SELECTIVE UPTAKE OF CESIUM BY HYBRID ADSORBENTS ENCLOSING HETEROPOLYACID

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Abstract
The selective separation and recovery of heat-generating nuclide ($^{137}$Cs) from high-level liquid waste (HLLW) containing highly concentrated HNO$_3$ and NaNO$_3$ are vital issues in relation to the partitioning of radionuclides. Ammonium molybdophosphate ((NH$_4$)$_3$PO$_4$・12MoO$_3$, AMP), a fine crystal of heteropolyacid, having a high selectivity toward Cs$^+$ ions, is one of the most promising adsorbents for this purpose. In order to granulate the fine AMP crystals, they can be incorporated into the macropores of zeolite (mordenite) by sol-gel method using alginate gel polymer matrices. The present paper deals with the novel preparation methods for the hybrid adsorbents enclosing AMP fine crystals, their stability and the selective uptake properties for Cs$^+$. The mordenite enclosing AMP (AMP-M), a kind of inorganic/organic composites, was easily prepared by the successive impregnation of 1) PMA (H$_3$Mo$_{12}$O$_{40}$P) and 2) kneaded sol (NH$_4$NO$_3$ and sodium alginate (NaALG)) into the mordenite macropores. The synthetic reaction of AMP could be expressed as H$_3$Mo$_{12}$O$_{40}$P + 3NH$_4$NO$_3$ $\leftrightarrow$ (NH$_4$)$_3$PO$_4$・12MoO$_3$ + 3HNO$_3$, and the XRD intensities of AMP were almost constant up to third loading run. Here the AMP-M composites obtained by 1$^{st}$ to 3$^{rd}$ cycles were abbreviated as AMP-M-1, -2 and -3, respectively. AMP-M composites were stable up to 200°C and had high uptake ability for Cs$^+$ up to 2.1×10$^7$ R irradiation ($^{60}$Co).

The uptake of Cs$^+$ for AMP-M from HNO$_3$ and NaNO$_3$ solutions was examined by the batch method. The uptake of Cs$^+$ for AMP-M in the presence of 0.01~5 M HNO$_3$ attained equilibrium within 5 h, and a relatively large uptake percentage above 90% ($K_d$ > 10$^2$ cm$^3$/g) was obtained; the uptake rate and uptake (%) of Cs$^+$ for AMP-M were markedly enhanced compared to those for mordenite matrices. The AMP-M composites also exhibited relatively large $K_d$ values above 10$^2$ cm$^3$/g for Cs$^+$ even in the presence of 0.01~3 M NaNO$_3$. The uptake ability of different metal ions for AMP-M was compared in the presence of 0.01~5 M HNO$_3$. The order of $K_d$ value was Cs$^+$ >> Rb$^+$ > Ag$^+$; significant difference in $K_d$ value between Cs$^+$ and other cations was observed. The maximum separation factors of Cs$^+$/Rb$^+$ ($K_{d,Cs}/K_{d,Rb}$) and Cs$^+$/Ag$^+$ ($K_{d,Cs}/K_{d,Ag}$) were estimated to be 23.9 and 100, respectively. The selective uptake (%) of Cs$^+$ from simulated HLLW (SW-11E, 28 components, 2 M HNO$_3$, 1 M NaNO$_3$, JAEE, 1 M NaNO$_3$, JAEE) was estimated to be 70~80% for AMP-M-1~3.

For the practical use, the column adsorption properties (breakthrough and elution) were examined in the presence of 2.5 M HNO$_3$. The breakthrough and total capacities were estimated to be 0.081 and 0.22 mmol/g from the symmetrical S-shaped curves, respectively. Further, the adsorbed Cs$^+$ on the AMP-M-3 column can be eluted by passing the eluent of 5 M NH$_4$NO$_3$ solution and the elution (%) was estimated to be 95.4%.

Thus, the AMP-M composites seem to be effective for the selective separation of Cs$^+$ ions from HLLW.