

Coordination study of lanthanide and yttrium in aqueous nitrate solutions

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Removal of rare earth element (REE) from sea (river and lake) water by Fe-Mn oxyhydroxides is an important geochemical process in the hydrosphere. Although REE adsorbed on the materials lacks long-range order, elucidation of their disordered structures is a very interesting theme. The extended X-ray absorption fine structure (EXAFS) spectroscopy above the L_{III} edges is a useful method to characterize the local structure of REE on such materials. However, the reliable determination of a disturbed structure is not easy. We have therefore examined hydration structures of all REE^{3+} to establish the higher reliability EXAFS measurement for the short-range order structure because REE's hydration structures have been obtained from several measurements (X-ray, neutron diffraction, and EXAFS) and reported by many researchers.

Yttrium K-edge and lanthanide L_{III} -edge EXAFS spectra were recorded at the BL12C of KEK-PF. A Si(111) double-crystal monochromator was used to produce a monochromatic X-ray beam. The 1000-ppm solutions of REE with 1N HNO_3 were recorded in a fluorescence mode using a 19-element pure-Ge Solid State Detector in atmosphere at room temperature. EXAFS signals of $REE^{3+}_{(aq)}$ weighted by k^3 were characterized by a simple oscillating curve, which reveals existence of a first shell local order around the REE site. However, small irregular spectra were superimposed on the main oscillation in the k range of 5-7 \AA^{-1} for light REEs. These anomalous spectra are caused by a multielectron excitation (MEE). The MEE of light REEs has a broad peak that located at 120-160 eV from the L_{III} edge. The MEE peak decreases and shifts to the higher-energy side as the atomic number increases. The MEE was treated as a glitch and removed from the data prior to background removal. The MEE does not affect seriously the determination of structural parameters even in $La^{3+}_{(aq)}$. The determined interatomic distance (REE-O) and coordination number changed from 2.55 \AA and 9.5 for La to 2.31 \AA and 7.7 for Lu, which are very consistent with the reported values. The Y^{3+} has the similar hydration structure to Ho^{3+} . The number of coordination sphere of $REE^{3+}_{(aq)}$ changed from 9 to 8 between Sm and Gd. The Debye-Waller factor (σ) also decreased gradually from 0.095 \AA for La to 0.074 \AA for Lu.