Eu(III) Complex Formation with Organic Ligands in Artificial Cement Porewaters

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Introduction

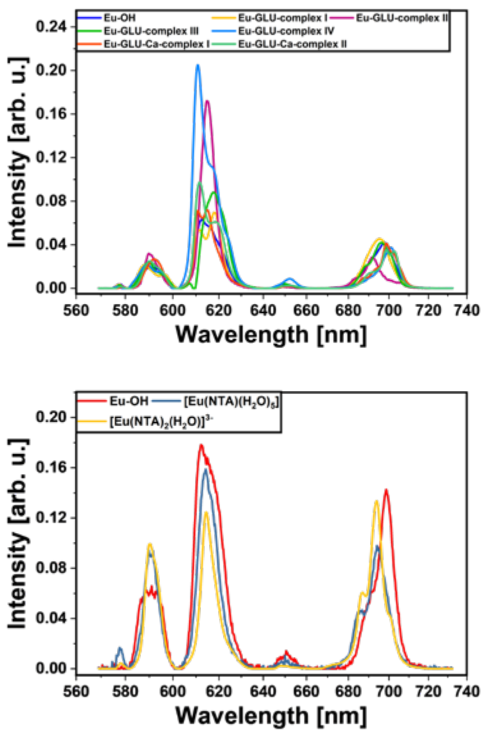
The long-term storage of highly reactive nuclear waste from various applications has been a hot topic in the international scientific community for decades. The use of a multi-barrier concept in underground repositories is considered the most promising solution. Hydrated cementitious systems, particularly Calcium Silicate Hydrates (C-S-H), are extensively studied as technical barriers due to their ability to uptake radionuclides and provide a highly alkaline environment that reduces radionuclide mobility. However, besides radionuclides, underground repositories also contain numerous organic substances like cleaning agents and cement additives that on the other hand might increase the mobility of radionuclides. Nitrilotriacetic acid (NTA) and gluconate (GLU) are examples of such substances with strong complexation properties in alkaline media. Consequently, thermodynamic and kinetic data are required for predicting the long-term impact of these compounds on the safety of a future repository. Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS) is an analytical techniques, capable of directly identifying different species based on their emission spectra and luminescence decay times. Therefore, based on TRLFS, thermodynamic data can directly be obtained and subsequently used in a speciation analysis (e.g., by using chemometric data analysis (here PARAFAC) and the PHREEQC software package).

This study examined the coordination of trivalent europium (as a natural analog for actinides in the +III oxidation state) with NTA and gluconate in artificial cementitious pore water (APW). TRLFS data were analyzed using the multi-way data evaluation method PARAFAC to identify europium species. The goal was to deepen the understanding of lanthanides and actinides behavior in APW of cementitious repositories and to guide future speciation studies. A special emphasis has been put on the influence of calcium ions present in cementitious pore waters on the europium speciation.

Experimental

The two APW solutions were prepared by synthesizing C-S-H species with C/S ratios of 1.65 and 0.8, which correspond to C-S-H solids in cement alteration stages two and three. After equilibration, the C-S-H samples were filtered and the pH values of the obtained pore waters were measured. The pH values were determined to 12.0 ± 0.1 for C/S = 1.65 and to 9.8 ± 0.1 for C/S = 0.8. To distinguish between the two APW solutions, they will subsequently be referred to as APW-1.65 and APW-0.8 to account for the different C/S ratios in the preparation. The Eu(III) concentration in the APW samples was adjusted to 50 µM. The stock solutions of the organic ligands were prepared by directly dissolving NTA and GLU in the APW. The luminescence of Eu(III) in the APW samples was measured using a pulsed 10 Hz Nd:YAG laser (Quanta Ray, Spectra Physics) combined with an optical parametric oscillator (primoScan, GWU). The excitation wavelength was adjusted to 394 nm, which corresponds to the $^5L_6 \leftarrow {}^7F_0$ transition of Eu(III). The luminescence signals were detected with an iCCD camera (iStar iCCD A-DH320T-18F-93, Andor Technology) coupled with a spectrograph (Kymera 328i equipped with a 300 l/mm grating blazed at 760 nm, Andor Technology).

Discussion

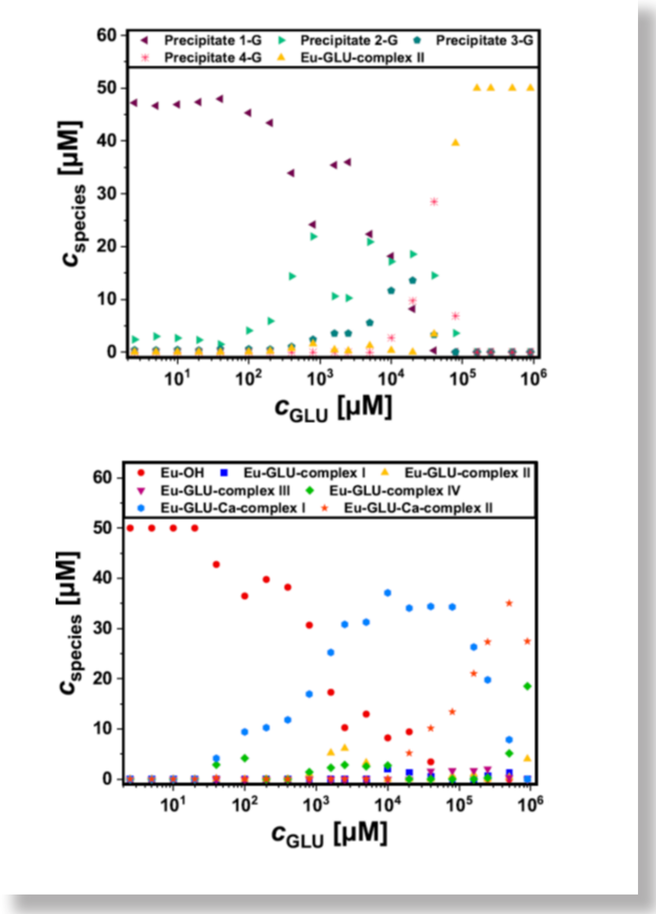


Luminescence spectra of Eu(III) complexes with gluconate (GLU, left) and NTA (right). The spectra of the single species are the result of the PARAFAC analysis of the TRLFS data of APW-1.65. For GLU two different ternary complexes with Ca(II) were identified. The luminescence was excited at λ_{ex} = 394 nm.

It was found that the composition of cementitious pore waters derived from C-S-H samples with different C/S ratios has a distinct effect on the europium speciation. This finding underlined the importance of the C/S ratio on the speciation of +III actinide ions. Depending of the alteration stage of the cement the C/S ratio (and consequently also the pore water chemistry, e.g., the concentration of Ca(II) ions) is changing, which will affect the +III actinide speciation and subsequently their retardation/mobility in cement barriers. Using NTA as organic ligand, it was observed that high concentrations of Ca(II) ions directly compete with Eu(III) in the formation of soluble NTA complexes. At a calcium concentration of over 20 mM (found in cement porewaters at high C/S ratios typically found in cement alteration stage two), NTA did not form any soluble Eu-NTA complexes under the experimental conditions applied. Instead, the europium ions quantitatively formed hydroxide species of low solubility (this finding is supported by thermodynamical speciation calculations). In the absence of calcium as an control experiment, the formation of the $[Eu(NTA)_2(H_2O)]^{3-}$ complex was readily observed at low ligand concentrations of around 10 µM at pH = 12. Additionally, the formation of the 1:2 complex between Eu(III) and NTA was found to be generally favored in alkaline environments, the 1:1 complex was only observed at a lower pH value of 9.8 in minor quantities (see Figure 1, right).

Using gluconate (GLU) as the organic ligand instead of NTA, the presence of calcium ions had an opposing effect on the europium speciation. Calcium ions were found to favor the complex formation between europium and GLU, reducing the required ligand concentration for the formation of soluble complexes by a factor of ten. Moreover, experimental evidence has been derived for the formation of ternary or quaternary complexes between calcium, europium, gluconate and possibly hydroxide ions. Furthermore, the highly alkaline medium of cementitious pore waters favored the formation of a variety of different complexes between europium and gluconate. Including two ternary or quaternary complexes, six different Eu-GLU complexes could be identified under the present conditions (see Figure 1, left, for emission specra). A speciation diagram for APW-1.65 is shown in Figure 2 (right).

The combined presence of calcium and silica species in cementitious pore waters with low C/S ratios showed a very unique effect on the europium speciation (see Figure 2, left). The formation of white solid precipitates was observed in almost all samples in the APW-0.8. On further investigation, it was found that the structure of the solid changed with increasing organic ligand concentration, resulting in a total of four different insoluble species with similar emission spectra, mainly differing in the shape of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ peak. Furthermore, the four identified species were characterized by largely different luminescence decay times. Given the present results, it is tempting to attribute the novel solid phase to the formation of C-S-H like coprecipitates between dissolved europium ions together with Ca and Si. Work is in progress to further investigate this novel precipitate with respect to its composition and structure. In this context also the ubiquitous formation of $Eu(OH)_x$ species need to be re-considered with respect to the spectroscopic parameters since these will be part of the chemical inventory in the cement environment.



Speciation diagrams for Eu(III) in APW-0.8 (left) and APW-1.65 (right) in the presence of GLU. Data shown are based on a PARAFAC analysis of the respective TRLFS data.

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