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DECONTAMINATION OF TRU CONTAMINATED METALS

MASTER

Hanford Engineering Development Laboratory

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1.0 INTRODUCTION

This report summarizes laboratory work performed at the Hanford Engineering Development Laboratory (HEDL) on a study to evaluate the feasibility of a chemical etching system for decontamination of metals and metal equipment.

Failed metal equipment constitutes a large volume of radioactively contaminated waste. The ability to remove the contamination from the surfaces of metal equipment could greatly reduce the costs associated with disposal as well as the volume of waste requiring disposal.

A variety of cleaning solutions has been investigated for use in decontaminating equipment used in the nuclear industry. These have included solutions of permanganate, oxalic acid, detergents, and inhibited mineral acids, as well as very corrosive materials such as sulfuric, phosphoric, and hydrochloric acids. All of these agents work to various degrees and can be used to decontaminate equipment. Electropolishing in phosphoric acid electrolyte is being investigated as a method to decontaminate equipment.(1) The electropolishing process is very effective as a decontamination technique since it dissolves a surface layer of the metal and thus removes the surface contamination. The electropolishing process has the disadvantage that it produces a large volume of salt waste.

Corrosion of stainless steel and other metals in nitric acid can be accelerated by the presence of certain inorganic reduction-oxidation (redox) systems (i.e., systems which contain elements which can exist in two or more oxidation states). Earlier work(2) had shown that cerium(IV) in nitric acid effectively dissolved the outer surface of stainless steel objects. The rate of attack is quite rapid and is dependent upon effective regeneration of the cerium(IV). Regeneration can be effectively accomplished electrolytically.

The decontamination process being investigated at HEDL involves the dissolution of a surface layer of the metal to achieve decontamination. In the initial part of the study, dissolution of the metal surface by use of a nitric acid solution of cerium(IV) is being investigated. Cerium(IV), a strong oxidizing agent, oxidizes the metal causing it to dissolve into the nitric acid solution. The reaction reduces cerium(IV) to cerium(III); the cerium(III) is oxidized back to cerium(IV) electrolytically.

2.0 SUMMARY AND CONCLUSIONS

A laboratory study has been conducted to evaluate a metal decontamination process proposed by HEDL. The proposed process uses a nitric acid solution of a redox agent to etch or dissolve the surface layer of the contaminated metal and thereby remove the contamination. The oxidizing species is regenerated electrolytically.

Based upon the results obtained in this study it is concluded that a metal decontamination process based upon removal of contamination by treatment with a cerium(IV)-nitric acid solution (or other redox agent in nitric acid) is feasible and highly promising. This conclusion is based on the following considerations:

- The technique is effective in dissolving the surface layer of stainless steel. Dissolution rates of approximately 1.5 mils/hr have been demonstrated with cerium(IV)-nitric acid solutions.
- Removal of plutonium contamination from stainless steel has been demonstrated in laboratory tests with cerium(IV)-nitric acid solutions. In tests with plutonium contaminated metal specimens, activity levels were reduced from greater than 5×10^5 counts per minute to nondetectable levels in approximately one hour when treated with cerium(IV)-nitric acid solutions at 90°C.
- Removal of paint from stainless steel surfaces has been demonstrated with cerium(IV)-nitric acid solutions.
- Materials of construction are available for a cerium(IV)-nitric acid decontamination facility.
- This type of decontamination process has the following potential advantages over chemical solutions currently being used or tested:
    1) Nitric acid solutions are widely used throughout the nuclear industry and as such their properties are well known and understood. This should facilitate regeneration of the decontamination solution (e.g., by removal of plutonium and/or other contaminants by standard chemical separations techniques used routinely in the nuclear industry), and/or disposal of the solution following its use as a decontamination agent.

2) Cerium(IV) in nitric acid is a good dissolution agent for plutonium oxide(3-6) and could possibly be used for removal or recovery of plutonium from equipment highly contaminated with plutonium. Other redox systems in nitric acid might also be applicable to dissolution of PuO_2.

3) The systems proposed are not high salt systems; therefore, there is potentially less waste generated by this process than most others.

4) The decontamination is not sensitive to relative distance from an electrode as an electropolishing process is. Thus, the process should be more effective for irregularly shaped equipment than processes which are sensitive to the location of the cathode.

5) The process does not require immersion of the equipment being decontaminated, i.e., it could be effective as a spray or a flow-through system.

3.0 RESULTS AND DISCUSSION

3.1 Dissolution Rates

The dissolution rate of stainless steel in a nitric acid solution of the redox agent was considered to be one of the key factors in determining the potential success of this concept as a decontamination process. In their electropolishing work, PNL has reported that the removal of two mils of metal surface is normally sufficient to achieve decontamination(1). In the HEDL tests, penetration rates of approximately 1.5 mils/hr were demonstrated on stainless steel using cerium(IV)-nitric acid solutions having the following characteristics: 0.1-0.2 M Ce(IV), 2 to 4 M nitric acid and a temperature of 90°C.

Initially, a two-level factorial set of experiments was conducted to examine the effects of cerium concentration, the cerium(IV) to total cerium ratio, nitric acid concentration, and temperature. Stainless steel washers were used as the test specimens. The results of one-hour tests, listed in Table 1, showed that cerium concentration and temperature had the largest effect on dissolution rate. The dissolution rate increased with an increase in each of these parameters; however, nitric acid concentration in the range of 1-7M did not affect the dissolution rate significantly. (Later data at nitric acid concentrations as high as 13M confirmed this.)

Additional dissolution data showing the effects of ceric ion concentration and temperature are shown in Figures 1 and 2. The results show that penetration rates of approximately 1.5 mils/hr are achieved at 90°C with 0.2M Ce(IV). Dissolution data at various nitric acid concentrations are plotted in Figure 3 and show that nitric acid concentration has very little effect on the dissolution rate.

Although the nitric acid concentration did not effect the dissolution rate, it did affect the roughness of the resulting metal surface. At lower nitric acid concentrations the final metal surface is smoother.

TABLE 1

DISSOLUTION RATE OF STAINLESS STEEL IN CERIUM-NITRIC ACID SOLUTION

Run No.	Cerium Total, M	Ce^{+4}/Ce Total	HNO_3, M	Temp, °C	Weight Loss, Mgs(a)	Penetration Rate, mils/hr(b)
1	0.01	0.80	7	20	0.0	0.0
2	0.01	0.80	1	20	0.0	0.0
3	0.01	1.00	7	20	0.7	0.007
4	0.01	0.80	1	90	2.7	0.03
5	0.05	0.90	4	55	8.7	0.09
6	0.10	0.80	7	90	50.9	0.52
7	0.10	0.80	7	20	1.0	0.01
8	0.10	1.00	7	20	2.1	0.02
9	0.10	1.00	7	90	5.9	0.06
10	0.05	0.90	4	55	8.1	0.08
11	0.10	1.00	1	20	1.1	0.01
12	0.10	0.80	1	20	0.9	0.01
13	0.01	1.00	1	20	0.0	0.00
14	0.01	0.80	7	90	4.7	0.05
15	0.05	0.90	4	55	9.2	0.09
16	0.10	1.00	7	90	60.7	0.62
17	0.10	1.00	1	90	57.8	0.59
18	0.10	0.80	1	90	56.8	0.58
19	0.01	1.00	1	90	5.3	0.05
20	0.05	0.90	4	55	8.5	0.09

(a) After one hour of dissolution.

(b) Assuming constant surface area during dissolution.

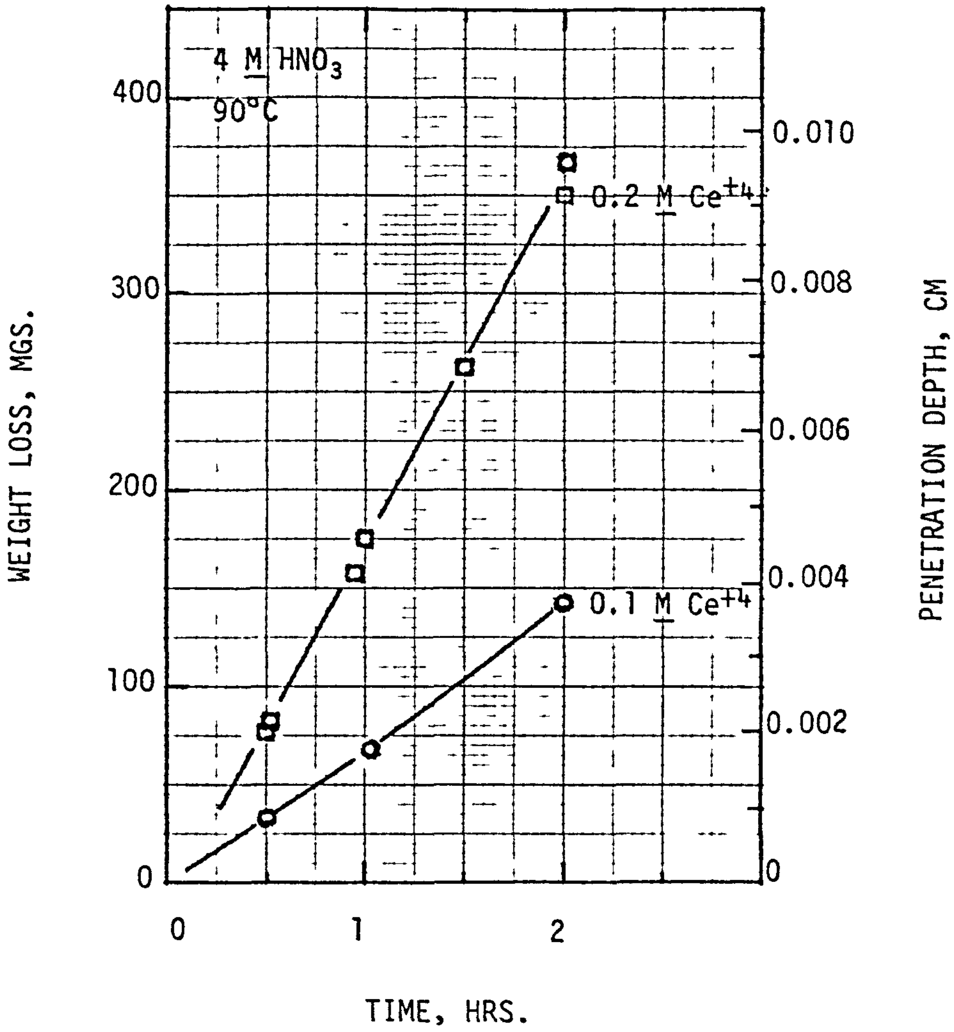


Figure 1: Dissolution of Stainless Steel in Cerium(IV) Solution. The Effect of Cerium(IV) Concentration.

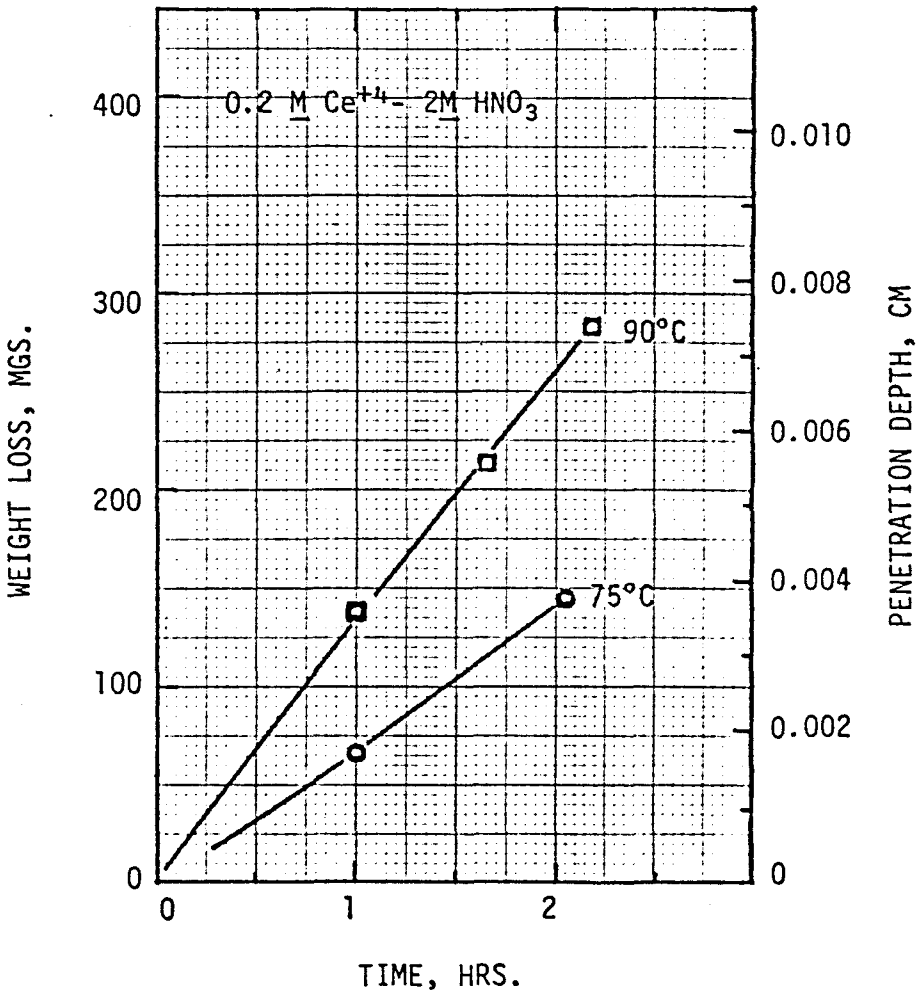


Figure 2: Dissolution of Stainless Steel in Cerium(IV) Solution. The Effect of Temperature.

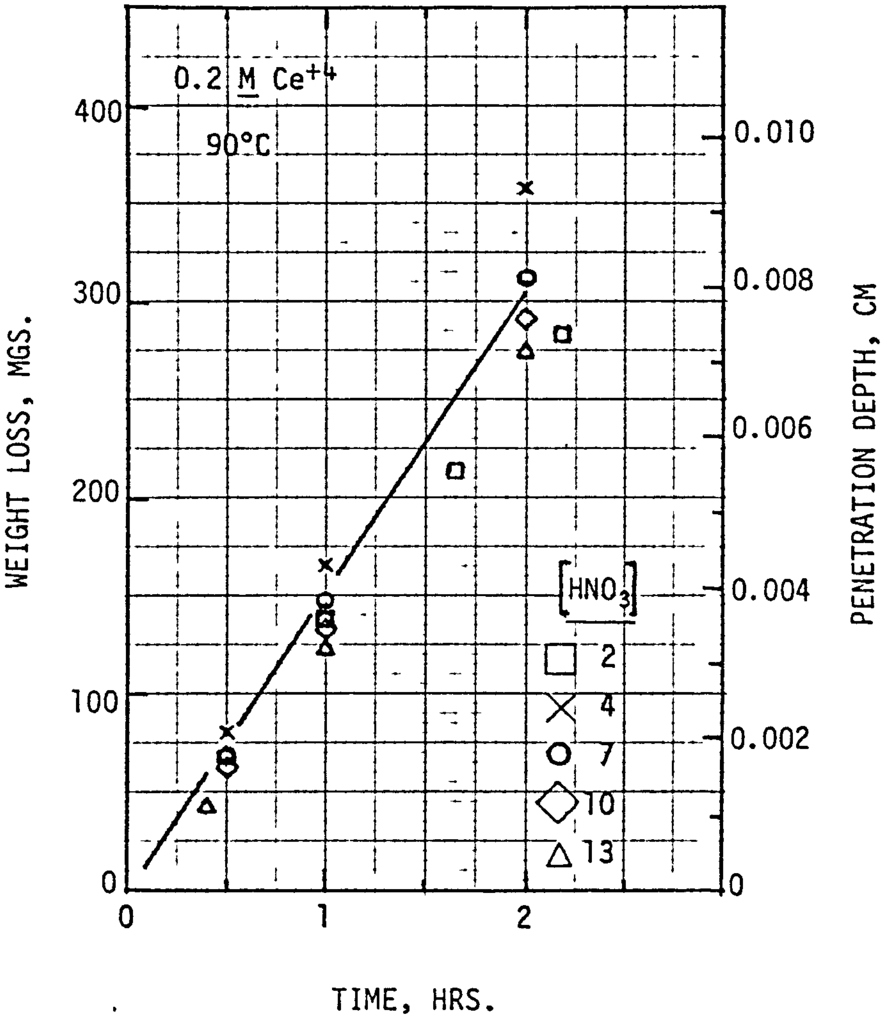


Figure 3: Dissolution of Stainless Steel in Cerium(IV) Solutions at Various Nitric Acid Concentrations

3.2 Paint Removal

Laboratory tests demonstrated that cerium(IV)-nitric acid solutions would also remove paint from stainless steel surfaces, thereby exposing the surface to further decontamination processing. Thus, a painted piece of equipment could be decontaminated with a cerium(IV) solution without first going through a separate pre-treatment operation to remove the paint. Or a treatment with a cerium(IV) solution to remove the paint could precede another decontamination process.

Tests were performed using two highly chemically resistant paints (Amercoat-33® and Amercoat-52®) and an alkyd enamel paint. The results are shown in Table 2. The rate of removal of the paint increased with increasing nitric acid concentration, although only removal of the Amercoat-33 was significantly improved in going above 7M in nitric acid concentration. Other tests demonstrated that the rate of paint removal increased with increasing cerium(IV) concentration and temperature, the same process parameters that cause an increase in metal dissolution rate.

Once the paint has been penetrated in a few places by the solution it is loosened from the metal surface and tends to come off as a film of paint. However, the solution continues to dissolve the film as the organic part of the paint is oxidized by the cerium(IV)-nitric acid solution.

TABLE 2

REMOVAL OF PAINT BY CERIUM(IV)-NITRIC ACID SOLUTIONS

Test Solution: 0.2 M Ce(IV) - HNO_3

Temperature: 90°C

	Time to Remove Paint From Washer			
Paint	4 M HNO_3	7 M HNO_3	10 M HNO_3	13 M HNO_3
Glidden Alkyd Enamel	49 min	12 min	17 min	11 min
Amercoat 33	225	85	< 59	12
Amercoat 52	48	7	19	9

3.3 Decontamination of Stainless Steel

Tests with plutonium contaminated stainless steel specimens have demonstrated the feasibility of using a cerium(IV)-nitric acid solution to decontaminate metal equipment. Alpha activity levels greater than 5×10^5 counts per minute on stainless steel washers were reduced to background levels using approximately one-hour treatments in cerium(IV)-nitric acid solutions.

Figure 4 shows decontamination results at two cerium(IV) concentrations and two nitric acid concentrations. There are two important aspects of these results that should be noted. First, the alpha activities were successfully reduced to non-detectable levels; and second, the activity levels decreased as a function of time in a nearly straight line manner (when plotted on a semi-log graph as in Figure 4). This means that the metal can be totally decontaminated in reasonable time periods.

Figure 5 shows the results from a test in which a plutonium contaminated washer was first treated with 2 $\underline{M}$ nitric acid at 90°C (that is, with no cerium in the solution). The nitric acid had reduced the activity level by only about one order of magnitude after 90 minutes and the rate of decrease in activity level was very low during the final 15 minutes of treatment. The washer was then placed in a 0.1 $\underline{M}$ Ce(IV)-2 $\underline{M}$ HNO_3 solution and the activity level dropped 3 orders of magnitude in the first 15 minutes and there was no detectable activity after 45 minutes of treatment in the cerium(IV) solution. Decontamination results are also shown in Figure 5 for a second washer which had been contaminated in a manner identical to that of the first washer. This second washer was treated only with the cerium(IV)-nitric acid solution which removed the contamination to non-detectable levels in 45 minutes. These results clearly demonstrate the effectiveness of the cerium(IV) in achieving decontamination of the stainless steel specimens.

A decontamination test with a stainless steel bolt and two nuts demonstrated the ability to decontaminate non-smooth surfaces such as bolt threads with a cerium(IV)-nitric acid solution. A 1" x 1/4" stainless steel bolt and two nuts, each having alpha contamination levels of $\geq 5 \times 10^5$ counts per minute, were treated in a 0.2 $\underline{M}$ cerium(IV)-4 $\underline{M}$ nitric acid solution. After one hour the activity level on each of the nuts had been reduced to background and after 75 minutes the activity on the bolt had been reduced to that level. Figure 6 shows the bolt and nuts after the decontamination test.

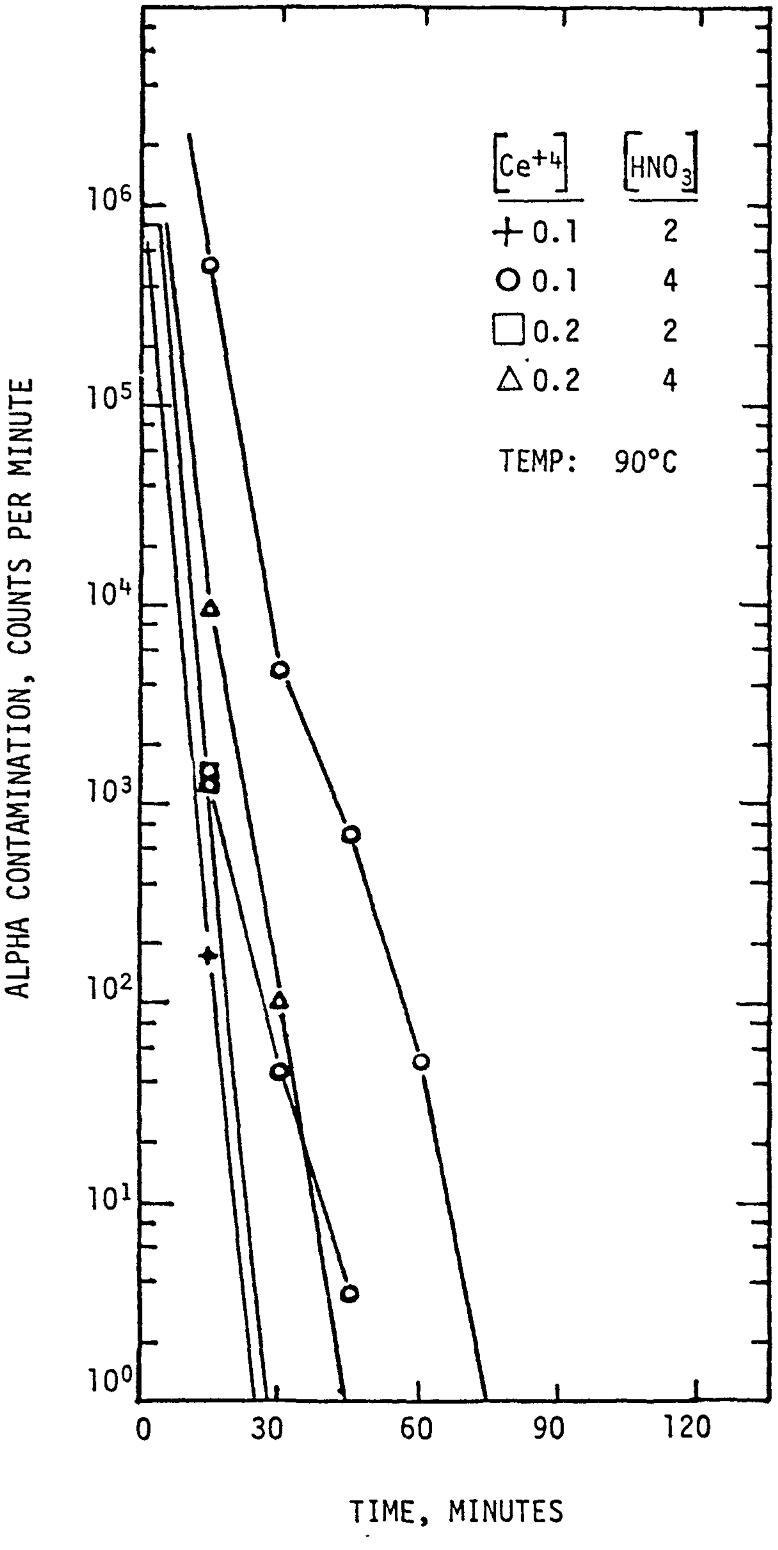


Figure 4: Decontamination of Plutonium Contaminated Stainless Steel With Cerium(IV) Solutions.

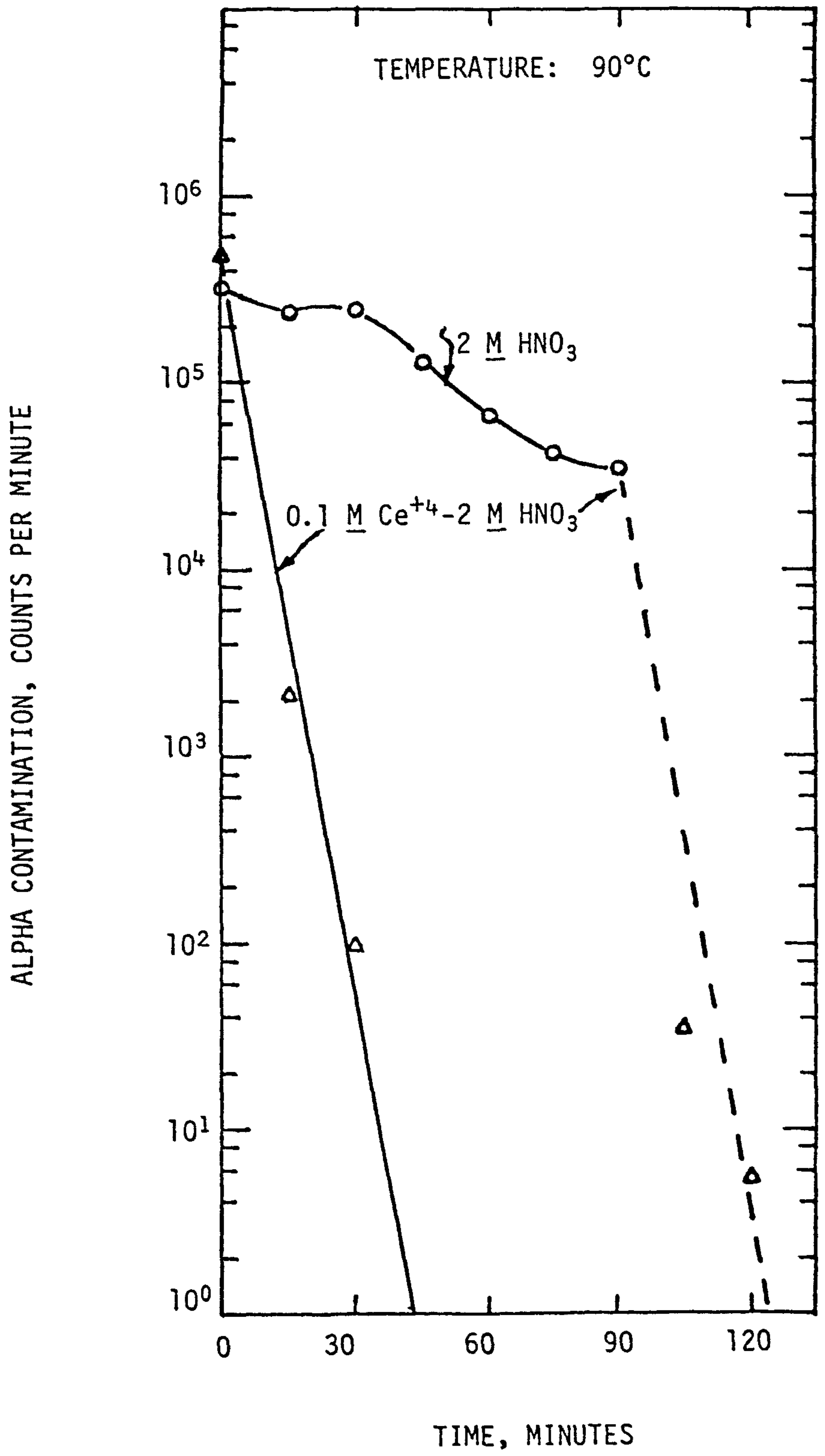


Figure 5: Decontamination of Two Stainless Steel Specimens.

TEST CONDITIONS

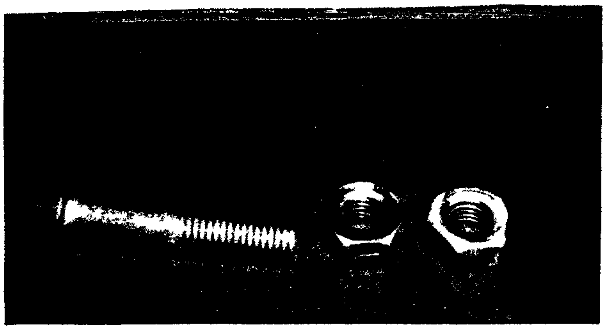
Solution: $0.2\underline{M}$ Ce(IV)-$4\underline{M}$ HNO_3

Temperature: 90°C

Treatment Time: Nuts, 60 minutes
Bolt, 75 minutes

Initial Contamination: $\geq 5 \times 10^5$ counts/min

Final Contamination: Background



Stainless Steel Bolt and Nuts
After Decontamination Test.

Figure 6: Decontamination Test With A Stainless Steel Bolt and Nuts

3.4 Materials of Construction

Scouting tests with materials specimens have shown some metals as well as plastics which are resistant to corrosion or attack by cerium(IV)-nitric acid solutions at elevated temperatures and thus would be suitable as materials of construction for a decontamination facility.

Tantalum, titanium, Zircaloy-2, and Zircaloy-4 are all very resistant to corrosion in cerium(IV)-nitric acid solutions. Corrosion tests run for 140 hours in 0.2 M Ce(IV)-4 M HNO_3 at 90°C indicate upper limits on the corrosion rates of 1×10^{-7}, 1×10^{-6}, 3×10^{-7}, and 7×10^{-7} cm/day for tantalum, titanium, Zircaloy-2, and Zircaloy-4, respectively.

Tests have been run on the attack of ceric-nitric acid solutions on various plastic coupons. In general, the fluoroplastics are the most resistant to attack by the solutions, with FEP (Fluorinated ethylene propylene), TFE (polytetrafluorethylene), and MFP-10 (fluoroethene) showing no attack after approximately 70 hours in 0.2 M Ce(IV)-4 M HNO_3 at 90°C. Several kinds of plastics did show attack as evidenced by physical deterioration and/or weight loss of the test specimen. The order of increasing weight loss was Lexan® < Kynar® < polyethylene < polypropylene < polyimide ∿ Hypalon.

4.0 AREAS REQUIRING FURTHER RESEARCH AND DEVELOPMENT

The following have been identified as areas of additional work for development of a metal decontamination process based upon use of a redox agent in nitric acid:

- Cell design for electrolytic regeneration of cerium(IV).
- Effect of metal contaminants in the cerium(IV) decontamination solution.
- In-situ decontamination.
- Effectiveness of other redox agents as decontamination agents.
- Clean-up and regeneration of the decontamination solution.
- Scale-up of the process to enable treatment of large pieces of equipment.
- Waste treatment.
- Materials of construction
- Equipment design for a full-scale facility.
- Plutonium recovery from the decontamination solution.

A program incorporating these factors has been formulated and proposed.

5.0 REFERENCES

1. R. P. Allen, H. W. Arrowsmith, L. A. Charlot, and J. L. Hooper, Electropolishing As A Decontamination Process: Progress and Applications, USDOE Report PNL-SA-6858, Pacific Northwest Laboratory, Richland, WA, April 1978.

2. R. E. Lerch, Corrosion of Stainless Steel in Solutions of Cerium(IV)-Nitric Acid, USAEC Report BNWL-CC-1646, Pacific Northwest Laboratory, Richland, WA, May 1968.

3. A. S. Wilson, "Method of Dissolving Plutonium Dioxide in Nitric Acid Using Cerium Ions," U.S. Patent 3,005,662 (Oct. 24, 1961).

4. A. L. Uriarte and R. H. Rainey, Dissolution of High-Density UO_2, PuO_2, and UO_2-PuO_2 Pellets in Inorganic Acids, USAEC Report ORNL-3695, Oak Ridge National Laboratory, Oak Ridge, TN, April 1965.

5. H. D. Harmon, Dissolution of PuO_2 with Cerium(IV) and Fluoride Promoters, USERDA Report DP-1371, Savannah River Laboratory, Aiken, SC, October 1975.

6. D. E. Horner, D. J. Crouse, and J. C. Mailen, Cerium-Promoted Dissolution of PuO_2 and PuO_2-UO_2 in Nitric Acid, USERDA Report ORNL/TM-4716, Oak Ridge, TN, August 1977