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Plutonium oxidation state speciation in aqueous solution studied by Pu L and M edge high energy resolution XANES technique

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In this work four electrochemically aqueous plutonium (Pu) species prepared in perchloric acid solution at different oxidation states (III, IV, V, VI) as well as Pu(IV) colloids are characterized for the first time by Pu L3 and M5 edge high energy resolution X-ray absorption near-edge structure spectroscopy (HR-XANES). A Johann type five-analyzer crystal spectrometer recently installed and commissioned at the INE-Beamline for actinide research at the ANKA synchrotron radiation facility, Karlsruhe, Germany was applied Different to conventional XANES several spectral features could be identified. The most intense absorption resonances (White Line, WL) have higher intensities for all Pu L3 HR-XANES spectra compared to the conventional XANES. Additionally, the Pu(V) and Pu(VI) L3 HR-XANES spectra exhibit better resolved post-edge features. The energy distance between the WL and this resonance is sensitive to the bond distance between the Pu and axial O atoms in Pu(V) and Pu(VI). Extended X-ray absorption fine structure (EXAFS) investigation is performed to correlate oxidation states with average Pu-O bonding distances. For the Pu(VI) M5 edge HR-XANES a feature at higher energy is well resolved, which might be sensitive to changes in Pu-O bond length and to the level of hybridization of metal and axial oxygen valence orbitals. A pre-edge 'shoulder'is detected in the Pu(III) spectrum. The origin of hitherto unresolved features is elucidated by quantum chemical calculations using the FEFF9.5 code. The HR-XANES experimental technique provides new insights into the actinides electronic structure and allows detection of minor contributions of Pu oxidation states in oxidation state mixtures.

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