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Studies on Solubility of Metal Ions and Complexes in Supercritical Fluids and Their Application to Nuclear Fuel Preparation and Radioactive Waste Treatment

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Chapter 1

Supercritical fluids (SCFs) have unique properties such as low toxicity, non-flammability, gas-like diffusivity, and liquid-like solubility. Supercritical fluids are used in various chemical fields as alternative to conventional solvents. In nuclear industry, many processing are used various kinds of solvent. Therefore, SCFs can be applied to nuclear industry. From this viewpoint, we have performed basic studies for developing novel low decontaminated MOX fuel preparation method using supercritical water (SCW) and decontamination of solid radioactive wastes using supercritical carbon dioxide ($scCO_2$).

Chapter 2

In order to develop preparation method of raw metal oxide particles for low decontaminated MOX fuels by supercritical hydrothermal synthesis (SHS), we have investigated the optimal conditions of conversion reaction from U(VI), Ln(III) (Ln: lanthanoid = Ce, Pr, Nd, Sm, Tb), Cs(I), and Sr(II) nitrate or chloride compounds to their metal oxide particles by SHS (temperature = 400 - 500 ℃, pressure = 30 - 40 MPa), and examined the conversion reaction mechanisms. As a results, it was found that $Ln(NO_3)_3$ (Ln = Ce, Pr, Tb) compounds produce LnO_2, that $Ln(NO_3)_3$ (Ln = Nd, Sm) compounds are hardly converted to their oxides, and that $LnCl_3$ (Ln = Ce, Pr, Nd, Sm, Tb), $CsNO_3$, and $Sr(NO_3)_2$ do not form their oxide compounds. Furthermore, HNO_2 species were detected in the liquid phase obtained after treating HNO_3 aqueous solutions containing $Ln(NO_3)_3$ (Ln = Ce, Pr, Tb) under SH conditions, and also NO_2 and NO compounds were found to be produced by decomposition of HNO_3. From these results, it was proposed that the Ln oxide (LnO_2) particles are directly formed with oxidation reaction by HNO_3 and HNO_2 species in the SH systems. Moreover, the uranyl species were found to form U_3O_8 and UO_3 depending on the concentration of HNO_3. From these results, it is expected

that the raw metal oxide particles are efficiently prepared from metal ions by SHS method.

Chapter 3

Furthermore, for development of decontamination methods of solid radioactive wastes using $scCO_2$, we have determined the solubility of Ln(fod or hfa)$_3$·2H_2O (Ln = Pr, Nd, Eu, Er; fod: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate, hfa: hexafluoroacetylacetonate) complexes in $scCO_2$ at 40 ℃ in the pressure range of 10 - 25 MPa by using UV-vis spectrophotometer equipped with high pressure-cell, and examined the control factor of their solubility in $scCO_2$. As a results, it was found that the solubility of Ln(fod)$_3$·2H_2O complexes is higher than that of the corresponding Ln(hfa)$_3$·2H_2O complexes and that the heavy Ln(III) complexes are more soluble than the light Ln(III) ones. This result indicates that the solubility of metal complexes increases with increasing the number of fluorine atom in their ligands and that the metal complexes largely shielded by the ligands are more soluble. Furthermore, we examined the differences in solubility from the viewpoints of interactions between Ln(fod or hfa)$_3$·2H_2O complexes and CO_2 molecules based on the Chrastil model. As a results, it was found that the solubility of Ln(fod or hfa)$_3$·2H_2O (Ln = Nd, Eu, Er) complexes are higher than that of Pr(fod or hfa)$_3$·2H_2O complexes in spite of small *k* values (*k*: the number of CO_2 molecules associated with metal-chelate complexes) and that the order of solubility of Ln(fod of hfa)$_3$·2H_2O is opposite to that of *k* values. This result suggests that the solvation of CO_2 is not the predominant factor for controlling the solubility of Ln(III) fluorinated *β*-diketonate complexes. Furthermore, it is proposed that the relatively high solubility of Ln(fod or hfa)$_3$·2H_2O is attributed to the specific interactions between $scCO_2$ and the fluorine groups in Ln(fod or hfa)$_3$·2H_2O such as the van der Waals interaction rather than the solvation of CO_2. From these results, it is expected that the fluorinated *β*-diketone (Hfod) is suitable compound for extracting Ln(III) species from the solid materials to $scCO_2$ phase.

Chapter 4

For the verification of feasibility of application of SCFs to nuclear industry, we have examined whether the fuel pellets can be prepared using metal oxide powders synthesized by SHS and the metal species can be extracted from the artificially contaminated materials to $scCO_2$ by using Hfod. As a results, it was clarified that the prepared fuel pellets have density about 80 % T.D. and that the particles size influences the density of the fuel pellets. From these results, it is expected that the raw metal oxide powders for low decontaminated MOX fuels are efficiently prepared by SHS method. Furthermore, it was

found that the Ln(III) species are extracted effectively by using $scCO_2$ containing Hfod as an extractant and methanol as modifier.

Chapter 5

Based on these studies, we have confirmed that the application of SCFs as reaction medium to nuclear industry is feasible.