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Study on Stabilization Technique of Wastes Polluted with Radioactive Cs and Sr for Interim Storage and Final Disposal

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No solidification method for the final disposal of decontaminated radioactive waste from the Fukushima Daiichi nuclear power plant accident has been established yet. Therefore, we studied solidification methods for soil-rich wastes containing relatively low radiocesium concentrations and for wastes containing high radiocesium concentrations such as incineration fly ash.

A quantitative estimate using a theoretical equation based on the competitive adsorption theory that was developed to estimate the elution ratio of Cs from soil was validated for wastes containing relatively high percentages of soil with an estimation error of a few percent. Based on a Langmuir-type competitive adsorption theory, and assuming the existence of three types of adsorption sites for Cs in soil, which are the So type: exchangeable adsorption sites mainly on organic matter; Ss type: exchangeable adsorption sites mainly in the clay matrix; and Sf type: almost unexchangeable adsorption sites in soil, called frayed edge sites. Thus, the Cs adsorbed is expressed by the following equations:

$$[Cs\text{-}S] = [Cs\text{-}So]+[Cs\text{-}Ss]+[Cs\text{-}Sf] \quad (1)$$

$$[Cs\text{-}So] = [So_{max}]b_{Cs\text{-}So}[Cs^+]/(1+ \Sigma_i b_{i\text{-}So}[M_i]) \quad (2)$$

$$[Cs\text{-}Ss] = [Ss_{max}]b_{Cs\text{-}Ss}[Cs^+]/(1+ \Sigma_i b_{i\text{-}Ss}[M_i]) \quad (3)$$

$$[Cs\text{-}Sf] = [Sf_{max}]b_{Cs\text{-}Sf}[Cs^+]/(1+ \Sigma_i b_{i\text{-}Sf}[M_i]) \quad (4)$$

where $[Cs^+]$ is concentration of Cs^+ in the eluate (meq/mL), $[M_i]$ is concentration of cation "i" in the eluate (meq/mL), $[Cs\text{-}S]$ is Cs adsorbed in the solid phase in the soil (meq/g); and $[Cs\text{-}So]$, $[Cs\text{-}Ss]$, $[Cs\text{-}Sf]$ are Cs adsorbed by So type, Ss type, and Sf type adsorption sites (meq/g), respectively. Considering the practical situation of incineration ash containing soil, the elution ratio E_{Cs} (%) by the standard heavy metal elution test used by the Ministry of the Environment (MoE), Japan, is expressed by the following equation:

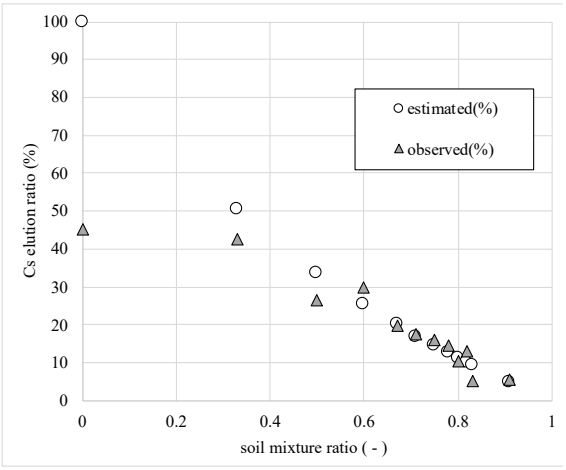

Fig. 1 Comparison of estimated and observed elusion ratios of Cs from incineration ash depending on its soil mixture ratio.

$$E_{Cs}=100/(1+(a/R)\ RIP/[K^+]) \quad (5)$$

where "a" is the weight content (or mixture) ratio of soil in the incineration ash, "R" is the weight ratio of incineration ash to eluate, $[K^+]$ is the concentration of K^+ in the eluate (meq/mL), and "RIP" is the radiocesium interception potential.

The efficiency of Equation (5) is considered by the following experiment: A quantity of Cs is added to refuse derived fuel (RDF), then it is mixed with a certain amount of forest soil, then it is incinerated at 500°C for three hours, and then it is eluted by the elution test method MoE uses.

The elution ratios estimated by equation (5) are compared with observed values in Fig. 1. This shows that Equation (5) can well estimate the elution ratio of Cs from incineration ash containing soil when

the soil mixture ratio is not small. Equation (5) also shows that it is not necessary to measure the soil mixture ratio "a" and the concentration of K^+, respectively, but it is enough to measure the value of $a/[K^+]$. We also showed that the ratio of $a/[K^+]$ can be estimated from the ratio of Si to K measured by a portable XRF instrument:

$$a/[K^+]=(M_K R)/(1000 r_{Si}([K/Si]-r_K/r_{Si})) \quad (6)$$

where M_k is the atomic mass of K, r_{Si} is the weight ratio of Si in soil, r_K is the weight ratio of K in the clay matrix and [K/Si] is the weight ratio of K and Si measured by XRF. It is expected that the elution ratio of each sample can be estimated on site using XRF measurement and equations (5) and (6). Furthermore, we showed that the necessary parameters in the theoretical equation, such as the ratio of potassium to soil, could be easily obtained using a portable X-ray fluorescence spectrometer. Finally, a classification method to control the elution ratio of Cs using highly concentrated ammonium solution to increase the recycling ratio of contaminated soil was proposed. The quantitative estimation of elution was effective for Cs the main adsorption sites of which were frayed edge sites, but it was difficult and more parameters were necessary to be observed for Sr the main adsorption sites for which were pH-dependent variable charge sites.

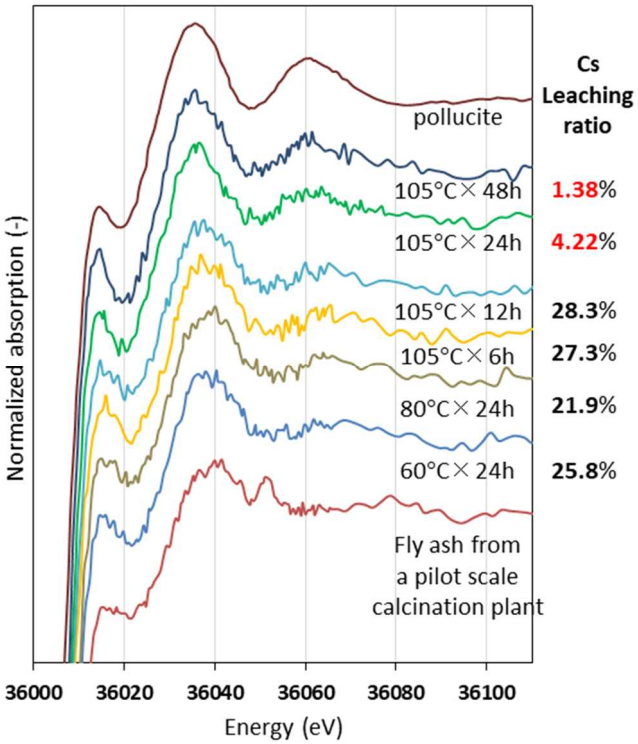

Fig. 2 Change in Cs- K XANES spectra in materials solidified with fly ash from a pilot scale calcination plant.

To reduce the volume and weight of decontaminated radioactive waste and concentrate radiocesium into a small fraction, the separation of Cs by high-temperature thermal processes such as melting or calcinating has been considered. Through this process, fly ash with a relatively high radiocesium concentration is generated. Therefore, it is necessary to dispose of the fly ash safely. In this study, a stabilization and solidification method using geopolymeriza-tion was developed for fly ash. Materials, mixing conditions and curing conditions were varied to make stable solidified materials. When fly ash, aluminosilicate material, NaOH solution and water glass were mixed in equal quantities and cured at 105°C for more than 24 h, the Cs leaching ratios from the solidified materials were less than 5%. The optimum NaOH concentration was present in the immobilization of Cs in the fly ash. The Cs immobilization mechanism in the solid was studied using X-ray diffraction, X-ray absorption fine structure and nuclear magnetic resonance analyses. When specific zeolites such as Chabazite were formed, the Cs leaching ratios were lower, suggesting that Cs was likely fixed as pollucite, which is a very stable Cs compound. The change in chemical form of Cs was confirmed from the change in Cs- K XANES spectra as shown in Fig. 2. This indicated that geopolymerization under optimal conditions was involved in not only simple solidification but also chemical stabilization. Under the same optimal conditions, the leaching behavior of radioactive Sr was examined. The release of Sr was also inhibited significantly. The behaviors of radioactive Cs and Sr were basically the same as those of stable Cs and Sr. Finally, the geopolymer solidification process was compared to cement solidification, washing and adsorption processes to determine its use for the final disposal of highly contaminated fly ash. As a result, future challenges in both processes were elucidated.