am(III) speciation; the maximum amount of $AmNO_3^{2+}$ under these experimental conditions is > 30% for $[NaNO_3] = 0.1$ mol/L [53, 54].

The effect of pH on the uptake of Am(III) by Triassic clay was studied using different mixtures of synthetic rain water (pH = 4.9) and synthetic rain water–cement water (pH = 11.6) as liquid phase. As the pH is adjusted by mixing solutions of different composition, increasing the pH is accompanied by an increase of the ionic content (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, CO_3^{2-}) of the aqueous phase and thus the ionic strength which increases from < 0.003 to > 0.025 mol/L. The Am(III) uptake increases with increasing pH up to pH = 8, at higher pH sorption decreases with increasing pH-value. The respective K_d value ranges between 30,000 and 80,000 L/kg [54].

Lastly, three batches of Triassic clay with different content and composition of reactive compounds (e.g. Calcite, Fe minerals) in their coatings were investigated regarding their interaction with Am(III). For all clay samples, high sorption rates were observed for the uptake of 3×10^{-11} mol/L Am(III) at pH 8.0–8.2. Also the K_d-values lies in the same range (3000–8000 L/kg) [55].

Conclusions

This literature review clearly points out the impact of different geochemical parameters on the uptake of americium by clay and clay minerals. The enormous variety of effects, which also influence each other, makes it almost impossible to generalize these sorption processes.

Independent of the sort of clay, the most important parameter is the pH value. Generally, Am(III) sorption increases continuously with increasing pH and becomes almost quantitative in the near neutral to basic pH range in the absence of CO_2. This is attributed to the increasing negative charge of the mineral surface leading to a stronger attraction towards positively charged ions (Am^{3+}, $AmOH^{2+}$, $Am(OH)_2^+$).

The partial pressure of CO_2 regulates the carbonate content in aqueous solution and can exceed the value of ambient air by more than one order of magnitude [56]. The presence of carbonate is a highly important factor at basic pH and generally decreases Am(III) uptake as a result of the formation of negatively charged Am(III)-carbonate species (compare Fig. 1). However, a proper investigation of this effect requires precise and accurate realization of the respective experiments. Usually it is not sufficient to prepare highly basic solutions under ambient air conditions as the dissolution of CO_2 is rather slow. This has been demonstrated by Turner et al. [25]. Therefore, the equilibration of carbonate containing solutions has to be accelerated by addition of solid Na_2CO_3 or $NaHCO_3$. The review shows that in some cases no effect of CO_2 is observed. Whereas this can be explained by the low metal concentration in some cases or a high solid-to-liquid ratio creating a high excess of sorption sites, some data has to be considered carefully if the experimental conditions are not reported very detailed.

Humic substances (especially humic acids) represent the second and most investigated group of anionic ligands in the context of Am(III) sorption onto clays. The range of investigated HAs includes commercial, natural and synthetic substances. Independent of their origin, two major effects can be distinguished: In the acidic pH range, sorption of HA itself increases strongly. This coating of the sorbent leads to the formation of new sorption sites which also increases the uptake of Am(III). At basic pH, sorption of Am(III) decreases in the presence of HA. This behavior is explained by the formation of soluble Am(III)-humate species, under ambient conditions the presence of mixed humate-carbonate complexes is also possible.

A factor which only affects sorption processes on distinct clays at acidic pH in a significant way is the ionic strength. Strong effects are observed for 2:1 minerals (e.g. smectite, illite) and heterogeneous materials which contain high amounts of these clays. At low pH values, the uptake by these sorbents is determined by cation exchange processes. As a result, the increase of the ionic strength increases the amount of cations (e.g. Na^+, Ca^{2+}, etc.) competing with Am(III) for interlayer sites and reduces the amount of Am(III) bound to the sorbent visibly. The presence of trivalent lanthanides like Eu(III) leads to concurrence processes in the entire pH range [31].

According to experimental findings, less important factors include the redox potential, the solid-to-liquid ratio and metal concentration. Due to the fact that + 3 is the only relevant oxidation state of americium, the Eh has no effect on the redox speciation and, thus, does not influence the sorption behavior of Am(III). The solid-to-liquid ratio and metal concentration play a minor role compared to other geochemical parameters. Generally, the distribution coefficient for the uptake of Am(III) by a sorbent is constant at given experimental conditions and independent of solid-to-liquid ratio and initial Am(III) concentration. However, in some cases it is observed, that sorption increases with decreasing metal concentration or increasing solid-to-liquid ratio, which is attributed to an increasing excess of sorption sites. In the case of heterogeneous sorbents, which allow to distinguish between sites of varying affinity for Am(III), it can also be concluded that an excess of high-reactive sites compared to less affine sites causes these differences.

Whereas the effect of temperature on sorption processes is highly interesting due to the expected release of heat from the stored nuclear waste, only one study focusses on this effect: Yu et al. [44] showed that Am(III) sorption on bentonite increases with increasing temperature. It can be expected that a change of temperature affects both, the properties of the sorbent (e.g. stronger deprotonation of surface sites) and the sorption process. However, more similar studies are necessary to clarify the attached mechanisms in detail.

Whereas the summarized data strongly improve the general understanding of Am(III) geochemistry and its affinity for certain minerals, it is unlikely that it will be possible to generalize the sorption behaviour of a heterogeneous natural material according to the properties of the different minerals it is composed of. The various studies clearly demonstrate the variety of effects, with experimental distribution coefficients ranging over several orders of magnitude. Therefore, the uncertainties which are attached to a bottom up approach are, in our opinion, too large to be the basis for the selection of a distinct storage site for high-level nuclear waste. Whereas the selection of a suitable backfill material might be possible on the basis of literature data, a detailed investigation of a potential host rock formation with respect to its characteristic chemical and physical properties regarding the retention of relevant radionuclides including Am(III) will always be essential.

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