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Complexation of Americium(III) with chloride – A high-temperature EXAFS study

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The long-term storage of high-level nuclear waste will be applied in deep geological formations, different host rock formations (salt, clay, crystalline formations) are investigated throughout Europe [1]. Due to their long half-lives, the long-term radiotoxicity will be determined by the transuranium elements (Np, Pu, Am) included in the waste materials. Therefore, a well-funded knowledge of the geochemical behaviour of these long-lived radioelements is of high relevance for a reliable safety assessment of a potential storage site. Due to the radioactive decay of the stored radionuclides, the temperature in the near-field of the repository will heat up significantly ($T_{\text{max}} = 200\text{ °C}$ (salt) [2]). As reducing conditions are expected in the near-field, +III will be the stable oxidation state of Am (and partly Pu). The strong increase in temperature will have a significant effect on the chemical properties of the trivalent actinides and therefore speciation studies at elevated temperatures are of particular interest.

As chloride will be the most abundant anion available for complexation reactions aim of the present work was to determine the structural parameters of Am(III)-chloride complexes as a function of the temperature up to 200 °C . The Am LIII-edge EXAFS measurements were performed at the INE-Beamline (ANKA, Karlsruhe, Germany) using a newly developed high-temperature EXAFS cell [3].

No differences in the EXAFS spectra and Fourier Transforms are observed for $T \leq 90\text{ °C}$. At $T = 200\text{ °C}$, the peak in the pseudo-radial distribution (Fig. 1, right) is visibly broadened which is attributed to a coordination of Am(III) by chloride, revealing that Am(III) is coordinated by 2.4 chloride ligands [3]. At 200 °C , a chloride concentration of 3 M is sufficient to cause a visible complex formation with Am(III). In contrast to this, room temperature studies showed that no chloride complexes are formed for $[\text{Cl}^-] < 8\text{ M}$ [4].

The present study points out that the impact of chloride on the speciation of trivalent actinides will increase significantly with increasing temperature. Furthermore, our results provide a new insight into the complex formation properties of actinides at elevated temperatures which is a valuable contribution to improve the molecular-level understanding of the related geochemical processes.

*Author for correspondence: daniel.froehlich@partner.kit.edu. [1] W. Kickmaier, et al., Nucl. Eng. Des. 176, 75 (1997).

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Primary author: Dr FRÖHLICH, Daniel (Physikalisch-Chemisches Institut, Universität Heidelberg, Germany)

Co-authors: Dr SKERENCAK-FRECH, Andrej (Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Campus Nord, Karlsruhe, Germany); Dr ROTHE, Jörg (Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Campus Nord, Karlsruhe, Germany); Dr DARDENNE, Kathy (Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Campus Nord, Karlsruhe, Germany); Prof. PANAK, Petra (Physikalisch-Chemisches Institut, Universität Heidelberg, Germany)

Presenter: Dr FRÖHLICH, Daniel (Physikalisch-Chemisches Institut, Universität Heidelberg, Germany)

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