

Local Structural Analysis of Rare Earth Complex in the Adsorbents for Extraction Chromatography

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Background

Recovery of trivalent minor actinides (MA: Am and Cm) from high level radioactive liquid wastes is an important task for reduction in volume and potential hazard of the final wastes, and an extraction chromatography has been under development as a promising technology for selective MA recovery. In this process, specific adsorbents which keep extractant molecules in the polymer coating over the porous silica matrix are used for column chromatographic separation. In a current promising flow-sheet, selective MA stripping from an adsorbent was achieved. However, washing out of loaded lanthanides (Ln) in the adsorbent after the MA recovery is required for repeated use of the adsorbent. To find out the best Ln washing condition effectively, extended X-ray absorption fine structure analysis on complexes of rare earth elements formed the adsorbents were carried out.

Experimental

The adsorbent was prepared by impregnating CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethyl)-phosphineoxide) and HDEHP (Bis(2-Ethylhexyl)hydrogen phosphate) into the polymer with molar ratio of 1 to 1. Eu in 3 mol/L nitric acid solution was loaded into the adsorbent through column operation. The adsorbent was mixed with DTPA solution at various pH which is an eluent for selective MA stripping, and then shaken for 3 h. The adsorbent washed with the DTPA solution was supplied to Ln washing experiments. In order to examine applicability of several carboxylic complex solutions for the washing solution, lactic acid, oxalic acid and citric acid solution with various pH were used for batch-wise washing operation. The adsorbents loading Eu, washed with DTPA and with DTPA and the wash solutions were supplied to EXAFS analysis. Eu L_{III} edge transmission EXAFS measurements on the adsorbents were carried out at BL-27B in Photon Factory of High Energy Accelerator Research Organization, Japan. An EXAFS oscillation was extracted using the cubic spline method and the structure function was obtained by the Fourier transformation. Structural parameters were derived from fitting based on the EXAFS equation.

Results & Discussion

The citric acid solution with high pH showed excellent performance for the Ln washing. By EXAFS of DTPA washed adsorbents at various pH conditions, coordination number of the nearest oxygen around an europium was 9 at pH=1 and decreases to 6 with increasing pH up to 3. This fact is considered to suggest that dominant europium complex after washing with DTPA at pH=1 is $\text{Eu}(\text{NO}_3)_3(\text{CMPO})_n$, while at pH=3 is $\text{Eu}(\text{H}(\text{DEHP})_2)_3$. EXAFS of citric acid washed adsorbents at various pH conditions showed that the coordination number around Eu decreases with increasing pH. This result must be due to weakening in Eu-extractant interaction with increasing of the pH of citric acid wash solution. These features are reasonably explained by elution behavior of europium by the citric acid. Based on the structural analysis, a promising flow-sheet was designed. Demonstration through column separation experiments on simulated and genuine high level liquid wastes will be carried out in near future.

Conclusion

EXAFS analysis on complex formed in the adsorbent for the extraction chromatography was shown to be one of powerful tools for design a flow-sheet. Demonstration of the optimized flow-sheet based on this study will be carried out soon.