REACTIONS OF IRON CRUD WITH METALLIC IONS UNDER BWR WATER CONDITIONS

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Objectives: Formation mechanisms and formation rates of $NiFe_2O_4$ and $CoFe_2O_4$ from amorphous Fe(III) hydroxide and α-Fe_2O_3, with Ni(II) and Co(II) ions, were studied experimentally to clarify the formation of spinel oxide on BWR fuel rod surfaces.

Comments: The reactions of the amorphous Fe(III) hydroxide with Ni(II) and Co(II) could be explained by a reaction model incorporating two phenomena: the dehydration of Fe(III) hydroxide, and the diffusion of ions into it. Cobalt (II) ions diffused into α-Fe_2O_3 to form $CoFe_2O_4$. Apparent activation energy for Co(II) diffusion into a α-Fe_2O_3 was obtained as 2.72-e5 J/mol. Formation of $NiFe_2O_4$ from α-Fe_2O_3 and Ni(II) was promoted by crystallization of Ni(II) and Fe(III) ions from dissolved α-Fe_2O_3 and NiO. The apparent activation energy for the nucleation of $NiFe_2O_4$ crystal was obtained as 6.38-e5 J/mol. When $Co(OH)_2$ coexisted with $Ni(OH)_2$ and α-Fe_2O_3, Co_3O_4 which has a spinel structure was formed and those particles became nuclei for $NiFe_2O_4$. This lowered the activation energy for the nucleation.

Remarks/Potential for dose limitation: The behavior of metallic ions (Ni, Co, etc.) and Fe crud (Fe(III) hydroxides and oxides) which enter the primary water by corrosion of structural materials is closely related to radioactivity in the reactor water. Most of these impurities are deposited on the fuel cladding surface in the reactor water where they become activated through neutron irradiation and represent a major source of radioactivity. Boiling on the fuel rod surface accelerates the deposition of Fe crud and ions. It is desirable to suppress the amounts of parent nuclides flowing into the reactor. Then main radioactive species are Co-58 and Co-60, which are produced by the reactions Ni-58(n,p)Co-58 and Co-59(n,γ)Co-60 respectively. The amount of Co can be reduced by using low Co content materials. However, reduction of the Ni amount is difficult due to dissolution from Ni based alloy in the reactor. Then, it is important to change the chemical form of the deposits into spinel oxides ($NiFe_2O_4$, $CoFe_2O_4$, etc.), which have lower solubility than mono-oxides (NiO, CoO, etc.). When spinel oxides form on the fuel rod surface, the release of radioactive species from them is depressed and those concentrations in the reactor water can be kept low.

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References: Nishino, Y. et al, "Reactions of Iron Crud With Metallic Ions Under BWR Water Conditions," *Water Chemistry of Nuclear Reactor Systems 6*, Vol. 1, pp. 63-68, British Nuclear Energy Society, London, 1992.

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