Decontamination of Zircaloy Cladding Hulls from Spent Nuclear Fuel

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Abstract

The feasibility of decontaminating spent fuel cladding hulls using hydrofluoric acid (HF) was investigated as part of the Global Energy Nuclear Partnership (GNEP) Separations Campaign. The concentrations of the fission product and transuranic (TRU) isotopes in the decontaminated hulls were compared to the limits for determining the low level waste (LLW) classification in the United States (US). The ^{90}Sr and ^{137}Cs concentrations met the disposal criteria for a Class C LLW; although, in a number of experiments the criteria for disposal as a Class B LLW were met. The TRU concentration in the hulls generally exceeded the Class C LLW limit by at least an order of magnitude. The concentration decreased sharply as the initial 30-40 μm of the cladding hull surface were removed. At depths beyond this point, the TRU activity remained relatively constant, well above the Class C limit.

1.0 Introduction

Reprocessing of spent nuclear fuel generates a cladding waste which would likely require disposal as a Greater than Class C LLW in the US [1-3]. If the cladding hulls could be treated to remove a majority of the actinide and fission product contamination, the hulls could potentially meet acceptance criteria for disposal as a LLW [4] or allow recycle of the Zr metal. Discard of the hulls as a LLW would result in significant cost savings compared to disposal as a Greater than Class C waste which currently has no disposition path. During fuel irradiation and reprocessing, radioactive materials are produced and deposited in the Zircaloy cladding. Due to short depths of penetration, the majority of the fission products and actinide elements are located in the ZrO_2 layer which forms on the surface of the cladding during fuel irradiation. Therefore, if the oxide layer is removed, the majority of the contamination should also be removed.

It is very difficult, if not impossible to remove all of the activity from spent fuel cladding since traces of U and Th in the unirradiated Zircaloy adsorb neutrons generating higher actinides in the bulk material. During fuel irradiation, ^{92}Zr is also converted to radioactive ^{93}Zr by neutron adsorption. Methods for decontaminating and conditioning irradiated Zircaloy cladding hulls have been investigated in Europe, Japan, and the US during the last 35 years [5-11]; however, a method to decontaminate the hulls to an activity level which meets US acceptance criteria for disposal as a LLW was not deployed on a commercial scale. The feasibility of decontaminating spent fuel cladding hulls was investigated as part of the GNEP Separations Campaign. Small-scale experiments were used to demonstrate the removal of the ZrO_2 layer from Zircaloy coupons using dilute solutions ($\leq$1.0 M) of HF. The most effective conditions resulted in dissolution rates which were less than approximately 2 mg/cm^2-min. With dissolution rates in this range, uniform removal of the oxide layer was obtained and a minimal amount of Zircaloy metal was dissolved [12]. To test the HF decontamination process, experiments were subsequently performed using actual spent fuel cladding hulls. Decontamination experiments were performed to measure the fission product and actinide concentrations as a function of the depth of the surface removed from the cladding hull. The experimental methods used to perform these experiments and a discussion of the results and observations are presented in the following sections.

2.0 Experimental

To test the effectiveness of an HF decontamination process, Zircaloy cladding hulls generated during the dissolution of spent fuel were used to perform a series of decontamination experiments. The spent fuel originated at the Big Rock Point Reactor, a 75 MW (electric) boiling water reactor of General Electric design. The fuel was discharged in 1984 with an estimated fuel burnup of 29,600 MWd/MTU. The UO_2 fuel was dissolved in 5.8 M nitric acid at 150 °C using a pressurized dissolver. Initially, three samples of the cladding were characterized using a hot cell at the Savannah River National Laboratory. A small ring of the cladding (with a mass of approximately 0.5 g) was removed from three randomly chosen pieces using a tubing cutter. The samples were subsequently removed from

the cell and dissolved in a Teflon® vessel at nominally 115 °C using concentrated HF. Radiochemical analyses were then performed for fission products and actinide elements of interest.

The decontamination experiments were performed in a 1 L Teflon® vessel using a hot plate/stirrer for heating and agitation. A Teflon® basket was designed to raise and lower the cladding hull into the HF solution using a compression fitting in the screw-top vessel lid. A thermocouple probe was used to monitor and control the HF temperature during an experiment. A water-cooled condenser was used to reduce evaporation losses. Prior to placing a piece of cladding into the vessel and following the experiment, the mass, length, diameter, and wall thickness of the cladding were measured using an analytical balance and a digital micrometer. Varying depths of the cladding surfaces were removed by adjusting the HF concentration, temperature, and reaction time. Following the experiment, a 0.5 g sample was removed from the hull, dissolved, and the resulting solution analyzed for isotopes of interest. A new tubing cutter was used to remove a sample from each hull to minimize the transfer of contamination from one experiment to another.

3.0 Results and discussion

Fission product and transuranic (TRU) concentrations measured in the three samples of cladding from the Big Rock Point Reactor fuel are summarized in Table 1.

Table 1 Cladding hull characterization.

Isotope	Hull-1	Hull-2	Hull-3	Average Conc.	Class A or C LLW Criteria[4]
	(GBq/m^3)	(GBq/m^3)	(GBq/m^3)	(GBq/m^3)	(GBq/m^3)
^{60}Co	445	483	624	518	25900 (A)
^{90}Sr	32700	46100	37900	38900	259000 (C)
^{137}Cs	63700	72400	67200	67800	170200 (C)
	(kBq/g)	(kBq/g)	(kBq/g)	(kBq/g)	(kBq/g)
^{238}Pu	432	1560	977	989	3.7 (C)
$^{239/240}Pu$	155	562	352	356	3.7 (C)
^{241}Am	93	203	187	161	3.7 (C)

From the data in Table 1, it can be seen that the concentrations of the fission products already meet the US criteria for disposal as a Class C LLW. However, the TRU activity greatly exceeds the 3.7 kBq/g criterion for disposal of the hulls as a LLW. The TRU activity also shows significant variation between the samples compared to the more consistent concentrations obtained for the fission products. The random deposition of the less soluble actinides during the fuel dissolution may have contributed to the variations in the measured activities.

The fission product and TRU concentrations following decontamination of the cladding hulls were compared against criteria for determining the LLW classification [4]. To facilitate the comparison, the activity of the decontaminated hulls was correlated with the depth of the surface removed during the experiment. The depth removed was estimated using the mass of the cladding hulls and physical dimensions. The concentrations of ^{60}Co, ^{90}Sr, and ^{137}Cs are plotted in Fig. 1. The Class A concentration limit for ^{60}Co and the Class B concentration limits for ^{90}Sr and ^{137}Cs are plotted on the figure for comparison. The figure shows that the cladding hulls meet the Class A limit for ^{60}Co and the Class C limits for ^{90}Sr and ^{137}Cs; although, in a number of experiments, the Class B limits for ^{90}Sr and ^{137}Cs were met. The concentration of the isotopes show only a slight decrease in concentration with an increase in depth of surface removed, which indicates the isotopes were deposited near the cladding surface probably by fission recoil or diffusion from the fuel. Increasing the surface removal depth beyond approximately 120 μm was generally successful in reducing the ^{90}Sr concentration below the Class B limit; however, ^{137}Cs concentrations below the Class B limit did not correlate with the dissolution of increasing amounts of the cladding hulls. It is possible that residual ^{137}Cs activity from previous work in the hot cell may have contaminated the hulls. The relatively constant ^{60}Co concentration was attributed to the formation of the isotope as an activation product throughout the cladding. Cobalt-60 is formed by neutron adsorption from trace quantities of ^{59}Co in the small amount of iron in the Zircaloy.

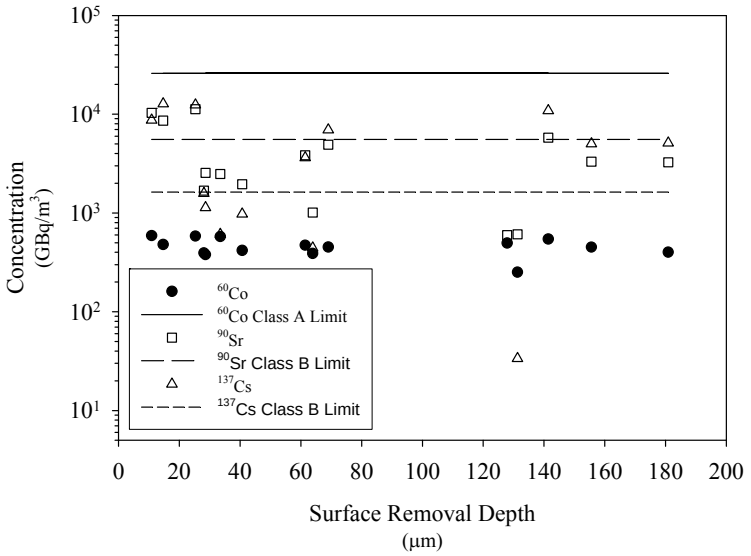

Fig. 1. Fission product concentrations in cladding hulls.

The sum of the concentrations of ^{238}Pu, $^{239/240}$Pu, and ^{241}Am in the cladding hulls is plotted as a function of the surface removal depth in Fig. 2. The figure shows an initial steep decrease in the TRU element concentration as the first 30-40 μm of the cladding hulls are removed. This observation is consistent with the removal of the majority of the TRU activity as the ZrO_2 layer is removed from the cladding hull. The ZrO_2 layer forms on the surface of the cladding during fuel irradiation. Short depths of penetration into the cladding are the result of both atomic diffusion and fission recoil [13]. The kinetic energy of the fission products provide the transport mechanism to carry clusters of TRU atoms into the oxide layer. At cladding hull surface removal depths beyond 30-40 μm, the TRU element concentration remained relatively constant. Removal of additional activity from the cladding hulls was likely limited by the contaminated environment in which the hulls were handled. The concentration limit for a Class C LLW was exceeded by an order of magnitude in most experiments. The order of the alpha activity was ^{238}Pu > $^{239/240}$Pu > ^{241}Am.

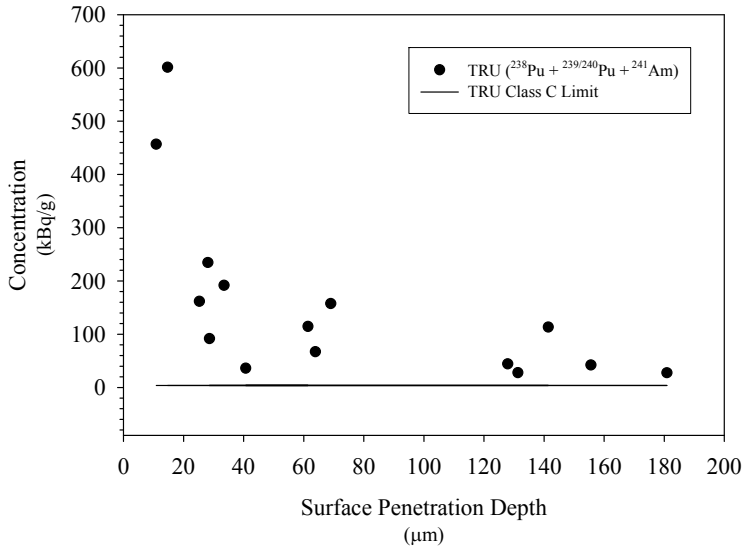

Fig. 2. TRU concentration in cladding hulls.

4.0 Conclusions

Characterization of the cladding hulls from the Big Rock Point Reactor demonstrated that fission product concentrations in the hulls met disposal limits for a Class C LLW in the US following fuel dissolution. However, the concentration of TRU isotopes in the cladding greatly exceeded the 3.7 kBq/g criterion for disposal as a LLW. Following a series of decontamination experiments, the concentrations of fission products and TRU elements were measured in the cladding hulls and compared to the limits for determining the LLW classification. The ^{90}Sr and ^{137}Cs concentrations in the hulls still met criteria for disposal as a Class C LLW; although, in a number of experiments the criteria were met for disposal as a Class B LLW. Correlation of the ^{90}Sr and ^{137}Cs, concentrations in the hulls with the depth of the cladding surface removed showed only a slight decrease in activity with increasing depth indicating the majority of the isotopes were deposited near the surface in the ZrO_2 layer. Based on this observation, the removal of the ZrO_2 layer during decontamination of cladding hulls from other reactors or from fuel with higher burn-up and shorter cooling time would be expected to generate a LLW which meets the Class C criteria for both ^{90}Sr and ^{137}Cs. The TRU isotope concentration in all experiments generally exceeded the Class C LLW criterion by at least an order of magnitude; therefore, it is doubtful that cladding hulls from any reactor or even fuel with lower burn-up would meet the criterion for disposal as a Class C LLW.

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