CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0548431 1

ORNL-TM-6

COPY NO. - 13

DATE - Sept. 20, 1961

R-10,735

DECONTAMINATION STUDIES

P. S. Lawson

ABSTRACT

The decontamination of mild steel, stainless steel, and aluminum from cerium, europium, americium, ruthenium, cesium, and iodine was studied in several possible decontamination reagents. Several of the contaminants were deposited from helium gas at elevated temperatures. Iodine was one of the nuclides most difficult to decontaminate completely. It is suggested that the pretreatment of metals with small amounts of cold iodine prior to exposure to radioactive iodine may be of value in decreasing residual activity.

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

RELEASE APPROVED
BY PATENT BRANCH
10-2-61 SMR.
DATE SIGNATURE

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

1.0 INTRODUCTION

This work was concerned with the decontaminability of various individual isotopes from carbon steel, 347 and 302 stainless steels, and aluminum. Initially, it consisted of a series of screening tests to aid in selecting a solution which would best remove contaminating species from the EGCR service machine and other components of gas-cooled reactors. Later, however, as it became evident that certain elements, notably iodine, were not adequately decontaminated by the test solutions, more elaborate procedures were tried in an attempt to demonstrate essentially complete decontamination. Part of the work was also devoted to determining the feasibility of producing isotopic transport and contamination from heated helium gas, under conditions simulating those in the EGCR.

2.0 GENERAL DECONTAMINABILITY TESTS

A series of tests was made using various isotopes in which pre-contaminated aluminum, carbon steel, and stainless steel samples were contacted at 95°C for 20 min with each of the following solutions:

(A) 0.3 M H_2SO_4-0.1 M $H_2C_2O_4$-1/2 g/liter 1-phenyl-2-thiourea,

(B) 1 M HNO_3,

(C) 1 M HNO_3-0.1 M NaF,

(D) 1 M HNO_3-0.1 M NaF-1 M H_2O_2

(E) 0.3 M ammonium oxalate-0.1 M ammonium citrate-0.1 M oxalic acid, and

(F) solution E with 0.35 M H_2O_2.

This particular procedure of the 20-min contact at 95°C was adopted because considerable previous work had been done in this manner and a relation between the results obtained with the above solutions and those with other isotopes and other solutions was considered desirable. This technique has one minor drawback, however, in that it tells nothing about the removal of the last few percent of the activity. This information is important in the case of iodine, for example, in which 85-90% of the activity is quite easily removed while the last 10-15% adheres very tenaciously to

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0548431 1

the metal; and, consequently, a solution which appeared most favorable in the 20-min test could possibly fail to decontaminate as completely as one which worked more slowly initially. Except in rare, anomalous cases such as this, however, the tests probably give good indications of the difficulties to be expected with the various isotopes. Samples of the results obtained from these tests are shown in Table 1.

2.1 Cerium and Europium

Cerium and europium were selected for the tests in order to obtain some index of rare earth behavior in decontamination. Cerium which had been plated on the samples from alkaline solution and baked under helium at 100°C appears to decontaminate almost completely with most solutions tested. Europium, however, which had been similarly plated, decontaminated poorly, giving decontamination factors of between 10 and 100 with final activities averaging on the order of 10^4 c/m/cm^2. Both elements appear to be decontaminated well by the H_2SO_4-$H_2C_2O_4$-phenylthiourea solution which gave D.F.'s of the order 2×10^3 for cerium and 100 for europium. These results were only slightly better, however, than those obtained with the oxalate-acetate solutions both with and without peroxide. Differences between the D.F.'s obtained for the various types of metals do not appear to be very great. Generally, they were slightly higher for aluminum and lower for carbon steel with the two stainless steels intermediate. This generalization does not hold, however, when corrosion is appreciable as was the case with the HNO_3-NaF solutions on aluminum. The reason for the tenacity of europium is not known; however, it does appear out of character with the other family members since cerium decontaminated well, and previous work with yttrium and praseodymium indicates that they decontaminate well.

2.2 Americium

Americium was the only actinide subjected to the test series; and, consequently, it is not known to what extent its decontaminability is indicative of that of the other family members. The samples were prepared in a somewhat unconventional manner in that they were contaminated by boiling in americium nitrate-nitric acid solution and then water washed until all smearable activity was removed. Only type 347 stainless

steel samples were used. Decontamination was excellent with all solutions tested; indeed, final activities were so low that reliable D.F.'s could not be calculated. The HNO_3-NaF solution gave significantly better results than did the other five solutions; however, all except the 1 M HNO_3 reduced the alpha activity to less than 50 c/m/in.^{2}

Assuming other actinides behave as well, their decontamination should pose no great problem.

2.3 Ruthenium

Ruthenium is normally considered as one of the more difficult fission products to decontaminate. It is a member of the relatively unreactive platinum family and has several valence states. Tests with samples on which ruthenium-106 in the +3 state had been plated from alkaline solution and baked on at 100°C under helium gave D.F.'s of less than 100 with final activities of usually greater than 10^4 c/m/cm^2. Decontamination factors for samples which had not been baked were usually slightly higher. The best results were obtained with the HNO_3-NaF-H_2O_2 solution, and it is believed that this was due primarily to the oxidizing power of the acidic peroxide rather than to corrosivity since the more corrosive HNO_3-NaF solution gave lower D.F.'s. The second best results were obtained with the oxalate-peroxide-citrate solution, which probably acted in the same manner, but to a lesser extent because its peroxide concentration was lower (1 M H_2O_2 vs. 0.35 M). With ruthenium as with the rare earths, the results do not differ appreciably between the metals being decontaminated.

2.4 Cesium

Due to the high reactivity of cesium as an alkali metal, it would not be expected that its decontaminability would present a major problem, and previous work by the group with drop plated samples bears this out. However, at the request of others who reported difficulty in decontaminating cesium deposited from the gas phase, scouting work was undertaken to determine whether it would decontaminate

with facility. Elemental Cs-137 was plated on 347 stainless steel by first vaporizing from a fused cesium chloride-calcium residue at 750°C under helium and then passing the Cs° laden helium through a tightly wound helix of the steel at room temperature. Activities of the order of 10^6 c/m/cm^2 were obtained by the vaporization of 10 millicuries of Cs-137. Twenty-minute decontamination tests with the oxalate-citrate-peroxide solution and a similar solution of oxalate-acetate-peroxide reduced this to about 10^3 c/m/cm^2, giving D.F.'s of the order 10^3. These results are good; however, they do not indicate whether complete activity removal could be easily accomplished. Due to insufficient time this was not demonstrated; however, it would probably be wise to do so.

3.0 TELLURIUM-IODINE PLATING STUDIES

An experiment was carried out to determine the nature and extent of tellurium and iodine plateout under conditions simulating those in the EGCR. Tellurium dioxide (138 mg) was irradiated in the ORR for 24 hr to form 10 millicuries of Te-125 plus other Te isotopes and iodine-131. It was then allowed to cool for three days to permit the decay of short-lived products. The quartz ampule containing the product was broken open in a dry box and about half of the material was transferred to a tube furnace where it was vaporized at 900°C under helium. The Te-I laden helium was then passed over stainless steel, carbon steel, and aluminum samples which had been placed downstream in a thermal gradient ranging from 900 down to 50°C. Iodine deposition was heavy, especially on those samples which had been held at about 100°C. Tellurium activity was so low as to be almost completely obscured by the high I-131 activity. Gamma scans indicated, however, that its plateout is maximum at about 500°C and decreases slowly with decreasing temperature. Considerable iodine activity was found in the 200-600°C range, and it is not known to what extent this was due to primary plateout and to what extent to the decay of plated tellurium.

These results indicate that the problem of iodine contamination on EGCR associated materials will be augmented by the decay of tellurium plated at high temperatures, in addition to the deposition of iodine at lower temperatures.

3.1 Iodine Decontamination Studies

Samples onto which elemental iodine-131 had been plated in a manner similar to that described above were submitted to the series of 20-min 95°C tests. The iodine appears to decontaminate with facility to the extent of about 90% (i.e., down to activity levels of about 10^3 c/m/cm^2). The remaining activity, however, appears to be in the form of a tightly compounded layer which is extremely difficult to remove.

Once it had been determined that this lower level activity presented the major problem, several experiments were undertaken in an attempt to effect complete decontamination. The 20-min 95°C tests were repeated, using more exotic solutions such as 5% H_2O_2-5% NH_4OH, 2% $KMnO_4$-5% NaOH, 0.4 M chromous sulfate, 0.1 M sodium azide in sodium sulfite, and oxalate-peroxide-acetate. Of these solutions, however, only the chromous sulfate reduced the activity substantially. Corrosivity of the chromous-sulfate on mild steel and solution instability probably make it impractical for large scale use. Attempts were also made to remove the activity by isotopic exchange with cold iodine, both as the elemental form in various organic solvents and as the iodide in acidic media. The interchange was very poor, however, and activities were never reduced to below 5×10^3 c/m/cm^2.

It was eventually found that moderate success could be attained either with Turco 4501-A, a strongly alkaline chelating agent, or the above described oxalate-citrate-peroxide solution when contacted for an extended period of time. The former solution reduced the activity to less than 500 c/m/cm^2 on steel samples which had been contacted for 20 min with the refluxing solution. A concentration of KOH equivalent to that in the Turco was at least equally effective. The oxalate-peroxide-citrate solution decontaminated aluminum samples essentially completely when contacted for 1 hr at 95°C. Experiments with steel samples and this solution, however, have not been extensive and the results are ambiguous. Steel does not appear to decontaminate as easily as the aluminum samples. Further work should be done to determine whether substantial D.F.'s may be obtained within reasonable periods of contact time with the steels.

4.0 CONCLUSIONS AND RECOMMENDATIONS

One of the major problems to be faced in connection with EGCR service machine decontamination is that of iodine which may well prove to be the bottle-neck in activity removal. Probably work along this line would be most profitable if devoted to the more thorough testing of the mildly corrosive standby reagents such as oxalate-citrate-peroxide and oxalate-acetate-peroxide to determine the time requirements for essentially complete decontamination. The continued testing of the more exotic reagents would probably not be worthwhile, at least as far as the EGCR work is concerned, for these are selected on the basis of their reactivity with macro amounts of iodine, and this reactivity does not appear to carry over very well to micro quantities of tightly held I-131.

One idea which should be given some consideration is that of pre-contaminating the service machine with trace amounts of cold iodine from the gas phase. Since the iodine binds tightly and will not exchange isotopically, one could make the stable layer of cold iodine with the result that the radioactive species would contaminate only superficially; and, consequently, could be removed easily. It is important to guard against overdepositing, however, as the presence of macro quantities of iodine could lead to corrosion.

Further effort should be devoted to ruthenium and cesium as complete decontamination of these elements has not been demonstrated. This work would probably most profitably take the form of prolonged contact times with solutions giving moderate success in 20 min, such as the oxalate-citrate-peroxide. Also, similar experiments with actinides other than americium should be tried. Finally, it would be worthwhile in connection with the EGCR work to study mild steel contaminated with the anticipated mixed fission products under conditions similar to those expected in the EGCR, as it is possible that the interactions of the contaminating species will alter the decontaminabilities observed for individual isotopes.

Table 1. Illustrative D.F.'s and Final Activities Obtained with Six Test Solutions on Stainless Steel

Solution / Isotope	0.3 M H_2SO_4 0.1 M $H_2C_2O_4$ 1/2 g/liter phenyl-thiourea	1 M HNO_3	1 M HNO_3 0.1 M NaF	1 M HNO_3 0.1 M NaF 0.1 M H_2O_2	0.3 M $(NH_4)_2C_2O_4$ 0.1 M $(NH_4)_2HC_6H_5O_7$ 0.1 M $H_2C_2O_4$	0.3 M $(NH_4)_2C_2O_4$ 0.1 M $(NH_4)_2HC_6H_5O_7$ 0.1 M $H_2C_2O_4$ 0.35 M H_2O_2
Ce^{144}						
D.F.	~2,000	~2,000	~600	~750	~500	~750
Final Activity	100 c/m	~200 c/m	~125 c/m	~750 c/m	~60 c/m	$\sim 1.09 \times 10^3$
Eu^{152-4}						
D.F.	~90	~50	~90	~90	~40	~140
Final Acitivity	$\sim 4 \times 10^4$ c/m	$\sim 5 \times 10^4$	$\sim 5 \times 10^4$	$\sim 4 \times 10^5$	1×10^5	4×10^4
Am						
D.F.	35	23	635	127	48	80
Final Activity	30 c/m	85 c/m	2 c/m	13 c/m	30 c/m	25 c/m
Ru^{106}						
D.F.	~15	~10	~20	~200	~10	~50
Final Activity	$\sim 5 \times 10^4$	5×10^4	3×10^4	2×10^3	4×10^4	8×10^3
Cs^{137}						
D.F.	-	-	-	-	-	2×10^3
Final Activity	-	-	-	-	-	2×10^3 c/m
I^{131}						
D.F.	~10	~5	~5	~11	~4	~10
Final Activity	$\sim 4 \times 10^3$	1×10^3	-	2×10^3	2×10^3	1×10^3

ACKNOWLEDGEMENT

This work was sponsored by Oak Ridge National Laboratory, under agreement with the University of Tennessee as part of the student cooperative program. It was conducted in the Equipment Decontamination Group, Section A of the Chemical Technology Division.

DISTRIBUTION

1. M. Bender
2. R. E. Blanco
3. J. C. Bresee
4. K. B. Brown
5. F. L. Culler
6. D. E. Ferguson
7. H. E. Goeller
8. H. B. Graham
9. A. B. Meservey
10. D. H. Newman
11. M. W. Rosenthal
12. J. L. Scott
13. M. J. Skinner
14. M. E. Whatley
15. Lab Records-RC

EXTERNAL

16. W. L. Albrecht, TVA, AEC Bldg., Oak Ridge
17. P. S. Lawson, Box 304, Kingston, Tenn.
18. Dr. D. A. Shirley, Dept. of Chemistry
    University of Tennessee, Knoxville, Tenn.

19-33. DTIE