

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 ($(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, 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 ($\text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P}$) and 2) kneaded sol (NH_4NO_3 and sodium alginate (NaALG)) into the mordenite macropores. In this procedure, both synthesis and loading of AMP into the macropores are simultaneously accomplished. The synthetic reaction of AMP could be expressed as $\text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P} + 3\text{NH}_4\text{NO}_3 \leftrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 + 3\text{HNO}_3$, and the XRD intensities of AMP were almost constant up to third loading run. Here the AMP-M composites obtained by 1st to 3rd 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% ($K_d > 10^3 \text{ cm}^3/\text{g}$) 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 $10^2 \text{ cm}^3/\text{g}$ 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 $\text{Cs}^+ \gg \text{Rb}^+ > \text{Ag}^+$; significant difference in K_d value between Cs^+ and other cations was observed. The maximum separation factors of Cs^+/Rb^+ ($K_{d,\text{Cs}}/K_{d,\text{Rb}}$) and Cs^+/Ag^+ ($K_{d,\text{Cs}}/K_{d,\text{Ag}}$) 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 , JAEA) 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_4NO_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.