Copy 4A
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
DECLASSIFIED

AEC RESEARCH AND DEVELOPMENT REPORT

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360734 5

ORNL 1826
Chemistry-General

Inv. 59

DECONTAMINATION OF STAINLESS STEEL

D. O. Campbell

Classification Cancelled
By Authority Of AEC 11-12-59
Date 3-16-72

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.

CLASSIFICATION CANCELLED
ORNL DD 20140328
DD Signature Date
Single review of CCRP-declassified documents was authorized by DOE Office of Declassification memo of August 22, 1994.

DECLASSIFIED

ONAL LABORATORY
ATED BY
N CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

RESTRICTED DATA

[redacted]

Report Number: ORNL-[redacted]

This document consists of 47 pages. Number 4 of 173 copies. Series A.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

DECONTAMINATION OF STAINLESS STEEL

D. O. Campbell

DATE ISSUED:

FEB 17 1955

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of
UNION CARBIDE AND CARBON CORPORATION
Post Office Box P
Oak Ridge, Tennessee

[redacted]

3 4456 0360734 5

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-11. Laboratory Records Department
12. Laboratory Records, ORNL R.C.
13. C. E. Larson
14. L. B. Emlet (K-25)
15. J. P. Murray (Y-12)
16. A. M. Weinberg
17. E. H. Taylor
18. E. D. Shipley
19-20. F. L. Culler
21. F. C. VonderLage
22. W. H. Jordan
23. J. A. Swartout
24. C. P. Keim
25. J. H. Frye, Jr.
26. S. C. Lind
27. A. H. Snell
28. A. Hollaender
29. M. T. Kelley
30. K. Z. Morgan
31. T. A. Lincoln
32. R. S. Livingston
33. A. S. Householder
34. C. S. Harrill
35. C. E. Winters
36. D. W. Cardwell
37. E. M. King
38. W. K. Eister
39. F. R. Bruce
40. D. E. Ferguson
41. H. K. Jackson
42. H. E. Goeller
43. D. D. Cowen
44. R. A. Charpie
45. J. A. Lane
46. M. J. Skinner
47. R. E. Blanco
48. G. E. Boyd
49. R. B. Keely
50. W. R. Winsbro
51. D. O. Campbell
52. R. B. Lindauer
53. E. M. Shank
54. J. L. Matherne
55. W. H. Lewis
56. S. E. Beall
57. P. M. Reyling
58-59. ORNL Document Reference Library, Y-12 Branch

EXTERNAL DISTRIBUTION

60. AF Plant Representative, Wood-Ridge
61-68. Argonne National Laboratory
69. Armed Forces Special Weapons Project (Sandia)
70. Army Chemical Center
71. Arthur D. Little, Inc.
72-76. Atomic Energy Commission, Washington
77. Battelle Memorial Institute
78-79. Bettis Plant (WAPD)
80-81. Brookhaven National Laboratory
82-83. Carbide and Carbon Chemicals Company (C-31 Plant)
84-86. Carbide and Carbon Chemicals Company (K-25 Plant)
87. Chicago Patent Group
88. Chief of Naval Research
89. Columbia University (Hassialis)
90. Division of Raw Materials, Washington

[redacted]

91. Dow Chemical Company, Pittsburgh
92. Dow Chemical Company (Rocky Flats)
93-96. duPont Company, Augusta (1 copy to D. S. Webster)
97-99. General Electric Company (ANPD)
100-106. General Electric Company, Richland (1 copy to F. Woodfield)
107-108. Goodyear Atomic Corporation
109. Hanford Operations Office
110. Iowa State College
111-114. Knolls Atomic Power Laboratory
115-116. Los Alamos Scientific Laboratory
117. Mallinckrodt Chemical Works
118. Materials Laboratory (WADC)
119-121. Mound Laboratory
122. National Advisory Committee for Aeronautics, Cleveland
123. National Bureau of Standards
124. National Lead Company, Inc. (Winchester)
125. National Lead Company of Ohio
126. Naval Medical Research Institute
127. Naval Research Laboratory
128. New Brunswick Laboratory
129. New York Operations Office
130-131. North American Aviation, Inc.
132. Nuclear Metals, Inc.
133. Patent Branch, Washington
134-138. Phillips Petroleum Company (NRTS) (1 copy to D. G. Reid)
139. Pratt & Whitney Aircraft Division (Fox Project)
140. Public Health Service
141. Rohm and Haas Company
142. Sandia Corporation
143. Sylvania Electric Products, Inc.
144. Tennessee Valley Authority (Walthall)
145. USAF Project Rand
146. U.S. Naval Radiological Defense Laboratory
147. USNA Medical Research Laboratory
148-149. University of California Radiation Laboratory, Berkeley
150-151. University of California Radiation Laboratory, Livermore
152-153. University of Rochester
154. Virginia-Carolina Chemical Corporation
155. Vitro Engineering Division
156. Vitro Laboratories
157. Western Reserve University (Friedell)
158-172. Technical Information Service, Oak Ridge
173. Division of Research and Medicine, AEC, ORO

CONTENTS

		Page No.
1.0	ABSTRACT	1
2.0	INTRODUCTION	2
3.0	PROCEDURES	3
4.0	CONTAMINATION EXPERIMENTS	4
4.1	Fission Products Responsible for Contamination	5
4.2	Dependence of Contamination on Concentration	7
4.3	Effect of Addition of Stable Isotopes to the Contaminating Solution	10
5.0	DECONTAMINATION EXPERIMENTS	11
5.1	The 3-20 Reagent	12
5.2	Alkaline Tartrate-Peroxide	14
5.3	Nitric Acid	18
5.4	Oxalic Acid	20
5.5	Ultrasonic Radiation	22
6.0	APPENDIX	24
6.1	Decontamination with Noncorrosive Reagents	28
6.2	Decontamination with Corrosive Reagents	31
6.3	Removal of Surface	33
6.4	Plant Experience	35
6.5	References	38

[redacted]

TABLES

Page No.

1. Radiochemical Analyses of Contamination on Type 347 Stainless Steel 6

2. Effect of Contaminant Concentration in Solution on Contamination Level of Stainless Steel 8

FIGURES

1. Contamination of Type 347 Stainless Steel with Various Concentrations of Purex IAW Solution (HNO_3 = 2.2 M) According to Freundlich Isotherm 9

2. Rate of Decontamination of Type 347 Stainless Steel by Sodium Hydroxide and Alkaline Tartrate-Peroxide 15

3. Rate of Decontamination of Type 347 Stainless Steel by Alkaline Tartrate and Alkaline Tartrate-Peroxide following Initial Decontamination by Nitric Acid 17

4. Rate of Decontamination of Type 347 Stainless Steel by 16 M Nitric Acid 19

5. Rate of Decontamination of Type 347 Stainless Steel with 5% Oxalic Acid 21

[redacted]

1.0 ABSTRACT

The contamination on stainless steel exposed to Purex process solutions is predominantly niobium, which is also the most difficult contaminant to remove. Zirconium accounts for a few percent of the contamination, and other fission products are relatively unimportant. Contamination of stainless steel with various dilutions of Purex waste followed the Freundlich adsorption isotherm relation between the amount of radioactivity adsorbed and its concentration in the contaminating solution. The addition of a fluoride solution of stable niobium and zirconium to the contaminating solution decreased the gamma activity adsorption by decreasing that of niobium and zirconium. Ruthenium then became relatively important.

The most effective noncorrosive decontaminant was alkaline tartrate-peroxide. After the initial application of this reagent, its action was improved by a pretreatment of the contaminated surface with nitric acid. Several alternate treatments with nitric acid and alkaline tartrate-peroxide gave the best decontamination with negligible corrosion. The most effective decontaminant, 3% HF in 20% HNO_3, was severely corrosive to stainless steel. The rate of decontamination is reported for sodium hydroxide, alkaline tartrate, alkaline tartrate-peroxide, nitric acid, and oxalic acid. The reagents decontaminated rapidly at first, but the rate dropped to about 6% removal of activity per day after several days. High-intensity ultrasonic radiation increased the decontamination rate, but the problem of getting the radiation into large equipment would be formidable.

A survey of the literature on decontamination is given.

 [redacted]

2.0 INTRODUCTION

Radioactive contamination on stainless steel is due to fission products, either adsorbed on the surface or very close to the surface, and a large part of the contamination may be removed without much difficulty. Water washing, even after it has washed away the contaminating solutions, will slowly remove a few percent of the contamination. It appears, however, that water is much more effective for removing isotopes emitting beta radiation than those emitting gamma.

Decontamination methods usually involve one or more of the following: detergent cleaning, complexing of the contaminant, solution of the contaminant in strong acid, and surface removal by physical or chemical means. Since the last two methods may present corrosion problems, a corrosion study is a necessary corollary to a decontamination study. Such reagents as complexing agents and strong acids easily remove most of the contamination--90 percent or more. Removal of the remaining contamination becomes increasingly difficult; eventually rather violent means must be applied and, very often, they meet with relatively little success. It is important that initial decontamination behavior be considered independently of the very difficult subsequent decontamination observed when only a little contamination remains.

The studies reported here were restricted to type 347 stainless steel, the metal most commonly used in radiochemical processing equipment. The chemical system from which contamination was obtained was restricted to nitric acid solutions, such as are found in a Purex chemical plant.*

This report supersedes ORNL memo CF-54-3-171 (March 16, 1954), in which some of the data were originally published.

---

*Studies with a uranyl sulfate system are given in ORNL-1839 (report in preparation).

[redacted]

3.0 PROCEDURES

Type 347 stainless steel coupons, about 6 by 8 by 11 mm, were contaminated by hanging them with type 309 stainless steel wires, 3 mils in diameter, in 5 to 10 ml of the contaminating solution in a stoppered bottle for at least two days. They were decontaminated by suspending them in the decontaminating solution in open 100-ml beakers. The decontaminating solutions were agitated only very gently or not at all. In some cases, when the contaminated sample was to be dissolved so that the contaminating isotopes could be determined by standard radiochemical analysis, the samples were 1- or 3-mil-thick sheets, about 1 cm^2 in area, of type 347 stainless steel. All experiments were carried out at room temperature.

The contaminating solutions studied were aqueous raffinate (IAW) from the Purex process first cycle, obtained from the Pilot Plant in February, 1953, and a nitric acid solution of a 60-day-cooled Hanford slug, obtained in November, 1953, dissolved to form feed to the Purex process. Both were HNO_3 solutions of fission products. The Purex feed solution contained uranium and plutonium; the IAW did not.

The coupons were prepared for contamination usually by grinding with carborundum paper until a clean surface without pits was obtained. Such a surface is representative of the stainless steel used in process equipment. In some cases the coupons were polished to a mirror finish so that the amount and type of corrosion by the decontaminating reagents could be studied.

The level of activity on the contaminated samples was measured with one or more of the various survey instruments. For high contamination levels (initially most coupons read about 500 beta mr/hr and 100 gamma mr/hr at contact) a cutie-pie was used. Several thicknesses of aluminum foil were placed between the coupon and the cutie-pie for

measuring gamma contamination. For lower levels (less than 20 mr/hr) a Victoreen survey meter was used. Since most of the beta radiation was of very low energy (Nb^{95} and Zr^{95}), the gamma and beta readings were about the same with the Victoreen. The weak beta radiation did not penetrate the glass wall of the probe; it did, however, register on the cutie-pie.

As soon as the coupons were decontaminated to a sufficiently low level, they were counted in a Geiger counter with an end-window tube. A lead and aluminum absorber was placed between the coupon and the counter tube for gamma counts. With the best geometry that could be conveniently obtained, approximately 1100 gamma c/min corresponded to 1 mr/hr with the Victoreen meter. The use of the survey instruments does not contribute to precision in the results, although it more nearly duplicates field experience. However, this may be a serious source of error, and possibly may be diminished by using more accurate instruments. Probably a single instrument will not be satisfactory for the entire range of radiation levels obtained during decontamination of a coupon, from perhaps 1 r/hr to less than 0.01 mr/hr.

4.0 CONTAMINATION EXPERIMENTS

The two contaminating solutions (Purex aqueous raffinate and Hanford slug dissolver solution) gave essentially the same level of contamination on the coupons after the same cooling time. After three to five coupons had been contaminated in a solution, however, the contamination level for later coupons decreased. This seems to indicate that some fission product is adsorbed out of the solution on the first

few coupons contaminated, but, since the important contaminants were niobium and zirconium in all cases (see Sec. 4.1), this cannot be true. It is possible that some niobium hydrolysis product initially present in the solution was adsorbed more strongly than the rest of the niobium, but this explanation is tentative at best. No study was made of deposition or removal of uranium or plutonium in the studies with dissolver solution.

4.1 Fission Products Responsible for Contamination

Although material balances were not good, with the contaminating solutions used niobium and zirconium accounted for 75 to 95 percent of the radioactivity adsorbed by stainless steel (see Table 1 for representative values). Very often, other fission products contributed less than 1 percent. In some cases the beta and gamma analyses did not agree; however, 95 percent of the gamma activity due to niobium is probably a realistic figure. The niobium contribution to the beta activity varied downward from the values of 74 and 68 percent given in Table 1, presumably depending on the counting procedure used since niobium has a very low-energy beta activity. The zirconium contribution to gamma contamination was relatively small, varying from less than 1 percent in most cases to as much as 5 percent. Zirconium contribution to beta contamination was usually about five times as great as its gamma contribution, depending again on the counting methods used. Other isotopes contributed less than zirconium and, even after extensive decontamination, did not become important.

The radiochemical analyses leave much to be desired. Most of the decontaminating solutions contained complexing agents, and some also contained dissolved type 347 stainless steel, both of which may affect the accuracy of radiochemical determinations. It is clear that the

Table 1

Radiochemical Analyses of
Contamination on Type 347 Stainless Steel

Type 347 stainless steel coupons immersed in contaminating solution for two days at room temperature, and rinsed with water; fission products determined by standard radiochemical analysis

Contaminating Solution	Percentage of Gross Activity Due to Components									
	Niobium		Zirconium		Ruthenium		Rare Earths		Strontium	Cerium
	β	γ	β	γ	β	γ	β	γ	β	β
Purex dissolver solution	74	87	5.6	0.8	0.6	0.2	0.1	---	0.06	0.1
Purex IAW solution	68	93	15	1.6	---	1.0	---	1.0	---	---
Purex IAW solution	---	79	---	4.6	---	2.0	---	0.5	---	---
Purex IAW solution	---	95	---	4.7	0.3	---	---	0.05	---	0.5

contaminants of primary importance, certainly with respect to gamma activity, are niobium and zirconium, and that the niobium is more important. The problem of decontamination of stainless steel equipment used with Purex solutions, at least, is the removal of niobium.

Contamination and decontamination characteristics of ground and polished surfaces were indistinguishable.

4.2 Dependence of Contamination on Concentration

The levels of contamination on coupons suspended in various dilutions of the IAW solution were in agreement with the Freundlich adsorption isotherm relation between the contamination per unit area and the concentration of the contaminating substance in the solution. If several elements contribute significantly to the contamination, no simple relation should exist between the contamination level and the concentration of the contaminants. However, with Purex solutions the contamination on stainless steel is quite selective, niobium being primarily adsorbed.

Contamination experiments were carried out with four successive fivefold dilutions, at constant acidity (2.2 M nitric acid), of the IAW solution, in which pieces cut from 3-mil-thick sheets were suspended for 10 days. The beta and gamma activities on the contaminated samples were measured with a Geiger counter and, from the dimensions of the sheets, the activity per square centimeter was calculated. The classical Freundlich adsorption isotherm may be written, for this case,

$$\text{contamination/cm}^2 = kc^{1/n}$$

$$\log(\text{contamination/cm}^2) = \log k + (1/n)\log c,$$

where k is a constant, c is the concentration of the contaminating element, and n is a constant greater than 1 which depends on the system. A plot of the logarithm of the contamination per unit area against the logarithm of the concentration of the contaminants should give a straight line if the Freundlich adsorption isotherm applies, and the data obtained (see Table 2 and Fig. 1) rather strikingly demonstrate this. The data do not fit the Langmuir adsorption isotherm.

Table 2

Effect of Contaminant Concentration in Solution on Contamination Level of Stainless Steel

Type 347 stainless steel sheets contaminated at room temperature for 10 days with dilutions, at constant acidity, of the Purex IAW; sheets counted with an end window beta counter using a lead and aluminum absorber for gamma activity.

Dilution Factor of IAW Solution	Activity ($c/m/cm^2$)	
	γ	$\beta + \gamma$
0	3,960	17,250
5	1,484	3,680
25	237	785
125	47	159
625	12.5	74

[redacted]

ORNL-LR-Dwg 4874

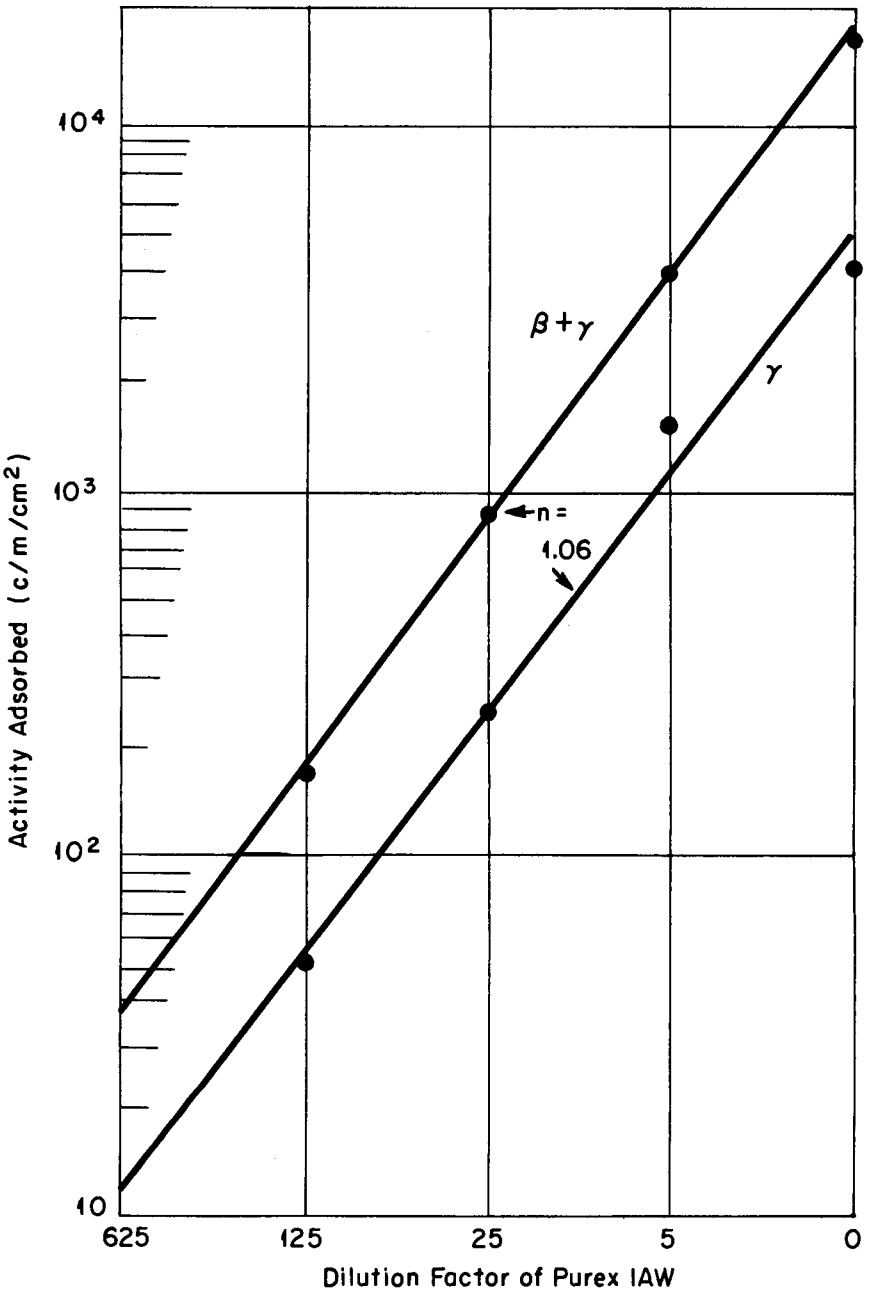


Fig. 1. Contamination of Type 347 Stainless Steel with Various Concentrations of Purex IAW Solution (HNO_3 = 2.2 *M*) According to Freundlich Isotherm.

4.3 Effect of Addition of Stable Isotopes to the Contaminating Solution

Decreasing the amount of contaminating material deposited on a surface is equivalent to achieving the same amount of decontamination. If only one or two elements contribute almost all the contamination, decreasing the contamination by decreasing the specific activity of the contaminant may be feasible since only a limited amount of an element, whether radioactive or not, is adsorbed on the surface from a solution of given concentration. The extent of adsorption by a solid surface from solution normally approaches a limit at higher concentrations. The addition to Purex waste solution of a fluoride solution containing less than 100 ppm of niobium and zirconium in 2.2 M nitric acid decreased the gamma contamination of an unpolished sample placed in the solution by a factor of about 7. The beta contamination, as measured with a Victoreen survey meter (only high-energy beta) was decreased by 30 percent compared to that with Purex waste similarly diluted with 2.2 M nitric acid alone. Radiochemical analysis of the dissolved coupon showed that there was a considerable decrease in niobium contamination. As a result ruthenium became the primary beta contaminant (90 percent), and it contributed 16 percent of the gamma activity instead of the usual 1 percent or less. Niobium was still the primary gamma contaminant, however, Zirconium contamination appeared to be decreased about the same as that of niobium. It is possible that the fluoride, by itself, would decrease niobium and zirconium contamination, but this has not been investigated. These experiments are considered to be incomplete.

Unfortunately, this method of decreasing the contamination probably is not applicable with nitric acid contaminating mediums because of the difficulty of keeping macro quantities of zirconium and niobium in nitric acid solutions without a complexing agent. Some success has

been obtained in dissolving zirconium in 2.2 M nitric acid, the acidity of the Purex first cycle aqueous raffinate, but zirconium is of secondary importance compared to niobium. So far, little success has been achieved in getting niobium into anything resembling Purex process solutions since nitric acid solutions present an extremely unfavorable environment for dissolved niobium.

5.0 DECONTAMINATION EXPERIMENTS

Numerous radiochemical analyses were made of solutions used for decontamination and of coupons in various stages of decontamination. Within the errors of the analyses, the results were always about the same as those in Table 1; i.e., niobium was the primary gamma contaminant throughout decontamination, and it contributed most of the gamma activity removed by the decontaminating solutions. The principal contaminant removed by the different reagents was niobium in all cases. Briefly, the problem in decontaminating stainless steel that has been in contact with Purex solutions is to remove niobium, and the effectiveness of a decontaminating reagent depends on its ability to do so. In the process of removing the niobium, the reagent also removes the other contaminants, which are of relatively minor importance.

The most effective reagent studied was 3 percent hydrofluoric acid in 20 percent nitric acid, "3-20 reagent." However, acid solutions of fluorides are corrosive and their use is thus limited. The next most successful reagent was a solution of sodium tartrate, sodium hydroxide, and hydrogen peroxide. Alkaline tartrate solutions have been described before (see Appendix, Sec. 6.0), but hydrogen peroxide definitely improved their effectiveness. Since niobium was the principal

contaminant, it is interesting that fluoride is the strongest complexing ion for niobium, and tartrate is next, although considerably weaker.

Since no cure-all has been found for contamination, and some reagents are corrosive, the problem of how long a given reagent should be used becomes important. Rate studies are also important in that they may aid in the understanding of the mechanisms of contamination and decontamination. Rate investigations should certainly prove useful to improve the economics of decontamination, with respect to both time and reagent cost. Previous investigations have been concerned almost exclusively with decontamination achieved in a predetermined fixed time by the first reagent used. The rate of removal of contamination for the promising reagents when used both initially and following each other was investigated. The results of such studies are considered in the discussion of the particular reagents. Such data permit choosing a decontamination procedure to fit the circumstances of the problem.

5.1 The 3-20 Reagent

Solutions of hydrofluoric acid in nitric acid have often been reported to be superior to all others in decontamination (see Appendix, Sec. 6.0). Acidic fluoride solutions are extremely corrosive, and 3-20 reagent (3 percent HF—20 percent HNO_3) is generally used because it combines good decontamination with minimum corrosion. Acidic fluoride decontaminants should probably be used only as a last resort, but corrosion was found to be negligible in the first few minutes, and very-short-time treatments may be useful for some applications.

A contaminated stainless steel sample was decontaminated with 3-20 reagent by decontamination factors of 3.3 after 10 sec, 4.6 after 30 sec, 6.6 after 1 min, and 12 after 5 min. With several contaminated

coupons that had been decontaminated to a few tenths of a milliroentgen per hour by various other treatments, 3-20 reagent gave a further decontamination factor of about 2 in 5 min. In one case a coupon decontaminated to 0.01 mr/hr by eight treatments with nitric acid followed by alkaline tartrate-peroxide (d.f. greater than 10^4) was treated with 3-20 reagent for 2.5 hr. The entire surface was corroded, but the d.f. was greater than 5. The coupon (~ 4 cm^2) had a gamma activity of less than 2 c/min above background. The overall d.f. was greater than 10^5; this is the most nearly complete decontamination attained in any experiment.

A contaminated stainless steel sample that had stood for 5 min in 3-20 reagent showed no corrosion when examined microscopically. In 20 min, shallow pits were beginning to form, especially along machine marks and surface irregularities. With further exposure the pits increased rapidly in area, but not in depth, until the entire surface was being corroded. After 117 hr the depth of corrosion was 0.6 mil as measured by a micrometer and 0.62 mil as measured by weight loss. Microscopic examination showed numerous shallow pits, mostly 1 to 2 mils deep and relatively large in area. There were no deep pits and there was no evidence of intergranular corrosion. This sort of uniform corrosion is much less damaging to equipment than the usual pitting and intergranular corrosion. This coupon was later contaminated, and it was no more difficult to decontaminate than coupons not so treated.

The 3-20 reagent is notably different in one respect from all other decontamination solutions tested. The beta d.f. is, in general, somewhat smaller than the gamma with 3-20, while it is larger, especially for the first few seconds, with the other reagents. It is not known whether this is because of decreased decontamination of beta emitters or increased decontamination of strong gamma emitters (niobium, in particular), but the latter appears likely. No radiochemical

analyses of 3-20 solutions used in decontamination were made, and gamma-scintillation-spectrometer analyses of coupons decontaminated with 3-20 were inconclusive since fission products other than niobium and zirconium were always at or below the limit of detection.

5.2 Alkaline Tartrate-Peroxide

The most effective noncorrosive reagent studied was a solution of sodium hydroxide, sodium tartrate, and hydrogen peroxide. Concentrations of components did not appear to be critical, but 5 percent sodium hydroxide, 1 percent sodium tartrate, and 1.5 percent hydrogen peroxide appeared to be reasonable minimums. Increased concentration of sodium hydroxide improved the effectiveness of subsequent decontamination somewhat but had little effect on the initial treatment.

Decontamination factors obtained with sodium hydroxide were much smaller than those with alkaline tartrate-peroxide. With the alkaline tartrate-peroxide the beta d.f. was greater than the gamma (see Fig. 2). This appeared to be caused by the increased beta decontamination during the first few seconds, which is multiplied throughout the subsequent decontamination. Beta and gamma d.f.'s were about the same after the first 0.1 min. This conclusion is consistent with the previous statement that niobium and perhaps zirconium are the important contaminants. Apparently, any strong beta emitters which may be present are very quickly removed by the alkaline tartrate-peroxide. The 3-20 reagent (Sec. 5.1) did not show this effect. In Fig. 2 the d.f.'s are plotted against a logarithmic time scale so that the d.f. for very short times and for long times can be represented on the same graph. The curves must be interpreted with care to avoid misleading conclusions. For example, an increase in d.f. from 25 to 50, which took several days, is really a further d.f. of only 2, the same amount of decontamination

[redacted]

ORNL-LR-Dwg 4875

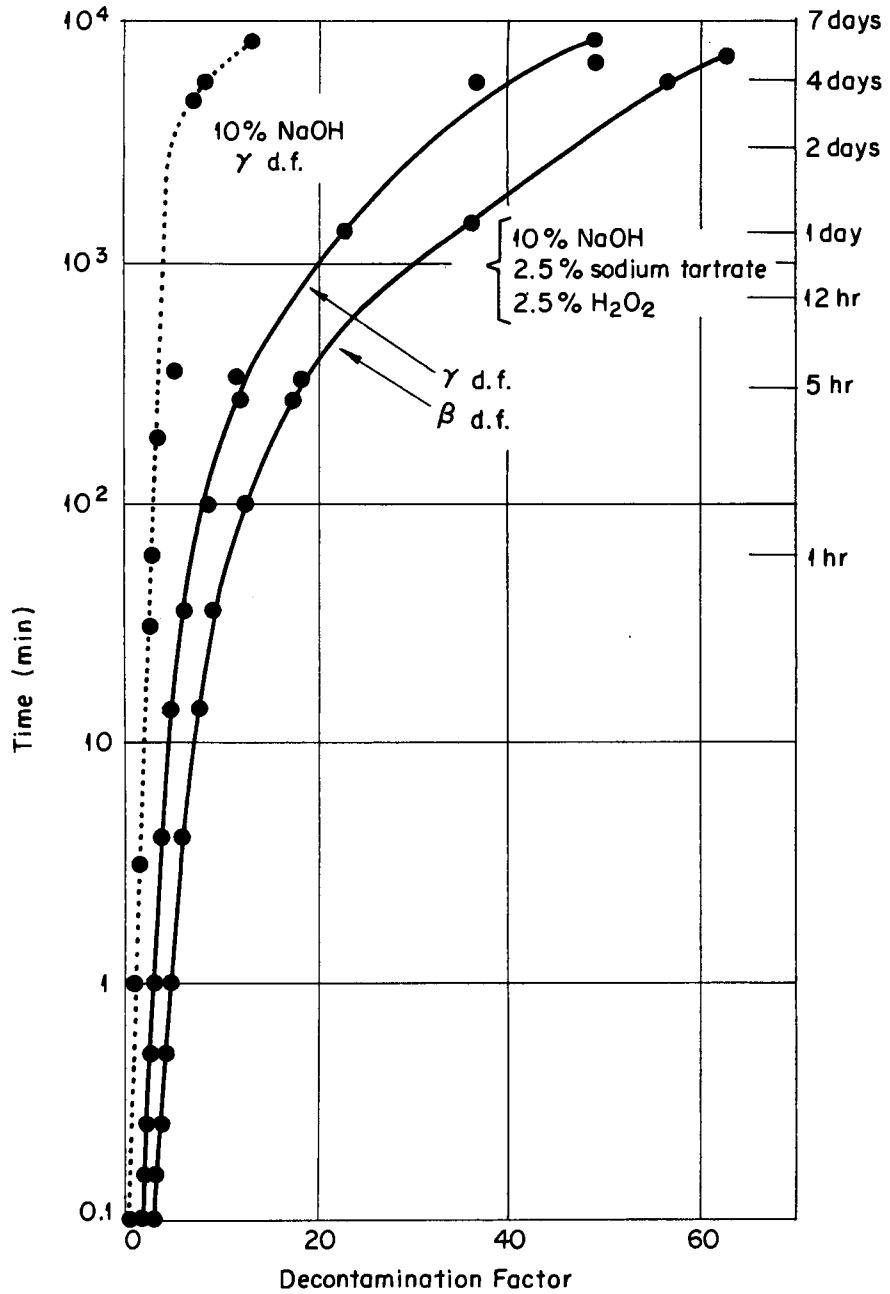


Fig. 2. Rate of Decontamination of Type 347 Stainless Steel by Sodium Hydroxide and Alkaline Tartrate - Peroxide.

that initially took about 10 sec.

The alkaline tartrate reagent without the peroxide was half, or less, as effective as that with peroxide (see Fig. 3). Also, the addition of hydrogen peroxide, after one day, to the alkaline tartrate greatly improved the decontamination. In these experiments contaminated samples were first decontaminated with nitric acid, with a d.f. of 2 to 3 and then treated with either alkaline tartrate or alkaline tartrate-peroxide. The alkaline tartrate-peroxide was as effective following the nitric acid treatment as when used first (see Figs. 2 and 3).

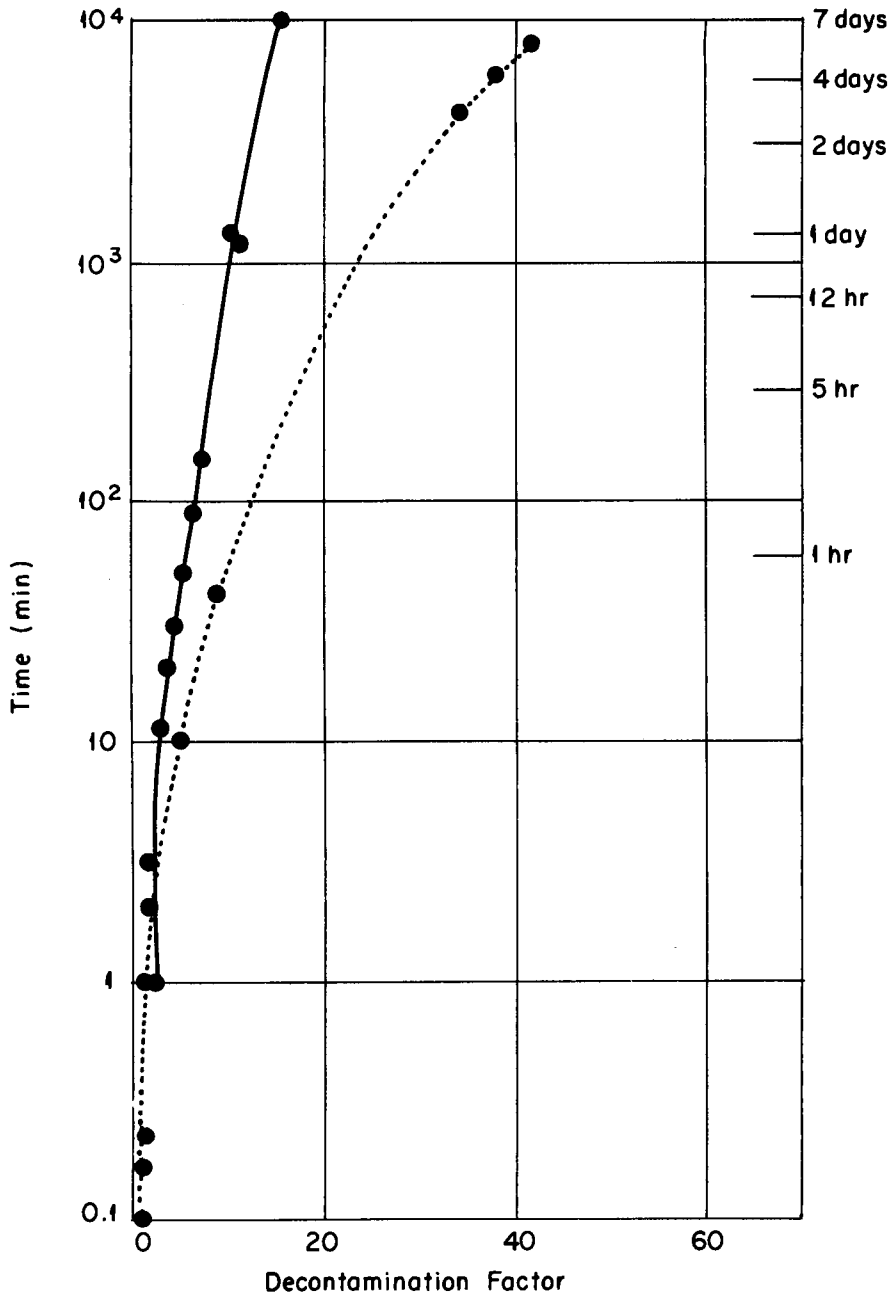
Alternate treatment with nitric acid for a few hours and alkaline tartrate-peroxide overnight gave d.f.'s of the order of 10^4 after about seven cycles. Decontamination continued slowly with further treatment, the d.f. being about 1.3 per cycle.

One coupon that had been initially decontaminated for 5 min in 3-20 reagent, with a d.f. of 12 (see Sec. 5.1), and showing no evidence of corrosion upon microscopic examination, was further decontaminated with alkaline tartrate-peroxide. This second treatment was not quite so effective as it was following nitric acid (the d.f.'s were between the values of the two curves of Fig. 3). This treatment, however, gave the greatest decontamination in a short time (d.f. greater than 50 in 0.5 hr) that has been obtained without measurable corrosion.

The substitution of fresh reagent did not increase the rate of decontamination by the alkaline tartrate-peroxide, even after a d.f. greater than 60 had been obtained with the old reagent. After the contamination level had been reduced to less than 0.1 mr/hr by treatment with various reagents, the alkaline tartrate-peroxide solution used for the initial decontamination would not recontaminate the coupon. It is possible, therefore, that this reagent could be used repeatedly for decontamination, being stored while other reagents were used, rather than fresh solution being

[redacted]

ORNL-LR-Dwg 4876



——— 10% NaOH, 2.5% sodium tartrate after 2 hr in 16*M* HNO_3 with d.f. of 2.0.

····· 10% NaOH, 2.5% sodium tartrate, 2.5% H_2O_2, after 1 day in 8*M* HNO_3 with d.f. of 3.3.

Fig. 3. Rate of Decontamination of Type 347 Stainless Steel by Alkaline Tartrate and Alkaline Tartrate–Peroxide following Initial Decontamination by Nitric Acid.

[redacted]

made up each time. This could effect a considerable saving in cost since the reagent could probably be used many times during a plant decontamination. The hydrogen peroxide would have to be replaced from time to time since it decomposes slowly. It should be pointed out that alkaline tartrate-peroxide continues to decontaminate, although very slowly, for weeks. Even after 20 days it was still removing 5 to 6 percent of the remaining activity per day; decay of niobium would account for about 2 percent per day. If time is not an important factor, there is no reason that equipment should not be contacted with this reagent for days.

Corrosion with alkaline tartrate-peroxide was negligible. Microscopic pits, barely visible under 500X magnification, appeared on a polished surface after a day, but they did not increase in size even after two weeks of treatment (eight treatments) with alkaline tartrate-peroxide and nitric acid, alternately.

5.3 Nitric Acid

Nitric acid is almost always the first reagent used in decontamination since it is put in the equipment to clean it out and, in particular, to dissolve any uranium that might have precipitated. It is often used between the various other reagents in decontamination procedures. However, nitric acid was the least effective reagent tested. On the other hand, it seemed to affect the surface so that it became susceptible to further decontamination by other reagents, especially the alkaline tartrate-peroxide.

The decontamination factor for the initial treatment with nitric acid for periods from an hour to a day was usually about 2 and less than 3 (see Fig. 4). Decontamination continued, although slowly, for days, and the factor approached unity for subsequent treatments. After

[redacted]

ORNL-LR-Dwg 4877

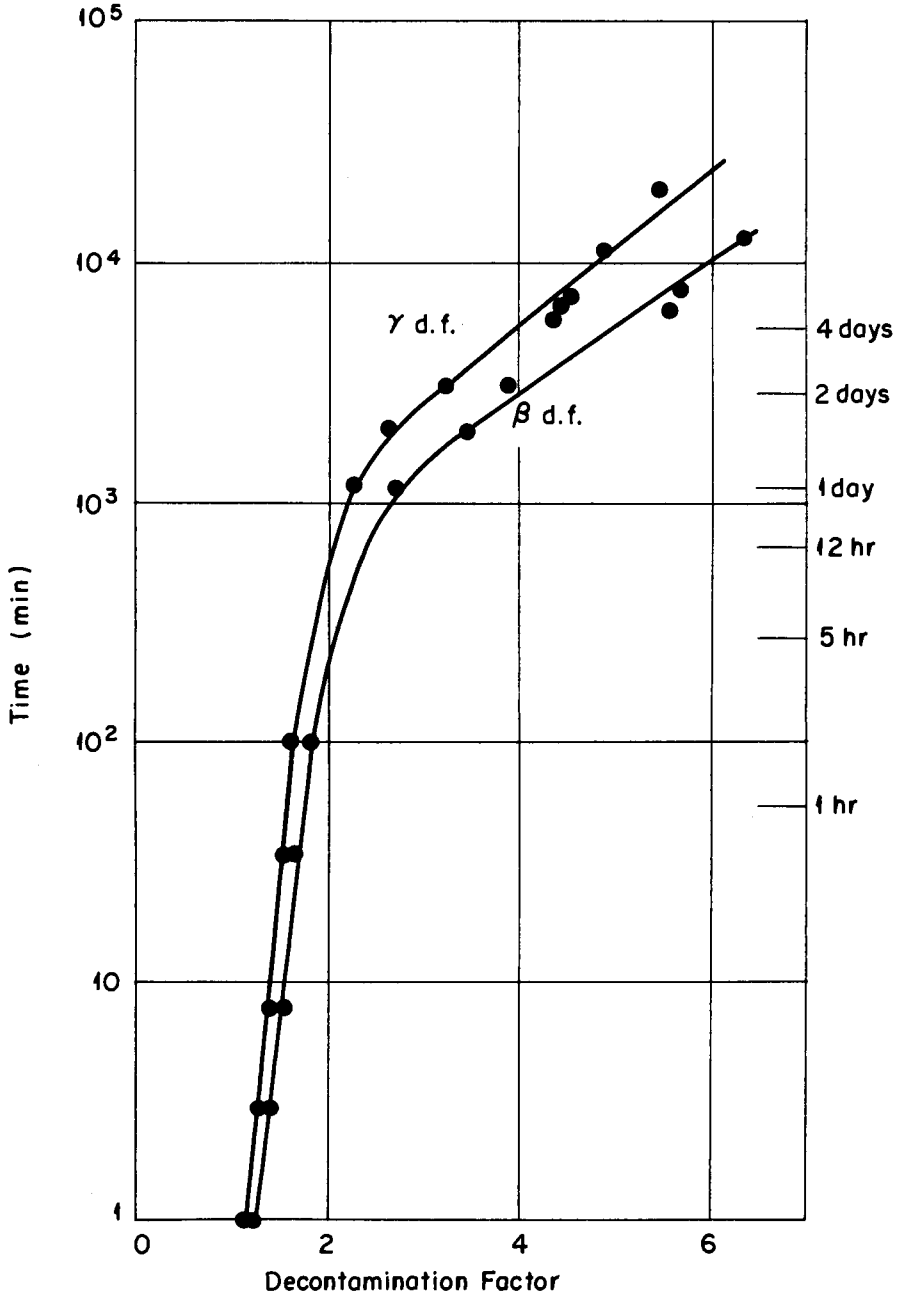


Fig. 4. Rate of Decontamination of Type 347 Stainless Steel by 16*M* Nitric Acid.

a week the activity was still being removed, at a rate of about 6 percent per day. The initial decontamination factor obtained on the first two or three coupons contaminated with a fresh contaminating solution was larger by a factor of perhaps 5; this fact cannot be explaned with certainty, but it is probably related to the higher contamination level on such coupons, as discussed in Sec. 4.0. Because of this, and the fact that dissolution of solids in the equipment normally releases large amounts of radioactive materials, the decontamination factor observed in practice with the first nitric acid treatment may be much larger than that indicated in Fig. 4.

The addition of 1 percent potassium permanganate to 8 and 16 M nitric acid improved decontamination considerably, but it resulted in a very severe intergranular corrosion. A precipitate of manganese dioxide formed on the surface of the coupon, and the decontamination was achieved when it was dissolved. Oxalic acid was very effective for the dissolution of the manganese dioxide. However, the corrosion was so severe that this solution cannot be considered for practical decontamination.

5.4 Oxalic Acid

Five percent oxalic acid was a much more effective decontaminant than nitric acid (see Fig. 5). There is quite a bit of confusion about corrosion by oxalic acid. It has been reported to be corrosive to stainless steel, but in our work, a polished coupon after two weeks' contact with the reagent at room temperature showed no corrosion when examined microscopically (500X) and no weight loss. After coupons had been decontaminated to a few tenths milliroentgen per hour by various treatments including oxalic acid, oxalic acid gave a further d.f. only a little greater than 1, as do most reagents. However, in an experiment

[redacted]

ORNL-LR-Dwg 4878

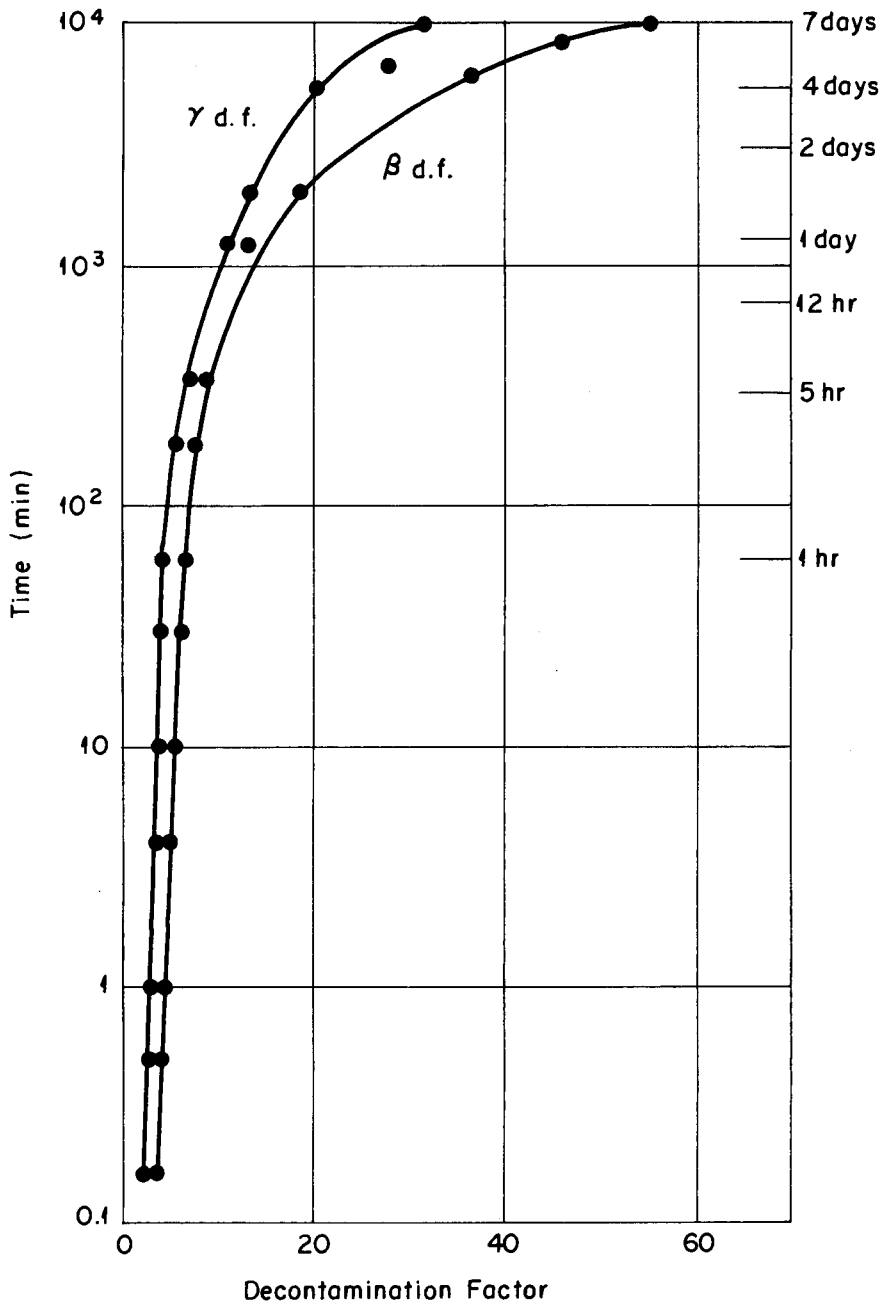


Fig. 5. Rate of Decontamination of Type 347 Stainless Steel with 5% Oxalic Acid.

in which oxalic acid was used for the first time after the coupon had been decontaminated to 0.03 mr/hr by several treatments with nitric acid, alkaline tartrate-peroxide, and 3-20 reagent, a further d.f. of 2.3 was obtained by overnight treatment with oxalic acid. Such a d.f. is excellent for this stage of decontamination.

Other organic acids, such as citric, were not tested in these experiments. They appear to rate between nitric and oxalic acids. None of them show any great specificity for niobium. Alkaline solutions of salts of the organic acids are in general more effective than the acids themselves, with the effectiveness approaching that of the alkaline tartrate. An alkaline solution of sodium gluconate, in particular, may become useful because it has been found to be about as effective as alkaline tartrate and it may be more readily available and less expensive.

5.5 Ultrasonic Radiation

With all reagents tested, the rate of decontamination was increased, although by varying amounts, by ultrasonic radiation of sufficient intensity. The decontamination appeared to be more nearly complete, also, but, in view of the continued slow decontamination by most reagents, this may not be so. If it has any effect on a reaction, ultrasonic radiation generally increases the rate, and this should be true with respect to decontamination, also.

Hydrogen peroxide decomposes in a short time in the presence of ultrasonic radiation, so most work was done with alkaline tartrate without the peroxide. Usually, the gamma d.f.'s were about 1.7 times the values indicated by the gamma d.f. curve for alkaline tartrate-peroxide in Fig. 2. After one coupon had been decontaminated by a factor of 25 without ultrasonic radiation, alkaline tartrate-peroxide was used. After 3 and

6 hr (total time) with ultrasonic radiation, d.f.'s of 2.4 and 3.2, respectively, were obtained. Then a d.f. of only 1.2 was obtained in 16 hr with the same reagent without ultrasonic irradiation. Finally, a d.f. of 1.4 was observed after another 6 hr with ultrasonic irradiation. Decontamination with nitric acid was affected in much the same way by ultrasonic radiation.

The addition of the solids--resin, carborundum, or Filtrol--to the various solutions, or even to water, improved decontamination considerably. The solids, with ultrasonic radiation, microscopically roughen the surface of the coupons. Decontamination factors of 2 to 3 were obtained in a few minutes with freshly contaminated coupons in suspensions of these solids in distilled water, and d.f.'s of 3 to 4 were obtained with suspensions in nitric acid. After the coupons had been decontaminated to such a low level that the usual reagents gave d.f.'s of only about 1.5 even with long treatment, d.f.'s of 2 to 3 were normally obtained with suspensions of these solids in the reagent with ultrasonic radiation for about an hour.

The major problem with ultrasonic radiation is to get it into the system with sufficient intensity to be useful. A rather high energy density is apparently necessary. For large pieces of equipment this would certainly be a major problem. To further complicate the problem, stainless steel appears to be a poor conductor of ultrasonic energy, as indicated by its heating in an ultrasonic field and by the relatively small amount of mixing of solutions that occurs in stainless steel tubes exposed to ultrasonic radiation.

6.0 APPENDIX*

SURVEY OF DECONTAMINATION LITERATURE

Although the experiments discussed in this report were carried out with stainless steel only, the literature was examined for decontamination procedures used with other materials also, since the decontamination characteristics of many smooth, nonporous surfaces, as long as they are not attacked by the reagents used, are similar. The reason for the increased use of relatively inert materials, such as stainless steel, in areas where contamination is likely, is not that they are less susceptible to contamination or more easily decontaminated, but rather that more reactive decontaminating reagents may be used with less destruction of the surface. In process equipment, of course, corrosion-resistant materials must be used to contain the process solutions. There are several bibliographies (1-6), surveys, and discussions (1, 7-9) on decontamination. Surveys on related subjects, such as organic complexing agents for fission products (10), and the fission product isotopes contributing significantly to the activity of mixed fission products at various times after fission have been tabulated (see, for example, reference 11).

Many reports on decontamination are not discussed here since there has been much duplication of experiments, and the results of much of the work were not conclusive. Certainly, none of the work has been completely satisfactory since there is not yet a really successful

---

* This appendix was originally published as ORNL memo CF-53-5-233 (May 18, 1953). Some more recent references are included.

decontamination procedure. Most of the reports examined in this literature search are concerned with the decontamination achieved in one treatment, and such results are of limited application to the practical problem in which repeated treatment is usually necessary. In most cases the gross decontamination was studied on samples of materials that had been contaminated with mixed fission products in either neutral or nitric acid solution, and results of experiments on decontamination with mixtures of radioactive contaminants are somewhat ambiguous unless the behavior of each element is investigated. The length of time of contamination varied considerably in the different investigations, as did the method of application of the contaminating solution. In some cases the experimental procedures and conditions were not clearly indicated.

The elements contaminating types 347 and 309 stainless steel that has been exposed to ORNL Purex pilot plant aqueous first cycle raffinate (IAW) are reported in reference 12. The beta activity adsorbed on the surface reached a maximum within 6 hr and remained nearly constant after that, but the gamma activity continued to increase even after 600 hr. Nearly all the activity was accounted for by rare earths, zirconium, and niobium, with zirconium and niobium responsible for about 75 percent of it. The most striking trend, however, is the reported increase in niobium activity during the first 24 hr, the maximum time investigated, this increase being largely at the expense of zirconium. The increase in niobium, a hard gamma and soft beta emitter, is given as the reason for the gamma activity not leveling off with the beta. After a long time, niobium was the primary contaminant on stainless steel.

Before an attempt is made to understand the mechanism and processes of decontamination, the specific processes involved in contamination and the general interactions between ions in solution and on surfaces,

especially metallic ones, should be considered. This is an exceedingly complex and difficult field (for reviews, see references 13 and 14), but a few significant observations may be pointed out. The rate of adsorption of orthophosphoric acid, labeled with P^{32}, on glass has been measured (15), and kinetically the process is not a simple one. There are three different exponential phases, corresponding to three different processes. A very rapid initial adsorption, with a half-time of the order of seconds, is attributed to electrostatic adsorption or ion exchange at the outer boundary of the electric double layer at the solid-liquid interface. Two slower phases, with half-times of about 10 min and 9 hr, respectively, were attributed to successive steps, one of which would be diffusion through the double layer. The slowest step accounts for about 75 percent of the ultimate adsorption in this case. This sort of stepwise adsorption has been generally observed.

It is very likely that the contaminating species are generally bound to the metal in several different ways. Some are adsorbed at the outer boundary of the double layer, and this part should be loosely held and easily removed. Complexing agents and isotopic carriers should be effective for removing this since they decrease readsorption of the contaminant. Some of the contamination, however, will be bound by "surface valences" and may be very tightly held. Part may be chemically bonded as a result of ion exchange with the material of the surface, and part may have diffused into the solid, or into any pores or imperfections in the surface. If it has diffused into the solid it cannot be removed without removal of some of the metal. Regardless of the mechanism, some of the contaminant is, for practical purposes, irreversibly held.

The problem of decontamination is quickly reduced to the removal of this essentially irreversibly attached material. There are two

possible methods of attack: (1) finding some way to accelerate the attainment of the equilibrium and (2) controlled surface removal, thereby exposing the adsorbed species to the action of the solution. It is not obvious how the first method may be applied. Greatest success, as far as decontamination is concerned, has been observed with the second method. Unfortunately, surface removal can seldom be controlled sufficiently to prevent rather severe corrosion. In any case, the answer to the problem, complete decontamination without destruction of the surface, has not been found. It certainly should be possible to improve on present procedures, however, both in respect to improved decontamination and decreased corrosion.

Decontamination procedures of the following types have been investigated:

1. Treatment with noncorrosive reagents, such as detergents and complexing agents.

2. Treatment with corrosive reagents, such as nitric acid or nitric acid-hydrofluoric acid mixtures.

3. Removal of the surface of the material by chemical or physical means, such as by removing part of the surface electrochemically or by removing strippable coatings with which the material is covered prior to use.

The first method is relatively mild and is effective during the early stages of decontamination when the less tightly held material may be removed. The last two methods are rather vigorous and might be expected to be more effective during the removal of the more tightly held contaminant. Unfortunately, they also damage the surface.

6.1 Decontamination with Noncorrosive Reagents

Such reagents are useful for the removal of the loosely held contaminant, usually 90 to 99 percent of the activity. Beyond that point they are essentially useless (15). These materials, especially the complexing and chelating agents, should be effective because they displace the equilibrium

$$\text{activity on surface} \rightleftharpoons \text{activity in solution}$$

to the right by tying up the activity in the solution. Unfortunately, however, the activity apparently must be removed from the surface and somehow put into solution before such reagents may act. The removal of the largest part of the contamination is easy, and for this, mild reagents are as effective as more corrosive ones. There are indications that chelating agents are the most effective of the mild reagents (16).

The stability of complexes has been investigated by means of ion exchange on resins, and attempts have been made to apply this knowledge to decontamination (see, for example, 7, 17-19). Since complexing agents are entirely ineffective for removing part of the contamination, it must be concluded that the mechanisms of ion exchange on a resin and at least a part of the decontamination of a surface such as stainless steel are entirely different. In short, the removal of part of the contamination is not an equilibrium process but a rate process. (This was stated (20) as early as 1930 for the general problem of surface interactions.) Complexing agents and isotopic carriers are therefore useless for removing the part of the contamination that is tightly bound to the surface and is not in equilibrium within reasonable time with the solution. They can displace the equilibrium, but they do not affect its rate of attainment.

The military organizations have tested numerous detergents, complexing agents, and surface-active compounds. Their problem has been

the decontamination of airplanes, ships, and, potentially, extensive land installations, for which inexpensive and noncorrosive reagents must be used. The decontamination of stainless steel and Alclad aluminum by more than 50 commercially available materials has been investigated (21). In the studies 1-in. disks of the metals were each contaminated with 300 μl of a neutral solution of yttrium, strontium, zirconium, and niobium in sea water, which was spread over the disks and evaporated under an infrared lamp. The disks were decontaminated, without first being rinsed with water, by being placed in 250 ml of the reagent, which was stirred for 20 min. Experiments were carried out at 20 to 25°C and 70 to 76°C.

For purposes of comparison, decontamination with dilute hydrochloric acid and sodium hydroxide, in the same pH range as the reagents, was also investigated. For stainless steel these solutions of pH greater than 7 removed about 70 percent of the activity. As the pH was decreased below 7, the decontamination increased, reaching about 97 percent at pH 2. The most effective of the decontaminating reagents were nitrilotriacetic acid (Antarane X-195, General Aniline and Film) and ethylenediaminetetraacetic acid (Versene, Sequestrene), and their salts, giving 98 to 99 percent decontamination at the lower temperature and 99 to 99.9 percent at the higher. Both these compounds are chelating agents.

Several formulas containing mixtures of pyro-, poly-, and metaphosphates as well as other cleaning agents were investigated. The pH varied from 11.8 to 6.8, depending on the compounds mixed together, and the decontamination varied from 80 percent at the higher value to 99 percent at the lower. It seems, then, that the mixtures are more effective at lower pH, at least down to 6.8. If the decontamination may be attributed to the phosphates, this is consistent with the observation (22) that $H_2PO_4^-$ and $H_2P_2O_7^=$ are adsorbed on all sorts of surfaces but the other

ortho- and pyrophosphate ions are not. On this basis the phosphates would be expected to be most efficient in the pH range 4 to 6.

A large number of metals and alloys have been compared in contaminability-decontaminability behavior (23). Polished disks of the metals were contaminated with one-year-old Hanford dissolver solution and were decontaminated with acidic, neutral, and basic citrate solutions. The different metals showed similar characteristics except when corrosion was evident, but, in general, the alkaline citrate solution was inferior. For stainless steel the acid citrate was superior; it removed about 90 percent of the radiation that was not rinsed off with water. Neutral and alkaline solutions removed 55 and 74 percent, respectively.

Similar studies have been made for a variety of materials: vitreous enamels (24, 25), aircraft paints (26), weathered aircraft paints (27), Navy gray deck paint (28), blue airplane lacquer (29), painted steel (30, 31), resins and plastics (32), composition decking materials (33), rubbers and some miscellaneous materials (34), woods (35), painted wood (36), painted concrete (37), and several papers (38).

In a test of 50 materials for contamination susceptibility and ease of decontamination (39), the effects of 5 percent Versene-1 percent Triton (pH 8 to 9), alkaline citrate (1 percent sodium citrate, 5 percent sodium hydroxide), neutral citrate (2.5 percent sodium citrate, 0.2 percent Aerosol D.T., pH 7), and acidic citrate (0.3 M citric acid, 0.1 percent Aerosol D.T., and 0.5 M hydrochloric acid) were investigated. The materials were contaminated with 100 μl of a three-year-old mixed fission product solution which was allowed to dry on the surface. They were then flushed with tap water. The materials were decontaminated by being placed in the appropriate solution and scrubbed with a brush for 2 min. The acidic citrate was most effective for stainless steel, decontamination factor 120, but it corroded the surface. The alkaline

wash was least effective.

Recently the Naval Radiological Defense Laboratory has published several reports (40) resulting from a reinvestigation and extension of some of this work. A more realistic contaminating solution has been developed (41) which has approximately the chemical composition of sea water, and the radioisotopes are more representative of fission products present shortly after fission (atomic bomb detonation) than the Hanford dissolver solution used in the earlier tests. There have also been a number of reports on contamination resulting from fall-out and on airplanes flying through the cloud after an atomic explosion, but they are not considered here because interest is restricted to contamination from solution.

Organic acids and their salts have often been suggested; these include oxalic, citric, and tartaric acids, especially. Soaps and detergents have been used at ORNL, especially for decontamination of tools and machines (9).

The use of stable isotopes of the adsorbed materials has been notably unsuccessful (1, 9, 15, 42).

6.2 Decontamination with Corrosive Reagents

The designation of reagents as "noncorrosive" or "corrosive" is quite arbitrary. Reagents which remove the protective oxide coating, and thereby expose the surface to attack, are included in the "corrosive" category. This category includes, therefore, such reagents as oxalic acid, which is also a complexing agent.

The degree of corrosion and of decontamination are not necessarily related. Although some surface removal may be necessary for removal of the tightly bound contaminant, corrosion is not always accompanied

by good decontamination. For example, the decontamination factor with HCl is often small although corrosion may be extreme. It seems likely that an appropriate complexing agent must be in the solution, along with the surface removing reagent, so that the contamination which is released from the surface will not be readsorbed on it. Thus, $HF-HNO_3$ mixtures, or any decontaminants containing fluoride ion, probably owe their effectiveness to the fact that, besides being corrosive, the fluoride ion forms very stable complexes with certain fission products. The association constant for $ZrOH^{3+}$ with F^- is 3.16×10^5 in 2 M perchloric acid (43). Tartrate similarly complexes some of the fission products. Thus, the presence of a complexing agent in a corrosive solution is very likely essential to good decontamination.

Corrosive reagents have been in general use in AEC installations for decontamination of stainless steel. Very often concentrated nitric acid is used for the first treatment since it will dissolve uranium left in the equipment. It is used intermittently, as are other reagents, until a sufficiently low level of activity is obtained. Far more nitric acid than anything else has been used, but it is likely that this is because of its availability rather than because of its effectiveness.

Two reagents found to be considerably more effective than any others are a solution of sodium tartrate in sodium hydroxide (1, 9, 42, 44) and a solution of hydrofluoric acid in nitric acid (1, 9, 12, 45). The reagent with the optimum concentrations of hydrofluoric and nitric acids, 3 and 20 percent, respectively (maximum decontamination and minimum corrosion), is generally called "3-20 reagent." The concentrations of sodium hydroxide and sodium tartrate are less well defined, but they are not so critical since corrosion is not so important a factor. Five to 20 percent sodium hydroxide and 1.25 to 10% sodium tartrate have been recommended; the 5 and 1.25% figures are probably the minimum concentrations to give good decontamination. Increasing the concentration of

sodium hydroxide, or of both constituents, with successive treatments seems to improve the results.

The 3-20 reagent is reported to have a low corrosion rate, and apparently it attacks the surface rather uniformly. It shows little or no intergranular corrosion and little pitting. Unfortunately, it seems to have a high solubility for welding flux. It presumably attacks, and opens, faulty welds which were kept from leaking by included flux; but such welds do hold most process solutions. Good welds are not attacked any more than normal stainless steel.

Another reagent that has been recommended (46) as giving essentially complete decontamination is a solution of 1.5 percent hydrogen peroxide in 5 percent sodium hydroxide, which is alternated with nitric acid. The stainless steel used in the experiments on which this recommendation is based may not have been properly contaminated to start with, since it was only dipped several times in a solution of two-months'-old fission products.

Sodium hydroxide and carbonate have been used, sometimes with organic acid salts added (1). One percent hydrogen peroxide in 35 percent nitric acid has been found effective for the removal of cerium (9). For mixed fission products, repeated cyclic treatment with 6.5 M sodium hydroxide containing either 0.67 M sodium tartrate (preferred) or 0.1 M sodium fluoride, followed by a solution 1 M in oxalic acid and 0.1 M in sodium fluoride, has been recommended (47). Each solution is left in contact with the surface for half an hour at 85°C. Successive treatment with several different solutions has been very effective.

6.3 Removal of Surface

a. Electrochemical Decontamination. The possibility of electrochemical decontamination has been investigated (12, 48-50). Anodization

in 2 percent sulfuric acid has given somewhat less corrosion and about the same decontamination as electropolishing. Small laboratory apparatus has been decontaminated from several hundred milliroentgens per hour to background. Some equipment contaminated in the pilot plant during several years of operation was further decontaminated after chemical methods had become ineffective.

Under properly controlled conditions electrodecontamination is quite successful. Unfortunately, owing to the complex shapes and numerous interconnections of process vessels, it is not practical in existing plants. A process plant would have to be designed with electrodecontamination in mind if this method is to become practical. In view of the complications arising in chemical decontamination, corrosion, and incomplete decontamination, the electrochemical procedure may eventually prove to be more feasible than it now appears.

b. Removable Coatings. Numerous reports have been written concerning coating of areas which may be exposed to contamination with substances that may be more easily decontaminated or removed by dissolution or mechanical means. Such coatings, under proper conditions, protect the coated material from at least a large part of the potential contamination. If the coating cannot be decontaminated, its removal also removes the greatest part of the contamination, and ordinary decontamination procedures may then be applied. The important thing is that a large decontamination factor may be obtained before chemical methods are necessary. The initial advantage so attained can tremendously simplify the remaining decontamination.

It is not possible, in general, to apply a coating to the inside of process vessels since coatings have not been found which are sufficiently resistant to the process solutions and conditions. However, they can be applied to the outside of equipment, to cell walls, and any area that may become contaminated because of spills, etc. As an example, stainless

steel samples painted with Navy gray paint and then contaminated lost well over 99 percent of their activity when treated with 5 percent NaOH, which softened the paint so that it was easily washed off (30). A decontamination factor of several hundred could be obtained by removing the paint without its being necessary to treat the surface with more reactive and corrosive chemicals.

In view of the ease of application and removal of such coatings and the decontamination so attained, compared to the difficulty in decontaminating exposed stainless steel, it would seem that these coatings should be used whenever feasible. Most of the contamination on the coating can be removed easily; that on the steel can be removed only with difficulty and some of it, not at all. It is essential that this last part be minimized. It is necessary, of course, that the proper coating be used so that contaminants will not permeate it or get between it and the coated surface.

It is almost essential that concrete surfaces exposed to contamination be protected by some coating since otherwise the contamination will soak into the cement. Chemical decontamination only drives the contaminants deeper. Painting the concrete helps, as long as the paint lasts. At the ORNL Pilot Plant it is the present practice to line radioactive cells with stainless steel. Once contamination gets into the concrete it can be removed only by some process such as sandblasting if it has not soaked in too far, or by chipping out the concrete, sometimes to a depth of several inches, if it has.

6.4 Plant Experience

Much information is available from decontamination of pilot plants. The interpretation of the data is difficult for two reasons:

1. Decontaminating reagents have sometimes been chosen because of

availability instead of effectiveness.

2. Process vessel decontamination cannot be determined unambiguously because of general cell background, radioactive spots, etc.

The decontamination experience at ORNL until 1948 has been summarized (9). The reagents steam, nitric acid, nitric acid with HF or ammonium fluosilicate, ammonium bifluoride, $KMnO_4$ followed by $NaHSO_3$, citric, oxalic, and tartaric acids, NaOH, Na_2CO_3, 5 percent NaOH-1.25 percent sodium tartrate, ammonium citrate, ammonium oxalate, some soaps, detergents, and organic solvents are mentioned. The procedure recommended for stainless steel at that time was:

1. Wash with water.

2. Treat with boiling 5 to 60 percent HNO_3 for 30 min, followed by boiling 15 percent Na_2CO_3 for 30 min. Repeat several times, increasing the nitric acid concentration each time.

3. Treat with 10 percent ammonium fluosilicate at room temperature for 30 min followed by boiling 15 percent Na_2CO_3 for 30 min; repeat 10 to 15 times.

4. Treat with steam for several hours.

This procedure reduced the activity from about 100 r/hr to 50 mr/hr.

Decontamination of the ORNL pilot plant has been considered in several other reports (for example, 52-53). In all cases several different solutions were used repeatedly and the decontamination was far from complete. The most successful reagents, after initial treatment by nitric acid to remove uranium, were alkaline tartrate solution and nitric acid—hydrofluoric acid. It might be well to point out that these reagents have been known for a number of years. They have recently been recommended for the Idaho Chemical Processing Plant (44). For comparison,

the decontamination procedure recommended follows:

1. Treat with a boiling 1 percent solution of the synthetic detergent Tide.

2. Reflux with 10 percent HNO_3 for 16 hr.

3. Treat with 20 percent NaOH—10 percent sodium tartrate at 80 to 90°C for 4 hr.

4. Treat with 10 percent oxalic acid at 80 to 90°C for 4 hr.

5. Repeat steps 2, 3, and 4.

If this does not give satisfactory decontamination, the following procedure is then used:

1. Treat with 10 percent citric acid at 80 to 90°C for 4 hr; follow by water wash.

2. Treat with 3 percent HF—20 percent HNO_3 at room temperature for 1 hr; follow by water wash.

3. Repeat the cycle.

Occasionally, HCl, H_2SO_4, and other acids have been used, but they are extremely corrosive on stainless steel (9, 54). This may be especially serious if the solution must be stored. Storage of fluoride-containing solutions presents a similar problem. For this reason the Idaho Chemical Processing Plant requested halide and sulfate-free decontamination reagents. The use of corrosion inhibitors in the storage tanks might diminish this problem.

The procedures used for pilot plant decontamination have caused corrosion of the process equipment. Each successive decontamination would therefore be expected to be more difficult and less effective than the preceding one because of the increase in surface area and the formation of pits and crevices, into which the decontaminating solutions

cannot easily penetrate. The fact that this has not been observed, recently, at least, might indicate that a maximum roughness of surface has already been obtained; further corrosion destroys as many pits, by removal of the material around them, as it forms. Even so, corrosion cannot be continued indefinitely without eventual destruction of the equipment. Surprisingly little is known about corrosion of stainless steel under process and decontamination conditions, either empirically or theoretically, and it seems that a parallel corrosion study is as important as a decontamination study.

6.5 References

1. G. E. Desetti, W. L. Kay (Hanford), "Decontamination of Product and Fission Product Activity from Various Surfaces," M-3270 (SE-PC-92) (Feb. 26, 1946).

2. H. E. Voress, "Surface Decontamination Methods: A Bibliography of Report Literature," TID-3025 (March 25, 1952).

3. Armed Services Technical Information Agency, "Radioactive Contamination and Decontamination of Surfaces of Various Construction Materials," NP-4081 (Apr. 28, 1952).

4. O. Plaat, J. F. Cosgrave, J. L. Evans, "Bibliography of USNRDL Reports, with Abstracts," AD-312(A) (March 31, 1951).

5. Plutonium Project (J. M. Siegel), "Nuclei Formed in Fission: Decay Characteristics, Fission Yields, and Chain Relationships," J. Am. Chem. Soc., 68: 2411 (1946).

6. R. L. Curtis, "Decontamination: A Literature Search," unclassified abstracts, Y-964 (May 19, 1953); classified bibliography taken partly from TID-3025, Y-965 (May 22, 1953).

7. S. W. Mayer, "Complex-Ion Formation with Fission Products. I. A Review of Recent Developments Relating to Decontamination," AD-16(C) (Feb. 26, 1948) [abs. in AD-312(A)].

8. W. W. Hawes, "Survey of Decontamination Methods," AD-48(C) (Oct. 21, 1948) [abs. in AD-312(A)].

9. F. N. Browder, "Summary of Surface Decontamination Experience at Oak Ridge National Laboratory," ORNL-158 (Aug. 20, 1948).

10. W. E. Shelberg, "A Recent Literature Survey of Organic Compounds Complexing Fission Elements," AD-58(C) (Dec. 28, 1948) [abs. in AD-312(A)].

11. H. F. Hunter, N. E. Ballou, "Simultaneous Slow Neutron Fission of U^{235} Atoms. I. Individual and Total Rates of Decay of the Fission Products," AD-65(C) (Feb. 24, 1949) [abs. in AD-312(A)].

12. "Chemical Technology Division Progress Report for Period August 1, 1951 to February 10, 1952," ORNL-1311, pp. 69-73 (Sept. 30, 1952).

13. O. Hahn, "Applied Radiochemistry," Cornell Univ. Press, Ithaca, N. Y., 1936.

14. A. C. Wahl, N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, 1951.

15. P. C. Tompkins, O. M. Bizzell, "Radioactive Decontamination Properties of Laboratory Surfaces. I. Glass, Stainless Steel, and Lead," ORNL-381 (Sept. 21, 1949); ibid. and C. D. Watson, "II. Paints, Plastics, and Floor Materials," ORNL-382 (Sept. 26, 1949).

16. H. Levin, "The Proper Role of Detergents in Relation to Radiological Decontamination; Technical Command Interim Report," Army Chemical Center, TCIR-627 (Feb. 5, 1951).

17. E. R. Tompkins, S. W. Mayer, "Ion Exchange as a Separations Method. III. Equilibrium Studies of the Reactions of Rare Earth Complexes with Synthetic Ion Exchange Resins," J. Am. Chem. Soc., 69: 2859 (1947).

18. G. E. Boyd, J. Schubert, A. W. Adamson, "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. I. Ion Exchange Equilibria," J. Am. Chem. Soc., 69: 2818 (1947).

19. E. R. Tompkins, J. X. Khym, W. E. Cohn, "Ion Exchange as a Separations Method. I. The Separation of Fission-Produced Radioisotopes, Including Individual Rare Earths, by Complexing Elution from Amberlite Resin," J. Am. Chem. Soc., 69: 2769 (1947).

20. L. Imre, "Adsorption leicht- und schwerlöslicher Elektrolyte an aberflächenvorgängen," Z. angew. Chem., 43: 875 (1930); Adsorptionsvorgängr an koagulierenden Nieder-schlägen. II. Uber den Mechanismus der Adsorption in Elektrolytlösungen," Z. physik. Chem., A153: 127 (1931) et seq.

21. W. Shelberg, R. Fuller, L. Graham, B. Lane, J. Mackin, L. Wentzler, "Chemical Decontamination of Stainless Steel and 24ST Alclad Aluminum," AD-337(C) (July 24, 1951).

22. D. O. Campbell, M. L. Kilpatrick, "A Kinetic Study of the Hydrolysis of Pyrophosphates," J. Am. Chem. Soc., 76: 893 (1954).

23. W. W. Hawes, L. Leventhal, "Survey of Decontamination. III. Decontaminability of Metals and Alloys," AD-75(C) (March 3, 1949). [abs. in AD-312(A)].

24. Ibid., "V. Decontaminability of Vitreous Enamels. Interim Report," AD-99(C) (April 8, 1949).

25. W. W. Hawes, B. Singer, E. C. Arbuckle, A. M. Branch, "Survey of Decontamination. XII. Decontaminability of Vitreous Enamels," AD-162(C) (Aug. 11, 1949).

26. W. W. Hawes, L. Leventhal, "Survey of Decontamination. II. Decontaminability of Aircraft Paints," AD-64(C) (Jan. 28, 1949) [abs. in AD-312(A)].

27. W. W. Hawes, B. Singer, E. C. Arbuckle, A. M. Branch, "Survey of Decontamination. XI. Decontamination of Weathered Aircraft Paints. Interim Report," AD-154(C) (Aug. 8, 1949).

28. L. Graham, B. Lane, J. Mackin, W. Shelberg, L. Wentzler, "Chemical Decontamination of Navy Grey Paint," AD-323(C) (May 16, 1951).

29. S. W. Mayer, "Notes on the Decontamination of Gray Deck Paint and Blue Airplane Lacquer," AD-186(Z) (Dec. 28, 1949) [abs. in AD-312(A)].

30. Ibid., "Notes on the Decontamination of Painted Steel. Interim Report," AD-47(Z) (Sept. 15, 1948).

31. H. Wellhouser, "Decontamination of Painted Surfaces by Steam Cleaning. Interim Report," AD-314(T) (April 19, 1951).

32. W. W. Hawes, L. Leventhal, "Survey of Decontamination. I. Decontaminability of Resins and Plastics," AD-86(C) (March 22, 1949) [abs. in AD-312(A)].

33. W. W. Hawes, B. Singer, "Survey of Decontamination. IX. Decontaminability of Proposed Composition Decking Material (Fibron). Interim Report," AD-143(C) (July 30, 1949).

34. Ibid., "VIII. Decontaminability of (1) Several Miscellaneous Materials and (2) Natural and Synthetic Rubbers," AD-141(C) (July 18, 1949).

35. Ibid., "X. Decontaminability of Woods," AD-146(C) (Aug. 10, 1949).

36. Ibid., "XIV. Behavior of Painted Wood. Interim Report," AD-202(C) (Feb. 21, 1950).

37. H. F. Mathiesen, P. E. Zigman, "Studies Concerning the Contamination and Decontamination of Painted Concrete," AD-107(X) (April 15, 1949) [abs. in AD-312(A)].

38. W. W. Hawes, B. Singer, "Survey of Decontamination. XIII. Relative Behavior of Several Papers. Interim Report," AD-196(C) (Feb. 7, 1950).

39. C. D. Watson, T. H. Handley, G. A. West, "Decontamination and Corrosion Resistance Properties of Selected Laboratory Surfaces," ORNL-732 (Aug. 29, 1950) (AECD-2996 Rev., Oct. 3, 1950).

40. (a) C. F. Miller, D. Bomberger, L. B. Werner, "Preliminary Report on Synthetic Sea Water Contaminants," USNRDL-391 (Sept. 19, 1952).

(b) W. E. Shelberg, J. L. Mackin, W. B. Lane, "Contamination Decontamination Characteristics of Clean and Soiled Navy Gray Paint Contaminated at Operation Jangle," USNRDL-437 (Sept. 28, 1953).

(c) C. F. Miller, R. Cole, W. J. Herman, M. Nuckolls, "Decontamination of Fission Products and Other Atomic Bomb Detonation Debris," USNRDL-439 (Nov. 24, 1953).

(d) C. F. Miller, R. Cole, R. K. Fuller, L. J. Graham, W. B. Lane, M. Nuckolls, J. F. Pestaner, D. Sam, "Influence of Some Decontamination Conditions and Methods on Decontamination Ratios," USNRDL-441, (Nov. 4, 1953).

(e) W. E. Shelberg, W. B. Lane, R. K. Fuller, L. J. Graham, "A Laboratory Scale Investigation of the Decontamination of Glossy Sea Blue Aircraft Lacquer by Hosing," USNRDL-442 (Feb. 11, 1954).

41. C. F. Miller, R. Cole, W. J. Heiman, "An Investigation of Synthetic Contaminants for an Atomic Burst in Deep Sea Water," USNRDL-411 (Aug. 6, 1953).

42. W. H. Baldwin, "Equipment Decontamination. Final Report," CN-2208 (for period July 15 to Dec. 1, 1944).

43. R. E. Connick, W. H. McVey, "The Aqueous Chemistry of Zirconium," J. Am. Chem. Soc., 71: 3182 (1949) (AECD-2272; UCRL-101, March 1, 1948).

44. C. D. Watson (ORNL), "A General Decontamination Manual for the Idaho Chemical Processing Plant," IDO-26081 (March 11, 1953).

45. M. D. Peterson, "Equipment Decontamination," CN-1617 (May 29, 1944).

46. A. J. Cruikshank, "The Removal of Adsorbed Fission Products from Stainless Steel," CI-180 (January, 1950).

47. "Chemical Technology Division Quarterly Progress Report for Period Ending February 20, 1953," ORNL-1494, p. 13 (March 24, 1953).

48. "Chemical Technology Division Quarterly Progress Report for Period Ending November 20, 1950," ORNL-936 (Jan. 31, 1951).

49. M. R. Bennett, "Electrodecontamination of Stainless Steel," ORNL-1608 (Oct. 13, 1954).

50. D. G. Reid, "Pilot Plants Section Report for August and September, 1949 (Technical Division, Chemical Technology Department)," ORNL-490 (Dec. 27, 1949).

51. J. M. Smith, J. G. Bradley, "Observations and Evaluation of the Decontamination Procedures Employed at Oak Ridge National Laboratories Redox Pilot Plant Equipment," HW-14532 (Sept. 19, 1949).

52. D. G. Reid, "Pilot Plants Section Report for September-October, 1950 (Chemical Technology Division)," ORNL-885 (Nov. 28, 1950).

53. H. P. Wood, "Decontamination of the Purex Pilot Plant," ORNL-1242 (May 5, 1952).

54. L. A. Welsch, E. J. Reber, "SPRU Cell No. 1 Decontamination during December, 1950," KAPL-493 (March 10, 1951).