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Decontamination of Control Rod Housing from Palisades Nuclear Power Station
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Introduction

Argonne National Laboratory has developed a novel decontamination solvent for removing oxide scales formed on ferrous metals typical of nuclear reactor piping. The decontamination process is based on the properties of the diphosphonic acids (specifically 1-hydroxyethane-1,1-diphosphonic acid or HEDPA) coupled with strong reducing agents (e.g., sodium formaldehyde sulfoxylate, SFS, and hydroxylamine nitrate, HAN). To study this solvent further, ANL has solicited actual stainless steel piping material that has been recently removed from an operating nuclear reactor. On March 3, 1999 ANL received segments of control rod housing from Consumers Energy's Palisades Nuclear Plant (Covert, MI) containing radioactive contamination from both neutron activation and surface scale deposits. Palisades Power plant is a PWR type nuclear generating plant. A total of eight segments were received. These segments were from control rod housing that was in service for about 6.5 years. Of the eight pieces that were received two were chosen for our experimentation—small pieces labeled Piece A and Piece B (see Figure 1).

The wetted surfaces (with the reactor's pressurized water coolant/moderator) of the pieces were covered with as a scale that is best characterized visually as a smooth, shiny, adherent, and black/brown in color type oxide covering. This tenacious oxide could not be scratched or removed except by aggressive mechanical means (e.g., filing, cutting).

Figure 1. Photos of as-received Pieces A and B from Palisades Nuclear.

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Gamma spectroscopy description

A baseline gamma-ray assay was performed in the as-received condition. The samples were placed individually at a distance of 35 cm from an EG&G ORTEC High Purity Germanium (HPGe) detector with a multi-channel analyzer. The spectra were collected for 24 hours and the respective isotope species identified and their activity quantified. Piece A contained a variety of isotopes including Co-60, Sb-125, Ag-110m while Piece B activity was derived almost exclusively from Co-60.

Decontamination methodology

The make-up of the scales on the Palisades pieces was perceived to be of the toughest oxide scales -- i.e., spinel structure containing nickel, columbium, tantalum, chromium and iron oxides. Therefore, an aggressive mixture of HEDPA, SFS, and HAN was employed. The solution was heated to $85\pm3^{\circ}\text{C}$ and monitored over a couple of days. The pieces were removed from the solution after two days of cleaning and gamma analyzed.

Post-decontamination analysis

In Figures 2 and 3, photos of Pieces A and B, respectively, show the complete removal of the brown/black oxide scale. For Piece A, the entire piece is shiny without any sign of corrosion or scaling. A post-decontamination gamma-ray analysis was used to quantify the decontamination factor (DF).¹ In Table 1, initial and final peak counts are displayed along with the corresponding DF. It is evident that within the constraints of (very sensitive) low detection limits in our counting system, the piece has been completely decontaminated of the surface oxides. The DF for suspected surface radionuclides of Eu-152, Sn-113, Sb-125, Ag-110m, Co-58, and Mn-54 are >7.8 , >70 , >79 , >36 , >111 , and >16 , respectively. The Cr-51, Fe-59, and Co-60 activity was reduced only by a factor of 1.5 but this is obviously due to internal activation of the sample. These three radionuclides are formed by the neutron activation of natural Cr-50, Fe-58, and Co-59, respectively.

Figure 2. Before and after photos of Piece A. The oxide scale has been completely removed.

¹ DF is computed by taking the total activity before decontamination divided by the total activity following decontamination. Where the activity after decontamination was below detection limits, a lower limit of DF was computed based on a detection limits of 3% counts above background. The contribution from suspected internal activation was not taken into account for Cr-51, Fe-59, and Co-60 but is estimated in the parenthetical values.

Table 1. Representative gamma-ray characterization and DF calculations for Piece A. The parentheses denote the DF taking into account internal activation.

Photopeak energy	Radionuclide	As-received counts	Post-decon counts	DF
122.6	Eu-152, 154	16,860	BDL	>7.8
319.9	Cr-51	16,928	11,506	1.5 (>5)
392.1	Sn-113	64,201	BDL	>70
428.4	Sb-125	69,117	BDL	>79
658.1	Ag-110m	19,616	BDL	>36
810.9	Co-58	80,049	BDL	>110
835.1	Mn-54	8,573	BDL	>16
1099.7	Fe-59	3,818	2,467	1.5 (>4)
1173.7	Co-60	422,612	276,372	1.5 (>340)

To show the contrast between a cleaned and an original surface, only half of Piece B was submerged in the HEDPA/SFS/HAN solution. The results are presented as a photo in Figure 3. One can easily discern the interface line between the submerged and non-submerged fraction. Some oxide material can still be seen on the cleaned fraction.

Figure 3. Photo of Piece B after decontamination of one-half the piece.

Discussion of results

From the gamma and visual characterization of Piece A and B, it is evident that the HEDPA decontamination solvent was effective. The surfaces of the pieces are effectively cleaned and for sample A, it was completely cleaned. The decontamination effectiveness was verified by gamma spectroscopy and the DF calculations.

Based on the complete success achieved with respect to these specimens, it has been decided to not continue the experimentation with the remaining six samples.

Management of Palisades Power station has been appraised of these results, and they have begun the decision making process to perhaps incorporate our (HEDPA + SFS + HAN) decontamination process technology for the disposal and decontamination of various components, currently being considered for disposal at Palisades.

Furthermore, it is stressed that even though the present experiments (i.e. decontamination process) were conducted over a two-day period, it is believed that the processing times can be reduced to less than 24 hours for stubborn surface oxides similar to the above pieces. This can be achieved by altering the chemical combinations and other processing variables such as, pressure, agitation and temperature. AISI type 347 stainless is a Cb-Ta containing steel. The spinels that form on this steel are chemically more inert than the chromium rich spinels that typically form on 304 and 316 type stainless steels. Therefore, these pieces are considered to be the "extreme case" of decontamination in so far as stainless steels are concerned. Shorter processing times and lower operating temperatures are anticipated for the decontamination of components made from standard AISI type 304 and 316 stainless steels.

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