Development of a Chemical Process Using Nitric Acid-Cerium(IV) for Decontamination of High-Level Waste Canisters

L. A. Bray

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SUMMARY AND CONCLUSIONS

At the West Valley Nuclear Services Co., Inc., in West Valley, New York, high-level radioactive waste will be vitrified into a borosilicate glass form. The molten glass will be poured into large, stainless steel (304L) canisters. During the filling process, small quantities of fission product compounds, principally ^{137}Cs , will volatilize and subsequently condense on the exterior of the canisters where they become sufficiently bonded to the oxidized canister surface. Decontamination techniques involving simple washing are not adequate to remove all of the smearable contamination from the canister surface. The smearable contamination that remains on the canisters after filling must be removed from the canisters' exterior surfaces prior to their storage and ultimate shipment to a U.S. Department of Energy (DOE) repository for disposal.

A simple and effective method was developed for decontamination of high-level waste canisters. This method of chemical decontamination is applicable to a wide variety of contaminated equipment found in the nuclear industry. The process employs an oxidant system $[\text{Ce(IV)}]$ in nitric acid (HNO_3) solution to chemically mill a thin layer from the canister surface. Contaminated canisters are simply immersed in the solution at a controlled temperature and Ce(IV) concentration level. The spent solution is discarded to the high-level waste stream and added to subsequent glass batches. The $\text{Ce(IV)}/\text{HNO}_3$ solution has been shown to be effective in chemically milling the surface of stainless steel, similar to the electropolishing process, but without the need for an applied electrical current.

West Valley (WV) staff had previously evaluated several canister decontamination methods, including electropolishing, liquid abrasive blast, high-pressure water wash, and ultrasonic cleaning, before the $\text{Ce(IV)}/\text{HNO}_3$ redox solution treatment was selected. The initial concept involved continuous electrochemical regeneration of the ceric ion. Extensive in-cell pumping and close-coupled heat transfer and electrochemical equipment were required. The objective of this study, performed at the Pacific Northwest Laboratory (PNL),

was to simplify the original concept. A summary of the major technical findings and conclusions is presented below:

- A single-use throwaway solution is recommended.
- An electrochemical cell is not required in the production of Ce(IV) for the decontamination facility.
- Three moles of Ce(IV) are required to dissolve one mole of iron. Approximately 0.65 to 1.4 moles of Ce(IV) will remove an -1.5- to 3- μm layer of stainless steel from -1 m^2 of surface to provide an effective radioactive decontamination.
- Nitric-acid-only solutions under similar test conditions provide inferior performance unacceptable to the Waste Acceptance Preliminary Specifications.
- Contact times of 3 to 6 h at temperatures $>45^\circ\text{C}$ are adequate.

The optimum Ce(IV) concentration in HNO_3 was determined for the decontamination of the WW stainless steel canisters. Stainless steel corrosion rates were determined as a function of the initial Ce(IV) concentration [0.0025 to 0.1 M Ce(IV)], the temperature (25°C to 78°C), and the time of contact (1 h to 12 h). The corrosion rates were determined by weight loss. The stainless steel surface-area-to-solution-volume was maintained at -4.9 m^2 (WW canister surface area) to 662 L of decontamination solution. The loss in weight increased with increasing temperature, time, and initial Ce(IV) concentration. The weight loss approaches the value expected from the theoretical Ce(IV)/Fe mole ratio of three with increasing contact time. This is based on the following reaction:

Tests were also conducted using contaminated coupons. Stainless steel coupons were installed on the outside of canisters being filled at PNL with radioactive glass. The coupons were then used to demonstrate the Ce(IV) decontamination method developed for use at WW. Various decontamination schemes

were applied, and the coupons were then reanalyzed to determine the decontamination factors (DFs) that resulted from the various decontamination methods.

The coupons were analyzed for their initial gamma activity. The activity for the twelve coupons varied from 10^7 to 10^{10} disintegrations per minute per 100 cm^2 of surface. Each specimen was then soaked in deionized water at 25°C for 1 min, air dried, weighed, and recounted. This was followed by a 2-min wash using a minimum volume of 0.5 M HNO_3 for 2 min at 50°C . Decontamination factors for the initial water soak ranged from 3 to 57. The average DF for the minimum treatment of H_2O and HNO_3 was 160. When four minimum treatment coupons were washed twice with a large volume of 0.5 M HNO_3 for 6 h at 65°C , the average DF was 8 for the first wash and <2 for the second wash. The average overall DF was 3140. When four minimum treatment coupons were washed twice with 0.007 moles of $\text{Ce(IV)}/100 \text{ cm}^2$ of surface, the DFs for the coupons averaged 30 for the first wash and 12 for the second wash. The average overall DF varied from 32,500 to 450,000. When two minimum treatment coupons were contacted once with 0.014 moles of $\text{Ce(IV)}/100 \text{ cm}^2$, the average DF was 416, with an overall DF of 40,000 (after including the water and acid treatments).

After the coupons were decontaminated, they were smeared to determine compliance with specifications. The results show that minimum treatment and 2 cycles of 0.5 M HNO_3 will not meet these specifications. When four coupons were treated once with 0.007 moles of $\text{Ce(IV)}/100 \text{ cm}^2$ to remove $\sim 1.5 \text{ }\mu\text{m}$ of surface, one coupon met the specifications. When they were treated twice with 0.007 moles of Ce(IV) to remove a total of $\sim 3 \text{ }\mu\text{m}$ of surface, all of the coupons met the specifications. When two coupons were treated once with 0.014 moles of Ce(IV) to remove $\sim 3 \text{ }\mu\text{m}$ of surface, both exceeded the specifications. Milling of the stainless steel (SS) surface of the canister with Ce(IV) is required to remove the contamination to a nonsmearable level. Nitric acid treatment alone will not meet the Waste Acceptance Preliminary Specifications (DOE 1987).

A scanning electron microscope was used to determine the extent of corrosion and etching of the SS coupons as a function of Ce(IV) dissolution of the surface layer. The photomicrographs show that intergranular attack is not extensive with a Ce(IV) milling or penetration of $<6 \text{ }\mu\text{m}$. Preliminary

examination suggests that as much grain and intergranular change takes place on the surface of the SS during vitrification heating as during the Ce(IV) removal of a 1.5- to 3- μm layer of oxide film. A more complete analysis will require metallurgical cross sections to determine depth and form of attack.

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1.0 INTRODUCTION

The reference process for vitrification of the West Valley (WV) high-level waste involves the preparation of a borosilicate glass. The molten glass will be poured into large, stainless steel canisters. During the filling process, volatile compounds of fission products, principally ^{137}Cs , will condense on the exterior of the canister. After filling and cooling, the smearable contamination on the canisters must be removed from the exterior surfaces prior to storing and shipping to a repository.

1.1 REVIEW OF PREVIOUS STUDIES

West Valley had previously evaluated several decontamination approaches including electropolishing, liquid abrasive blast, high pressure water wash, ultrasonic cleaning, and redox solution treatment and had completed a conceptual design of the canister decontamination station. The Ce(IV)/HNO_3 redox solution treatment was chosen for evaluation in this conceptual design.

The conceptual design called for immersion of the glass-filled waste canisters in a cylindrical tank of 0.1 M $\text{Ce(NO}_3)_4$ solution containing 2 M HNO_3 located in the hot cell. After removing a microlayer of stainless steel, the canister would be water-washed and tested for allowable smearable contamination. The rinse water would circulate through an ion-exchange column (outside of the hot cell) and back into the tank to reduce the total waste volume. To maintain the Ce(IV) concentration, the cerium decontamination solution would recirculate at a rate equivalent to approximately 5 volume changes per hour through an electrochemical regenerator (also located outside of the hot cell). It was noted that the reactivity of the Ce(IV) decontamination solution was temperature dependent at 50 to 100°C and that excessive etching and pitting of the canister material could occur. Therefore, the decontamination concept was designed to operate at 25°C and a heat exchanger was provided.

The above approach would require several pumps and extensive shielding around the electrochemical regenerator, water ion-exchange unit, and heat exchanger (due mainly to the 662 keV gamma from ^{137}Cs). The 0.1 M Ce(IV)

solution would be used until the radiation levels interfered with contact maintenance and/or the impurities had a deleterious effect on the decontamination efficiency.

During the initial study, Pacific Northwest Laboratory (PNL) exposed two coupons by suspending them in the inside of a canister neck during a glass pour in the 324 Building B-Cell vitrification facility. The two coupons were recovered and evaluated for radionuclide content, activity level, smearable activity, and effectiveness of the Ce(IV)/HNO₃ oxidation for decontamination. Two decontamination tests were conducted for 1 h at room temperature. Coupon BNW-1 was immersed in a 0.1 M Ce(IV) + 2 M HNO₃ solution, and Coupon BNW-2 was immersed in a 2 M HNO₃ solution as a control. After the coupons were air dried, they were smeared with cotton swabs to determine removable contamination. Activity on the BNW-1 swab could not be detected on a survey meter; the BNW-2 swab read over 600 counts/min. The BNW-1 sample had a surface thickness reduction, and the color was the same as fresh metal. The BNW-2 sample had no surface reduction and retained the gold color from the high-temperature oxidation. The ¹³⁴⁻¹³⁷Cs decontamination factor (DF) for BNW-1 was reported to be 164 to 417 as compared to 18 for BNW-2.

Based on the above tests, it was determined that -1 μm of stainless steel (6.4 mg) was removed from the -10 cm² surface of BNW-1 with 800 mL of 0.1 M Ce(IV) solution, which was being continuously reoxidized during the 1 h decontamination. This is equivalent to using 0.08 moles of Ce(IV) to dissolve 1.15 x 10⁻⁴ moles of Fe [a 232-fold excess of Ce(IV) ion]. This is based on the following reaction:

The amount of metal requiring removal to effect decontamination by phosphate electropolishing has been reported to range from 5 to 50 μm (Larson 1984). However, this may not apply to the stainless steel canisters exposed to radioactive contamination for very short time periods during glass filling.

1.2 STUDY OBJECTIVES

The overall objectives of the current PNL Ce(IV) cask decontamination flowsheet study were 1) to review the initial studies outlined above; 2) to provide an effective flowsheet that can be developed into equipment needed to decontaminate the WV canisters down to the Waste Acceptance Preliminary Specifications (DOE 1987); 3) to determine if a throwaway (after each canister is decontaminated) decontamination solution flowsheet is viable versus use of a close-coupled electrochemical cell as in the initial WV study; and 4) to test the process using additional radioactive contaminated coupons.

2.0 EXPERIMENTAL

This section describes the nonradioactive and radioactive testing of stainless steel (SS) coupons to predict the optimum cerium (Ce) concentration required to decontaminate the WV canisters.

2.1 NONRADIOACTIVE TESTING OF STAINLESS STEEL COUPONS

A test plan was prepared describing the steps required to determine the optimum Ce concentration in HNO_3 for the decontamination of 304L SS canisters. The study examined SS corrosion rates as a function of Ce(IV) concentration [0.0025 to 0.1 M Ce(IV)], temperature (25 to 78°C), and time of contact (1 to 12 h). The coupon corrosion rates were determined by loss of weight. The ratio of solution volume to SS surface area was maintained at 4.9 m² of canister surface area to 662 L of decontamination solution. This was based on the assumptions shown below.

2.1.1 Assumptions

1. West Valley canisters - 61 cm in diameter x 300 cm long, 304L SS
2. dip tank - 76 cm in diameter, 457 cm long, liquid level at 335 cm after inserting canister
3. decontamination criteria - Waste Acceptance Preliminary Specifications (DOE 1987), #3.6 "Specification for Removable Radioactive Contamination on External Surfaces," 220 dpm alpha/100 cm² and 2200 dpm beta and gamma/100 cm²
4. canister surface area - 4.9 m²
5. decontamination solution required - 662 L.

2.1.2 Initial Test Conditions

The following test conditions were used:

1. temperature - 25, 45, 65, and 78°C
2. time of contact - 1, 2, 6, and 12 h
3. coupon surface - 8.94 cm²

4. volume of solution/surface area ratio - -13.6 mL/cm^2
5. volume of solution - 120 mL
6. oxidant concentrations - 0.0025 to 0.1 M Ce(IV)
7. corrosion rates determined by weight loss, $\pm 0.001 \text{ g}$ accuracy
8. stainless steel coupon size - 2.54 cm x 1.52 cm x 0.15 cm thick with 0.30-cm diameter hole for hanging
9. stainless steel coupon weight - -4.5 g
10. stainless steel coupon marking - each sample will be marked with an identification number.

2.1.3 Preparation of Ce(IV) Solutions

Cerium (IV) nitrate solutions can be prepared by the dissolution of commercially available CeO_2 in nitric acid. The solution can also be prepared by oxidizing cerous nitrate (Ce^{3+}) to ceric ion in the anode compartment of a separated electrochemical cell. For WW plant use, a 0.5 to 1 M Ce(IV) solution could be added to a dilute nitric acid solution to give the composition desired for in-cell use. For these tests, a 2 M HNO_3 solution containing 0.1 M $\text{Ce}(\text{NO}_3)_3$ stock solution was oxidized by the use of an electrochemical cell (Bray and Ryan 1982). The resulting solution had a solution potential of -1.66 V . This is equal to or greater than 95% Ce(IV). The stock solution was then used as-prepared or after dilution with water.

2.1.4 Cerium Analytical Support

Two methods were found for the determination of the Ce(IV) concentration in process streams, in analytical samples, and to follow the oxidation/reduction process during decontamination. The first is a titration method using iron (II) and ferrous o-phenanthroline indicator. Pacific Northwest Laboratory has revised this method to use a potentiometric titration endpoint. This procedure provides an excellent analytical method for the initial stock solution. However, when SS (~18% Cr, 8% Ni) has been dissolved in the solution, the chromium (VI) produced during dissolution interferes with the titration.

To follow the oxidation/reduction process during decontamination, the solution potential can be determined. This second method can be used to follow the decontamination process in-cell, to determine the initial and terminal Ce(IV)/Ce(III) ratio, and to determine if a reductant such as NaNO_2 is required to be added to the spent decontamination solution before disposal (to prevent corrosion in plant piping systems). To determine the solution potential, a high-impedance digital volt meter was used in combination with two electrodes, a saturated calomel electrode, and a platinum metallic electrode.

2.1.5 Test Procedures

The general procedures used to determine the stainless steel corrosion rates are outlined below.

1. Add 480 mL of oxidant solution to a temperature-controlled beaker containing a magnetic stir bar. Bring to a specified temperature, $\pm 2^\circ\text{C}$ accuracy.
2. Place four (4) weighed, measured, and marked coupons on hangers in the test solution.
3. Remove one (1) coupon at the end of each specified time interval. Remove 120 mL of test solution with each coupon and place in a marked bottle. Wash the coupon with water and air dry.
4. Reweigh the coupon.
5. Determine the solution potential at 25°C for each sample.
6. Place coupons in marked bottles. Send selected samples to the laboratory for corrosion evaluation (pitting corrosion and excessive etching) by use of the scanning electron microscope (SEM).

2.2 TESTING OF RADIOACTIVE CONTAMINATED SS COUPONS

Radioactive contaminated SS coupons were obtained during actual high-level waste processing campaigns involving the Radioactive Liquid-Fed Ceramic Melter (RLFCM). Pacific Northwest Laboratory has operated the RLFCM since October 1984, when it became the first pilot-scale liquid-fed ceramic melter (LFCM) in the world to process radioactive liquid waste. Coupons were obtained during

canister production on behalf of the Federal Republic of Germany (FRG) during fiscal year 1987. The FRG work encompassed the immobilization of some 5.5 M curies of ^{137}Cs and another 3.9 M curies of ^{90}Sr , while producing over 5,000 kg of glass product. During the FRG canister-filling campaign, SS coupons were installed on both vertical and horizontal exterior surfaces of certain canisters. The purpose of the coupons was to provide samples from which information could be obtained on the extent and characteristics of canister contamination acquired during filling.

Initial coupons were removed from the canisters before being placed in the turntable to determine the contribution of airborne cell contamination to the total accumulation on the canisters. The remaining coupons were inserted with the canisters into the sealed turntable enclosure, which was vented to the off-gas system during pouring. After the canisters were filled and removed from the turntable, the coupons were removed and placed into bottles.

Following analysis of the coupons for quantities and characteristics of the contamination, a program was initiated on behalf of WW to evaluate the effectiveness of a Ce(IV)/HNO_3 solution as a canister decontamination agent. The contaminated coupons from the B-Cell RLFCM operations provided the opportunity to evaluate the effectiveness of the process under radioactive conditions.

2.2.1 Radioactive Coupon Testing Procedures

The general procedure is shown below.

1. The contaminated coupons were transported to the analytical hot cells from the RLFCM hot cells.
2. Each coupon was transferred into a clean marked bottle.
3. The coupons were gamma counted for ^{137}Cs .
4. The coupons were removed from the sample bottles and immersed in 10 mL of distilled H_2O for 1 min at 25°C .
5. The coupons were air dried, weighed on a 5-place balance, and placed in clean bottles for recounting. Several of the coupons were wiped with swabs to determine smearable contamination.
6. The swabs were counted by gamma energy analysis.

7. The water samples (10 mL) were analyzed for ^{90}Sr , gamma energy analysis, ^{99}Tc , alpha (Pu, Am, Cm). Technetium values were found to be less than background and were discontinued.
8. The H_2O -cleaned coupons were counted for ^{137}Cs and then returned for additional decontamination.
9. Two of the H_2O -washed coupons were uniquely treated: a) Sample 7-371 was contacted with 120 mL of 0.5 M HNO_3 containing 0.005 M Ce(IV) for 3 h at 65°C ; b) Sample 7-304 was contacted with 120 mL of 0.5 M HNO_3 for 3 h at 65°C .
10. Both coupons were dried, smeared for contamination, counted, and reweighed.
11. The aqueous solutions were analyzed as above (7).
12. All of the coupons were immersed in 10 mL of 0.5 M HNO_3 for 2 min at 50°C . The coupons were dried, smearable contamination was determined by swab smears, and the coupons were again counted for ^{137}Cs .
13. The acid samples were analyzed as above (7).

After completion of the above procedures for the RLFCM program, the partially decontaminated coupons were available for additional studies on behalf of WV. Selected samples were treated with 0.5 M HNO_3 or acid containing Ce(IV) . These studies were completed to determine the optimum conditions required to meet the Waste Acceptance Preliminary Specifications.

3.0 RESULTS

A test program designed to provide the experimental data needed to support the selection of an effective flowsheet for the decontamination of WW vitrification canisters has been divided into 3 parts: 1) nonradioactive testing of coupons to determine the effect of temperature, time, and Ce(IV) concentration on the dissolution of stainless steel, 2) testing of radioactive coupons to determine the effectiveness of the selected flowsheet, and 3) corrosion analysis of SS coupons.

3.1 NONRADIOACTIVE TESTING OF STAINLESS STEEL COUPONS

Nonradioactive SS coupons were contacted with Ce(IV) in dilute HNO_3 . Loss of weight was determined as a function of cerium concentration, temperature, and time. The results show that using 0.005 M Ce(IV) + 0.5 M HNO_3 for 3 h at 65°C , $-1.5\text{ }\mu\text{m}$ of the 8.94 cm^2 surface will be dissolved. Three moles of Ce(IV) are required to oxidize one mole of iron to Fe(III). The SS dissolution rate increases by a factor of ~ 2.5 for every 10°C between 25 and 78°C . Coupons heated to 750°C for 1 h in air to produce an oxide coat were treated using 0.01 M Ce(IV) for 3 h at 65°C . The oxide coat was completely removed and dissolution rates were found to be identical to coupons that had not been heat-treated prior to cerium decontamination.

An important finding of this investigation is that the decontamination solution can be adjusted [3 moles of Ce(IV) per mole of iron] to remove only the thickness of SS required for decontamination. By controlling the Ce (IV) concentration, no excessive corrosion can destroy the canister if the canister remains in the solution for an extended time or at elevated temperatures.

A Ce(IV) decontamination process for WW has been designed based on the above results, using 662 L of very dilute Ce(IV) in 0.5 M HNO_3 . The actual amount of cerium to be used will be based on additional radioactive testing. The minimum amount of HNO_3 required has not been determined. The decontamination solution will be placed in a titanium tank. After decontamination of the canister, the solution will be placed in a second holding tank for sampling and possible reduction of remaining Ce(IV) or Cr(VI) with NaNO_2 . The canister will

then be water-washed and inspected for waste acceptance. The water will be added to the cerium decontamination waste, and the waste will be returned to the vitrification process. The results are given below.

3.1.1 Details of Experimental Results

The laboratory corrosion tests were performed using a temperature range from 25 to 78°C, at contact times from 1 to 12 h. The test coupons were weighed before and after contact with 0.0025 M Ce(IV) to 0.11 M Ce(IV) nitrate solution. The results are shown in Table 1. The loss in weight increased with increasing temperature, time, and Ce(IV) concentration. Results for three concentrations of cerium, at four temperatures, and as a function of time, are shown in Figures 1 to 3. Previous initial tests that reported using a contaminated test coupon (BNW-1) were performed at 25°C for 1 h using 0.1 M Ce(IV). Figure 1 shows a weight loss of only 4 mg using similar conditions. This is equal to a 0.6-μm thick layer being removed from the SS surface, versus 1 μm found in the previous test.

When the results from Table 1 are plotted at 45°C (Figure 4) and at 65°C (Figure 5), as a function of cerium concentration, the weight loss approaches the theoretical Ce(IV)/Fe mole ratio of 3 with increasing temperature and contact time. A contact time of 3 h and 6 h at 45°C will consume 43% and 73% of the Ce(IV). At 65°C, a contact time of 3 h and 6 h will consume 68% and 82% of the available Ce(IV). When the 1 h results are plotted (Figure 6) as a function of temperature, the initial rate of dissolution can be approximated; the dissolution rate increases by a factor of 25 for every 10°C increase in temperature.

To follow the oxidation/reduction process during decontamination, the solution potential of the Ce(III)/(IV) couple can be determined using a standard saturated calomel electrode versus a platinum indicator electrode. The decrease in solution potential (V) during the dissolution of the SS coupons (Table 1) is shown in Figure 7. The initial value for a 5195% Ce(III)/Ce(IV) ratio was -1.42 V. As the Ce(IV) is consumed during the dissolution of SS to a final ratio of 9911% Ce(III)/Ce(IV), the voltage drops to <1.25 V. This should provide an excellent indication of the progress during plant operation.

TABLE 1. Results of Ce(IV) Contact with Stainless Steel

Conditions: 120 mL of solution, 0.0025 to 0.1 M Ce(IV) in 0.5 to 2 M HNO₃
 Coupon Surface, 8.94 cm²
 2.54 x 1.52 x 0.15 cm
 44 g 304L SS
 Loss of 333 mg = 50 μm = 2 mil

Temp., °C	Contact Time, h	Loss of Weight, mg					
		0.115 M Ce	0.057 M Ce	0.028 M Ce	0.01 M Ce	0.0025 M Ce	
25	1	3.85	1.89	0.5	--	--	
	3	13.75	7.1	3.0	--	--	
	6	34.6	15.4	6.4	--	--	
	12	88.4	36.8	15.9	--	--	
45	1	19.2	11.7	4.4	2.6	1.5	
	3	76.9	39.7	16.9	10.8	3.2	
	6	152.2	77.1	36.4	14.6	5.2	
	12	220.2	100.2	49.3	19.3	5.1	
65	1	101.5	41.0	15.4	7.1	2.9	
	3	139.8	113.0	44.0	9.4	4.0	
	6	228.0	100.0	54.7	17.0	4.6	
	12	276.7	100.0	54.1	26.0	4.7	
78	1	112.6	49.7	27.5	--	--	
	3	211.1	86.9	43.9	--	--	
	6	265.9	112.9	48.0	--	--	
	12	280.0	122.0	65.8	--	--	

Disposal of spent Ce(IV) solutions may cause corrosion to the downstream SS system. Therefore, it is recommended that a reductant such as NaNO₂ be added to the decontamination solution to reduce the cerium to (III) as follows:

However, since the Ce(IV) is nearly consumed during decontamination, this step may not be required on a routine basis.

FIGURE 1. Dissolution of Stainless Steel Using $\sim 0.1 \text{ M Ce(IV)}$

FIGURE 2 Dissolution of Stainless Steel Using $\sim 0.05 \text{ M Ce(IV)}$

3.2 RADIOACTIVE COUPON TESTING

Examination of 12 radioactive contaminated SS coupons (8.94 cm^2) contacted with H_2O , HNO_3 , and solutions containing Ce(IV) was performed. Coupons washed with a minimum treatment consisting of H_2O followed by 0.5 M HNO_3 , and those

FIGURE 3 Dissolution of Stainless Steel Using ~0.025 M Ce(IV)

washed for 3 to 6 h with 0.5 M HNO₃ at 65°C failed to meet the Waste Acceptance Preliminary Specifications of 2200 disintegrations per minute (dpm) gamma/100 cm² of surface. Coupons treated with two cycles of 0.005 M Ce(IV) or one cycle of 0.01 M Ce(IV) met or exceeded the specifications. These observations, in conjunction with the SS dissolution studies discussed previously, indicate that a 1.5- to 3-μm layer of SS was removed to meet these specifications [0.65 to 1.4 moles Ce(IV) per m²].

FIGURE 4. Effect of Cerium Concentration on the Dissolution of Stainless Steel, 45°C

The radioactive contaminated coupons were obtained during actual high-level waste processing involving the RLFCM. The coupons were made available to WV to test the effectiveness of Ce(IV) as a canister decontamination agent. The ^{137}Cs contamination condition of the original coupons, the initial H_2O and HNO_3 washes, and the Ce(IV) results performed during this study are reported below. The results are described in Tables 2, 3, and 4 and show 1) the ^{137}Cs counting data for the coupons as received and after attempts to reduce the

FIGURE 5. Effect of Cerium Concentration on the Dissolution of Stainless Steel, 65°C

contamination level using H₂O, HNO₃ and Ce(IV) solutions; 2) the analysis of the aqueous wash solutions to determine alpha, beta, and gamma levels of contamination removed from the coupon surface; and 3) the ¹³⁷Cs counting data of the smears used to determine if the coupons met the Waste Acceptance Preliminary Specifications after attempts to decontaminate their surfaces.

FIGURE 6. Loss of Weight During the First Hour as a Function of Temperature

FIGURE 7. Change in Solution Potential During the Dissolution of Stainless Steel

TABLE 2. ^{137}Cs Decontamination - Coupon Counting Data

All counting data reported as ^{137}Cs dls/min/100 cm^2 surface (DF listed in brackets)

Coupon ID	Initial Counts	After H_2O (a)	After 0.5 M HNO_3 Wash (b,e)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (b)	After 0.5 M HNO_3 Wash (c)	After 0.5 M HNO_3 Wash (d)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (d,e)	After 0.5 M HNO_3 Wash (d)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (d)	After 0.5 M HNO_3 + 0.01 M Ce(IV) Wash (d,f)	Total DF
Minimum Treatment											
7-265	3.5E7	4.7E ⁺ (7)	--	--	5.3E5 (9)	--	--	--	--	--	66
7-324	4.1E8	2.6E ⁺ (1E)	--	--	4.5E6 (6)	--	--	--	--	--	91
2-Cycles 0.5 M HNO_3											
7-303	4.5E9	2.7E8 (17)	--	--	5.8E7 (5)	6.5E6 (9)	--	3.6E6 (2)	--	--	1,250
7-304	1.8E10	4.8E8 (38)	1.0E7 (5)	--	8.9E6 (1)	5.1E6 (2)	--	--	--	--	3,530
7-367	6.4E9	2.1E8 (30)	--	--	1.8E7 (12)	1.8E6 (10)	--	1.0E6 (2)	--	--	6,400
7-370	2.9E9	1.6E8 (18)	--	--	2.7E7 (6)	3.1E6 (9)	--	2.1E6 (1)	--	--	1,380
2-Cycles 0.005 M Ce(IV)											
7-305	1.2E10	2.1E8 (57)	--	--	4.3E7 (5)	--	2.8E6 (15)	--	2.0E5 (14)	--	60,000
7-325	5.8E8	1.2E8 (5)	--	--	5.5E7 (2)	--	<2.0E5 (>270)	--	<1.3E3 (154)	--	450,000
7-368	2.5E9	1.2E8 (21)	--	--	1.3E7 (9)	--	7.0E5 (19)	--	7.7E4 (9)	--	32,500
7-371	2.5E9	3.2E8 (8)	--	5.7E6 (56)	1.6E6 (4)	--	2.5E4 (64)	--	--	--	100,000
1-Cycle .01 M Ce(IV)											
7-306	.9E9	1.8E8 (38)	--	--	3.3E7 (5)	--	--	--	--	9.1E4 (363)	75,600
7-419	.8E7	5.1E6 (3)	--	--	1.6E6 (3)	--	--	--	--	<3.4E3 (470)	>4,800

(a) 1.1 mL/ cm^2 surface for 1 min at 25°C.
 (b) 13.4 mL/ cm^2 surface for 3 h at 65°C.
 (c) 1.1 mL/ cm^2 surface for 2 min at 50°C.
 (d) 13.4 mL/ cm^2 surface for 6 h at 65°C.
 (e) 0.007 moles Ce(IV) /100 cm^2 .
 (f) 0.014 moles Ce(IV) /100 cm^2 .

TABLE 3. Solution Analysis After Decontamination of Test Coupons.
Results reported as dis/min/100 cm² surface.

Coupon ID	Initial Coupon ¹³⁷ Cs	Wash Conditions	Wash Solution Analyses					
			²³⁹⁻²⁴⁰ Pu	²⁴¹ Am	²³⁸ Pu	²⁴⁴ Cm	⁹⁰ Sr	¹³⁷ Cs
<u>Minimum Treatment</u>								
7-265	3.5E7	H ₂ O ^(a)	45		324	218	6.3E5	2.8E7
		HNO ₃ ^(c)	201		1029	436	2.2E5	4.3E6
7-324	4.1E8	H ₂ O ^(a)	694		3020	1074	2.8E6	3.1E8
		HNO ₃ ^(c)	1902		8277	2573	1.6E6	2.1E7
<u>2-Cycles 0.5 M HNO₃</u>								
7-303	4.5E9	H ₂ O ^(a)	67		626	235	1.4E6	3.6E9
		HNO ₃ ^(c)	268		917	257	7.6E5	2.2E8
		0.5 M HNO ₃ ^(d)	268		537	134	BD	5.2E7
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	2.1E6
7-304	1.8E10	H ₂ O ^(a)	123		1074	492	1.4E6	1.7E10
		0.5 M HNO ₃ ^(b)	408		1080	408	1.0E6	5.0E8
		HNO ₃ ^(c)	67		157	45	BD	7.1E5
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	2.9E6
7-367	6.4E9	H ₂ O ^(a)	11		224	134	5.0E5	5.5E9
		HNO ₃ ^(c)	56		660	347	3.5E5	1.3E8
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	1.6E7
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	6.6E5
7-370	2.9E9	H ₂ O ^(a)	34		200	90	1.1E6	2.5E9
		HNO ₃ ^(c)	100		447	157	1.5E5	1.4E8
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	2.4E7
		0.5 M HNO ₃ ^(d)	BD		BD	BD	BD	5.7E5
<u>2-Cycles 0.005 M Ce(IV)</u>								
7-305	1.2E10	H ₂ O ^(a)	324		3915	2349	1.0E7	1.1E10
		HNO ₃ ^(c)	503		3020	1342	3.4E6	1.8E8
		0.005 M Ce ^(d,e)	805		1880	805	BD	3.9E7
		0.005 M Ce ^(d,e)	BD		BD	BD	BD	3.4E6

TABLE 3. (contd)

Coupon ID	Initial Coupon ¹³⁷ Cs	Wash Conditions	Wash Solution Analyses					
			²³⁹⁻²⁴⁰ Pu	²⁴¹ Am	²³⁸ Pu	²⁴⁴ Cm	⁹⁰ Sr	¹³⁷ Cs
7-325	5.8E8	H ₂ O ^(a)	229		2125	1079	1.9E7	1.9E8
		HNO ₃ ^(c)	716		5481	3685	1.8E7	7.3E7
		0.005 <u>M</u> Ce ^(d,e)	7790		3.0E4	1.1E4	4.8E7	5.5E7
		0.005 <u>M</u> Ce ^(d,e)	BD		BD	BD	BD	2.3E4
7-368	2.5E9	H ₂ O ^(a)	56		436	123	2.1E6	2.3E9
		HNO ₃ ^(c)	224		973	291	6.4E5	1.1E8
		0.005 <u>M</u> Ce ^(d,e)	BD		BD	BD	BD	1.2E7
		0.005 <u>M</u> Ce ^(d,e)	BD		BD	BD	BD	8.3E5
7-371	2.5E9	H ₂ O ^(a)	386		5593	3860	3.6E7	2.1E9
		0.005 <u>M</u> Ce ^(b,e)	4900		2.6E4	1.2E4	2.7E7	3.3E8
		HNO ₃ ^(c)	22		45	BD	BD	1.8E5
		0.005 <u>M</u> Ce ^(d,e)	BD		BD	BD	BD	1.1E6
<u>1 Cycle 0.01 <u>M</u> Ce(IV)</u>								
7-306	6.9E9	H ₂ O ^(a)	45		447	290	9.4E5	6.1E9
		HNO ₃ ^(c)	56		313	123	3.5E5	1.5E8
		0.01 <u>M</u> Ce ^(d,f)	6442		1074	BD	BD	3.8E7
7-419	1.6E7	H ₂ O ^(a)	34		106	56	4.8E5	7.4E6
		HNO ₃ ^(c)	134		761	291	4.5E5	3.6E6
		0.01 <u>M</u> Ce ^(d,f)	5369		1342	BD	BD	1.5E6

- (a) 1.1 mL/cm² surface for 1 min at 25°C.
 (b) 13.4 mL/cm² surface for 3 h at 65°C.
 (c) 1.1 mL/cm² surface for 2 min at 50°C.
 (d) 13.4 mL/cm² surface for 6 h at 65°C.
 (e) 0.007 moles $\text{Ce}(\text{IV})/100 \text{ cm}^2$.
 (f) 0.014 moles $\text{Ce}(\text{IV})/100 \text{ cm}^2$.

BD = Below Detection Limit

TABLE 4. Sample Coupon Smear Counting Data

Results reported as ^{137}Cs dis/min/100 cm^2 surface									
Coupon ID	After H_2O Wash (a)	After 0.5 M HNO_3 Wash (b)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (c)	After 0.5 M HNO_3 Wash (d)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (e)	After 0.5 M HNO_3 Wash (f)	After 0.5 M HNO_3 + 0.005 M Ce(IV) Wash (g)	After 0.5 M HNO_3 + 0.01 M Ce(IV) Wash (h)	After 0.5 M HNO_3 + 0.01 M Ce(IV) Wash (i)
Minimum Treatment									
7-265	4.3E4	--	--	5.7E3	--	--	--	--	--
7-324	3.5E5	--	--	2.6E6	--	--	--	--	--
2 Cycles 0.5 M HNO_3									
7-303	2.6E6	--	--	1.0E10	6.3E4	--	--	--	--
7-304	ND	1.2E5	--	1.5E5	4.6E4	--	--	--	--
7-367	ND	--	--	1.1E5	1.7E4	--	--	--	--
7-370	1.8E6	--	--	3.0E5	1.9E4	--	--	--	--
2 Cycles 0.005 M Ce(IV)									
7-305	ND	--	--	3.9E5	--	9.7E4	4.3E3	--	--
7-325	ND	--	--	3.1E5	--	1.2E2***	1.2E3***	--	--
7-368	3.1E6	--	--	1.0E5	--	8.2E3	1.1E3***	--	--
7-371	ND	--	8.3E3	4.7E3	--	2.2E2***	--	--	--
1 Cycle 0.01 M Ce(IV)									
7-306	2.7E6	--	--	2.2E5	--	--	--	1.1E3***	--
7-419	ND	--	--	2.5E4	--	--	--	1.8E2***	--

(a) 1.1 mL/ cm^2 surface for 1 min at 25°C.
 (b) 13.4 mL/ cm^2 surface for 3 h at 65°C.
 (c) 1.1 mL/ cm^2 surface for 2 min at 30°C.
 (d) 13.4 mL/ cm^2 surface for 6 h at 65°C.
 (e) 0.007 moles Ce(IV) /100 cm^2 .
 (f) 0.014 moles Ce(IV) /100 cm^2 .

*** Meets Waste Acceptance Preliminary Specifications of 2200 dpm gamma/100 cm^2 surface.

ND = Not Determined
 -- = Not Applicable

3.2.1 Coupon Results

Counting data for ^{137}Cs were obtained for coupons prior to and just after being immersed in solution. Samples were counted on both sides and corrections were made for gamma penetration of the metal. Nearly all of the contamination was observed on the outward or exposed coupon surface. The results were adjusted to 100 cm^2 of surface area. The twelve initial coupons varied from 10^7 to 10^{10} dpm ^{137}Cs per 100 cm^2 of surface area. The DF for a 1 minute H_2O wash of each of the twelve coupons varied from 3 to 57, using 1.1 mL of $\text{H}_2\text{O}/\text{cm}^2$ at 25°C , for an average H_2O DF of 22. Ten of the samples were then immersed in 1.1 mL of $0.5\text{ M HNO}_3/\text{cm}^2$ at 50°C for 2 min. The average DF for 0.5 M HNO_3 was 6.

After the initial H_2O wash, two of the coupons (7-304 and 7-371) were treated for 3 h at 65°C with a volume of solution ($13.4\text{ mL}/\text{cm}^2$) equivalent to that required for the WV canisters. Coupon 7-304 was treated with 0.5 M HNO_3 while Coupon 7-371 was treated with $0.005\text{ M Ce(IV)}/0.5\text{ M HNO}_3$. Coupon 7-304 (dipped in HNO_3) did not change in weight. Coupon 7-371 [dipped in Ce(IV) solution] lost $-77\text{ mg}/100\text{ cm}^2$, equivalent to $-1\text{ }\mu\text{m}$ of surface removal. The ^{137}Cs DF for the acid-treated coupon (7-304) was 5, while that for the Ce(IV) treated coupon (7-371) was 56. The counting data for Coupon 7-371 indicated that the remaining contamination was only on one face. During inspection of the coupon, it was determined that the contamination was contained in one raised dot on the coupon and an $\sim 30\times$ picture (Figure 8) was taken of the contaminated DOT (note the 0.12-in. diameter hole in the coupon for size comparison). To confirm the contamination, the coupon was placed on a sheet of photographic film for 3 h. After development of the film, the autoradiograph was visible and was enlarged for comparison with the initial photograph. The spot contamination was removed during the second contact using the same Ce(IV) conditions.

Table 2 presents counting data for four types of treatment: 1) minimum ($1.1\text{ mL}/\text{cm}^2$) using H_2O and 0.5 M HNO_3 ; 2) 2-cycles of 0.5 M HNO_3 ($13.4\text{ mL}/\text{cm}^2$); 3) 2 cycles of 0.005 M Ce [$0.007\text{ moles Ce(IV)}/100\text{ cm}^2$] in 0.5 M HNO_3 ; and 4) 1 cycle of 0.01 M Ce [$0.014\text{ moles Ce(IV)}/100\text{ cm}^2$]. The average DF for minimum treatment for the 12 coupons was 160. When four minimum decontaminated

FIGURE 8. Photograph and Autoradiograph of Coupon 7-371

coupons were washed twice with 0.5 M HNO_3 , the average ^{137}Cs DF was 8 for the first wash and <2 for the second wash. The average overall DF was 3140. When four minimum decontaminated coupons were washed twice with 0.007 moles of $\text{Ce(IV)}/100\text{ cm}^2$, the DF for the coupons averaged >30 for the first wash and 12 for the second wash. The average overall DF varied from 32,500 to 450,000. When two minimum decontaminated coupons were contacted once with 0.014 moles of $\text{Ce(IV)}/100\text{ cm}^2$, the average DF was 416, with an average overall DF of -40,000.

3.2.2 Solution Analysis

During decontamination treatment, the coupons were analyzed using gamma analysis. The resulting wash solutions were also monitored since the Waste Acceptance Preliminary Specifications for smear contamination includes alpha and beta limits. The results are shown in Table 3. As expected, the results show decreasing activity with subsequent wash steps. The alpha and ^{90}Sr beta values for both 0.5 M HNO_3 and Ce(IV) were below analytical detection limits after the initial contacts. This was not the case for cesium, which if deposited as water-soluble CsCl would have washed off with H_2O or HNO_3 . As can be shown in Table 2, the second 0.5 M HNO_3 wash for ^{137}Cs produced only a DF of <2. Milling the SS surface of the coupon with Ce(IV) is required to remove the cesium contamination to a nonsmearable level.

3.2.3 Coupon Smear Analysis

After the coupons were immersed in a decontamination solution, they were dried and counted for gamma activity. The samples were then smeared three times on each face with two swabs, one held on each face. The swabs were then placed in counting bottles and gamma counted for ^{137}Cs activity. The results are reported in Table 4 as dpm per 100 cm^2 of surface. The results show that minimum treatment and 2 cycles of 0.5 M HNO_3 will not meet the Waste Acceptance Preliminary Specifications. When four partially decontaminated ($\text{H}_2\text{O} + \text{HNO}_3$) coupons were treated once with 0.007 moles of $\text{Ce(IV)}/100\text{ cm}^2$, one coupon (7-325) met the specifications. When they were treated twice, all of the coupons met the specifications. When two coupons (7-306 and 7-419) were treated once with 0.014 moles of $\text{Ce(IV)}/100\text{ cm}^2$, both exceeded the specifications.

3.2.4 Ce(IV) Coupon Milling Results

Radioactive contaminated coupons treated with Ce(IV) solution lost 0.110 g of weight when contacted with 0.007 moles of Ce(IV)/100 cm² of surface. This is equivalent to a 1.5- μ m layer of SS removed from the coupon surface (74.5 mg/100 cm²/ μ m was assumed for this report). The samples treated once with 0.01 M Ce(IV)/0.5 M HNO₃ [0.014 moles Ce(IV)] lost an average of 0.223 g of weight/100 cm² or -3 μ m of surface milling.

3.3 CORROSION AND ETCHING ANALYSIS OF STAINLESS STEEL COUPONS

Selected 304L SS coupons (Table 2) were used to determine the extent of corrosion and etching with Ce(IV) attack. The samples were subjected to Ce(IV) solutions with varying concentrations, temperatures, and contact times. Loss of weight for each coupon was determined. The weight loss was equated to surface milling which is reported as micrometers (μ m) of surface thickness dissolved. Scanning electron microscope photomicrographs (350X) show that intergranular attack will become more pronounced and slight pitting will occur on the grain surface with increased dissolution (Figure 9). Below 6 μ m, the surface of the coupons are similar to the standard untreated coupon. Between 6 and 13 μ m, more extensive intergranular attack occurs. At 17 μ m, the large individual grains still have portions of the original surface visible. Visually, without the use of the SEM, the coupon surface at 42 μ m appears dark brown with a mottled matte finish. A more complete analysis of all of the coupons using metallurgical cross sections is required to determine depth and form of attack.

3.3.1 SEM Examination of West Valley Canister Material

During the filling of canisters with radioactive glass at WV, the SS will be heated and an oxide layer will develop which may interfere with the removal of the radioactive contamination. Three samples of SS were provided by WV for examination; two had been cut from a canister (3 ft 6 in. from canister bottom) after it was filled with nonradioactive glass; a third (archive) sample was obtained to determine the SS surface structure prior to heating or fabrication. The SEM examination of the archive sample plate #27B is shown in Figure 10. The large sections, C27-A and B, were reduced to 4.5 cm x 4.5 cm coupons for

304L SS Standard (350X)

0.44 μm (2.9 mg)

FIGURE 9. SEM Examination of 304L Stainless Steel After Ce(IV) Contact

1.1 μm (7.1 mg)

2.3 μm (15.4 mg)

FIGURE 9. (contd)

13.3 μm (88.4 mg)

17.0 μm (113.0 mg)

FIGURE 9. (contd)

3.9 μm (26.0 mg)

6.2 μm (41.0 mg)

FIGURE 9. (contd)

41.5 μm (276.7 mg)

FIGURE 9. (contd)

examination followed by Ce(IV) milling. The exposed edges and the inside wall surface of the canister samples were covered with removable silicone rubber so that an accurate weight loss of the exposed surface could be determined. Samples C27-A and B were soaked in 300 mL of 0.005 M Ce(IV)/0.5 M HNO₃ for 6 h at 65°C. The initial oxidized surface (20.25 cm²) was removed (-1 to 1.4 μm). The original oxide layer appeared to remain attached to the surface of the coupons until they were washed off with a jet of water. The total weight loss after the samples were contacted for a second time corresponded to a total surface loss of -2.5 μm .

Photomicrographs of the archive (10 gauge) plate, the C27-A and B coupons "as-received" from WV after glass filling, and the coupons after the first and second Ce(IV) milling, are shown in Figures 10 through 16. The surface of the archive sample (Figure 10) appears to be similar to that used in the PNL study (Figure 9). However, the grain structure appears to have changed during vitrification heating of the canister wall (Figures 11 and 14). The grains and

FIGURE 10. SEM Examination of Archive Sample #27B (SA-240, 304L, 10 Gauge, HT#215606)

FIGURE 11. SEM Examination of West Valley Sample C27-A (canister wall after filling with glass)

200X

500X

FIGURE 12. Sample C27-A After First Milling, 1.0 μm

FIGURE 13. Sample C27-A After Second Milling, 2.4 μm

FIGURE 14. SEM Examination of West Valley Sample C27-B (canister wall after filling with glass)

FIGURE 15. Sample C27-B After First Milling, 1.4 μm

FIGURE 16. Sample C27-B After Second Milling, 2.6 μm

intergranular areas appear to be filled with a precipitate. When the C27 oxide-coated coupons were contacted with Ce(IV), the grains and grain boundaries appear to be cleaned (Figures 12, 13, 15, and 16).

Although the SEM results are a preliminary examination to determine the effect of Ce(IV) decontamination on 304L SS, it appears that as much grain and intergranular change takes place on the surface of the SS during vitrification heating, as during the Ce(IV) removal of a -1.5- to 3- μ m layer of oxide film. Complete analysis will require metallurgical cross sections to determine depth and form of attack.

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