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DECEMBER, 1964 to AUGUST, 1965

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DECONTAMINATION STUDIES - BATTELLE-NORTHWEST LABORATORIES,
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INTRODUCTION

This report describes the work done by Battelle-Northwest Laboratories on decontamination from the time of the last RDIEG meeting (December, 1964) to August, 1965. It is written for presentation at the Ninth Meeting of the USAEC Reactor Decontamination Information Exchange Group, September 1 and 2, 1965, Washington, D. C.

SUMMARY

The decontamination activity described in this report includes: (a) laboratory studies to evaluate reagents, and (b) actual decontamination of 2 steam generators at New Production Reactor.

A satisfactory reactor decontaminant must have 3 characteristics: (a) it must remove the films to the bare metal; (b) it must dissolve the films; and (c) it must not form a precipitate during the time it is in the reactor. Satisfactory test procedures have been developed to test these three characteristics and evaluate decontaminants more realistically.

In laboratory tests, a proprietary oxalic acid solution appeared to be more effective than any other tried. No excessive corrosion was noted.

Special reagents to dissolve high fired ceramic core materials (UO_2 and PuO_2) are being developed and evaluated. Phosphorous acid, sulfuric acid and a mixture of sulfuric and nitric acids were effective. Corrosion of 304 stainless steel was low.

Two N Reactor steam generators were decontaminated to facilitate inspection and repair. The APSUL procedure was tried, but control of concentrations was inadequate and decontamination factors were low, ranging from 1.6 to 9.0. No excessive corrosion was noted.

LABORATORY STUDIES

Efficiency of Decontaminating Solutions (R. D. Weed)

Variations of several two-step decontamination procedures (alkaline permanganate + acid or salt) were evaluated. The alkaline permanganate presently used is the 18,3 mixture (18% NaOH, 3% KMnO_4). A more dilute mixture would require less chemicals, be easier to use, simplify rinsing, result in less solid active waste to be disposed of, and probably be less corrosive. The actual results are shown in Table I. Note the very low D.F. obtained when the AP is not used. With sulfamic acid, the decontamination factor appeared to be unaffected by changes in concentration of the AP. In other cases the more concentrated AP appears more effective; these results are being checked.

TABLE I

Decontamination of Sections of N Reactor Steam Generators

	<u>Composition of</u> <u>AP Pretreatment</u>		<u>Activity Reading</u>		<u>Decontamination</u> <u>Factor</u>
	<u>% NaOH</u>	<u>%KMnO₄</u>	<u>Before c/m</u>	<u>After c/m</u>	
Oxalic*	0	*	25,000	17,000	1.5
60 g/l, 80 C	5	3	37,000	2,500	15
1 hour	10	3	32,000	1,500	21
	18	3	32,000	500	64
Sulfamic*	5	3	35,000	3,700	9.5
90 g/l, 60 C	10	3	35,000	3,200	11.0
1 hour	18	3	35,000	3,500	10.0
ACE*		*	32,000	26,000	1.2
20 vol %, 80 C	5	3	35,000	5,500	6.4
	10	3	35,000	5,000	7.0
	18	3	32,000	3,000	11.0
ACE*		*	32,000	20,000	1.6
20 vol %, 80 C	5	3	35,000	3,000	11.7
6 hours	10	3	35,000	2,500	14.0
	18	0	32,000	1,500	21.3

* Proprietary

The second step is a proprietary mixture containing an acid or a salt such as H_3PO_4 , HNO_3 , $NaHSO_4$, oxalic acid, sulfamic acid, or ammonium citrate (at various pH values with or without EDTA). Several of the reagents are ineffective or excessively corrosive. At present, 3 reagents are under test: a proprietary mixture of oxalic acid and other compounds, a proprietary compound of ammonium citrate + EDTA at pH 7, and a proprietary compound containing principally sulfamic acid. The oxalic acid reagent is a vast improvement over other proprietary oxalic reagents previously used, because it does not form an insoluble precipitate except after long standing (>40 hours).

A series of beaker experiments was run using sections ($\sim 1" \times 1/2"$) of PRTR jumpers. The variables which were evaluated were: concentration of AP, composition of acid or salt solution, and type of film on sample. The results are shown in Table II.

Again the effect of concentration of the NaOH in the AP appears to be of minor importance. Note, however, that the concentration of the $KMnO_4$ (3%) was not changed. The APOX procedure (alkaline permanganate followed by the proprietary oxalate solution) is clearly superior; the APSUL (alkaline permanganate followed by a proprietary sulfamic acid) gives a much lower D.F.; the APACERD (alkaline permanganate followed by the ammonium citrate-EDTA) is not very efficient.

The results using the different procedures are illustrated in Figures 1 and 2. The samples as received (Figure 1-a) had dark brown or black films. The loose activity and films were removed by scrubbing. The appearance, as shown by Figure 1-b, was not changed by these operations. In Figure 2 are shown the jumper sections after chemical decontamination. The samples in the illustration are arranged to accord with Table II. Note that those samples which were decontaminated to background levels were also completely defilmed.

In other tests using, as samples, sections of N Reactor steam generator tubing, decontamination factors were: APOX, 64; APSUL, 10; APACERD, 11. The APACERD is a potentially attractive decontaminant because it is less corrosive, since it is neutral (pH ~ 7). However, the efficiency is not as good as for the APOX, especially on the long-term films (e.g., PRTR jumpers). The efficiency can be increased by longer exposure; for example, for APACERD after 6 hrs, the D.F. is 21. Longer exposure will of course also increase D.F. for any other reagent; it will also increase corrosion.

Effect of Film Characteristics on Decontamination Efficiency (R. D. Weed)

It has been found consistently that ease of decontamination is related inversely to the length of exposure to high-temperature operation. The N Reactor tubing, which has been exposed for only a few months, is much easier to decontaminate than the PRTR jumpers, which have been exposed for 2 to 3 years or longer. This conclusion is illustrated in Tables I and II. The APACERD process is moderately effective in decontaminating N Reactor tubing (DF of 11) but is virtually without effect on PRTR jumpers (DF of 1.7).

In order to furnish samples for decontamination evaluations as well as to determine rates and patterns of activity buildup on PRTR primary system surfaces, bottom and/or top jumpers are removed periodically (one/3 months) from PRTR.

TABLE II

Decontamination of PRTR Jumpers with Various Reagents

Jumper Number	2049	1249	1253	1356	1546	1455
Months of Service	<u>26</u>	<u>22</u>	<u>22</u>	<u>20</u>	<u>6</u>	<u>6</u>

Ammonium Oxalate Treatment: 60 g/l, 1 hour, 76 C.

5% Caustic

Initial activity (mrad)	270	140	120	160	7	11
Final activity (mrad)	Bkgd*	23	21	42	Bkgd	2.5
D.F.	270	6.1	5.7	3.8	7	4.4

10% Caustic

Initial activity (mrad)	385	140	140	130	6.5	11
Final activity (mrad)	Bkgd	28	30	31	Bkgd	2.5
D.F.	385	5.0	4.7	4.2	6.5	4.4

18% Caustic

Initial activity (mrad)	600	150	140	140	8	12
Final activity (mrad)	Bkgd	28	33	27	Bkgd	2.5
D.F.	600	5.4	4.2	5.2	8	4.8

Ammoniated-EDTA Treatment: 25 volume %, 1 hour, 77 C.

5% Caustic

Initial activity (mrad)	420	130	160	145	5	11
Final activity (mrad)	60	70	100	100	1	5
D.F.	7.0	1.9	1.6	1.5	5	2.2

10% Caustic

Initial activity (mrad)	600	120	125	140	9	12
Final activity (mrad)	120	60	75	80	1	6
D.F.	5.0	2.0	1.7	1.7	9	2

18% Caustic

Initial activity (mrad)	800	115	130	155	7	9
Final activity (mrad)	140	60	75	90	1	4
D.F.	5.7	1.9	1.7	1.7	7	2.3

Sulfamic Acid Treatment: 90 g/l, 1 hour, 67 C

5% Caustic

Initial activity (mrad)	500	120	110	120	6	12
Final activity (mrad)	18	42	29	39	1	5
D.F.	28	2.9	3.6	3.1	6	2.4

10% Caustic

Initial activity (mrad)	370	120	140	130	8	12
Final activity (mrad)	16	31	41	40	1	4
D.F.	23	39	3.4	3.3	8	3

18% Caustic

Initial activity (mrad)	700	130	115	135	7	10
Final activity (mrad)	26	37	34	42	1	3
D.F.	27	3.5	3.4	3.2	7	3.3

*Background reading = ~1 mrad/hr

FIGURE 1. Coupons from PRTR Primary System Piping

a. As-received

b. After scrubbing

1746-T

a.

b.

1154-B

2049

1847-2

a.

b.

1253

1249

1546

a.

b.

1455

1548

FIGURE 2. FTIR Coupons Decontaminated by 2-Step Procedure Using Proprietary Compounds

* Proprietary

Sections of some of these jumpers were decontaminated using different procedures. The results, given in Table II and Figures 1 and 2, do show that consistent results can be obtained and relative efficiencies of different reagents may be determined using these samples. The most striking thing about Table II is the difference in degree of removal of activity from Jumpers 2049 and 1249. Both jumpers had been in the PRTR primary system since before the decontamination (November, 1962). This can best be illustrated by examples: Jumper 2049 was exposed for 26 months (Nov., 1962 to Jan. 7, 1965) and was decontaminated on June 9, 1965 using the APOX procedure. The activity level before decontamination was 600 mrad/hr; the decontamination procedure removed activity down to background. Jumper 1249 was exposed for 22 months (Nov., 1962 to Sept., 1964) and was decontaminated on June 9, 1965 using the APOX procedure (identical to procedure used for Jumper 2049). The activity level before decontamination was 150 mrad/hr and the activity level after decontamination was 28 mrad/hr. Thus, for Jumper 2049, the DF was >600 , while for Jumper 1249, the DF was 5.4. As seen in the table, the results are all consistent (600/5.4, 385/5.0, 270/6.1, 7.0/1.9, 5.0/2.0, 5.7/1.9, 23/3.9 and 27/3.5). It seems that there is an essential difference in the characteristics of the films on the 2 jumpers.

The only exposure experienced by Jumper 2049 and not by Jumper 1249 was during the period September, 1964, to January, 1965. It is interesting to note that during this same period, the activity of the PRTR primary system, as measured by the shutdown activity measurements, started to rise. As of now, no reason for change in characteristics of film or activity levels is apparent.

PRTR Shutdown Radiation Measurements (L. D. Perrigo)

The radiation coming from the buildup of activated corrosion products, wear products and coolant borne impurities in the PRTR impedes reactor operation and maintenance. The severity of this buildup problem increases with time and any period of off-standard operation results in increased amounts of material for activation.

Recent measurements have shown a marked change in the buildup of radioactivity in the PRTR Primary System. The radiation intensity variations at two representative sites during the last 20 months are shown qualitatively in Figure 3. The gradual increase in the 8/63 - 7/64 period represents a steady rate buildup of radioactivity following the 1962 primary system decontamination. An unknown change in operation occurred during August or September, 1964. The buildup following this change has been at a higher rate.

These buildup rate increases have been confirmed by the much greater radiation exposure experienced by operating and maintenance personnel in the past few months.

FIGURE 3. Shutdown Radiation Measurements at PRTR

Characteristics of a Satisfactory Reagent for Decontaminating Nuclear Reactors (J.A.Ayres)

Small pieces or components which are to be descaled, defilmed or decontaminated are usually placed in a tank filled with the decontaminating (or defilming) agent at elevated temperatures for a given time.

The first reaction of the decontaminant is the removal of the film or scale (usually by attack at imperfections) and undercutting. The film or scale as it is removed drops to the bottom of the tank and forms a layer of sludge. On long standing, this film may or may not dissolve, but this causes no concern. The defilmed piece with all the scale removed is withdrawn and rinsed. The decontamination factors are high.

When a reactor is decontaminated, however, it is necessary to fill the primary system with the decontaminant, recirculate (perhaps), empty the reactor and rinse by the same fill, recirculate, empty technique. Reactors are invariably built in such a way that there are many regions of low flow where debris can accumulate. This is especially true during a decontamination when pumps having a relatively small capacity are used for fill and drain. This unfortunate situation will probably exist for some time to come, so the engineer in charge of decontamination must take this into consideration when recommending chemicals or procedures for decontamination.

If the decontaminant removes but does not dissolve the film, this film will be transported around the system and settle in the low spots. Decontamination then will accomplish nothing but a redistribution of the activity with only partial removal. In fact, decontamination may actually make things worse, because the activity may be transported from the shielded core region to the unshielded region.

Therefore, a satisfactory decontaminant must accomplish 2 things:

- a. It must remove the film.
- b. It must dissolve the film.

If the film is dissolved and remains dissolved, the activity can be easily removed by draining the decontaminant and rinsing. It is necessary of course that the film remain in solution and no precipitate form before the decontaminant is drained. Therefore, as a corollary to b above, the decontaminant must not react with materials in solution or with the materials of construction to form a precipitate.

A realistic test program has been devised to evaluate candidate decontaminating chemicals, using the principles mentioned above.

Prototypical Testing of Decontaminants: ~~Sulfamic Acid~~ (R.D. Weed)

Three chemical decontaminants were tested to evaluate their capability for removing and dissolving the crud and film from portions of N Reactor steam generator tubing. The samples to be decontaminated were placed in a 50-ml graduate, which was then filled with the decontaminant, thus giving a relatively large surface area for a very small amount of decontaminant. The tests are discussed in detail below. The pretreatment in all cases was 1 hour in a 18,3 alkaline permanganate solution at 105 C.

Proprietary Sulfamic: 90 g/l, 60-70 C, 1 hour, surface area of sample = 135 cm², volume of acid solution used 40 ml, surface area/volume = 3.2 cm²/ml.* After treatment, undissolved flaky and flocculent material was observed settling to the bottom of the cylinder. The internal film on the tubing sample was only partially removed even though the color had been changed from black to red. About 95% of the activity was removed from the tubing, but some of the film remained as a sludge in the bottom of the graduate.

Proprietary Oxalic: 60 g/l, 70-80 C, 1 hour, surface area of sample = 133 cm², volume of acid solution used = 40 ml, surface area/volume = 3.2 cm²/ml.* After treatment, the solution was a yellow color with no observed precipitate. All of the film was removed from the internal as well as external surfaces of the sample. About 98% of the film and activity were removed (D.F. ~60) and no undissolved sludge remained.

Proprietary ACE: 60 ml to 190 ml of water, 80 C, 2.25 hours, surface area of sample = 138 cm², volume of acid solution used = 52 ml, surface area/volume = 2.6 cm²/ml.* After 1 hour, the solution was speckled with flaky material. The sample was still filmed. After 2.25 hours, the sample was defilmed; undissolved material was observed settling to the bottom of the cylinder. About 98% of the film and activity were removed from the tubing, but a considerable fraction of the film and associated activity remained as sludge in the bottom of the graduate.

The results are shown in Figure 4.

* The calculated ratio of surface to volume for a typical reactor is 1.3-3.2 cm²/ml.

FIGURE 4. Descaling of Sections of N Reactor Primary System Piping

Dissolution of High-Fired UO_2 - PuO_2 and PuO_2 (LD Perrigo)

Ceramic plutonium fuel decontamination processes are being developed to promote the utilization of the Plutonium Recycle concept since the operation and maintenance of such reactors can be severely restricted when they become contaminated with highly irradiated fuel rupture debris. Reagents commonly used for dissolving ceramic fuel materials are extremely corrosive to certain reactor components while standard reactor decontaminating solutions are safe but ineffective.

Three new decontamination processes have been developed in the laboratory. A boiling (136 C) 75% H_3PO_3 solution and non-aqueous 90% H_2SO_4 - 10% HNO_3 at 155 C dissolved both high-fired UO_2 -1% PuO_2 (~200 mesh Tyler sieve) and PuO_2 (~325 mesh Tyler sieve). High-fired PuO_2 was also effectively dissolved in 155 C, 100% H_2SO_4 . The results of these studies are given in Table III.

TABLE III

Plutonium Ceramic Dissolution Processes

<u>Material</u>	<u>Effectiveness, % dissolved</u>		
	<u>1 hr</u>	<u>4 hrs</u>	<u>21 hrs</u>
1. PuO_2			
(a) 75% H_3PO_3	17%	62%	100%
(b) 90% H_2SO_4 - 10% HNO_3	25%	69%	100%
(c) 100% H_2SO_4	65%	96%	100%
2. UO_2 -1% PuO_2			
(a) 75% H_3PO_3	5.3%	100%	95%
(b) 90% H_2SO_4 - 10% HNO_3	68%	95%	100%
(c) 100% H_2SO_4	ineffective		

Additional information on the effect of surface area and modes of fuel preparation on dissolution rates, corrosion, and the effects of ceramic fuel rupture debris distribution in flowing systems is being obtained. Evaluation of the corrosion effects on 304 stainless steel are underway. Preliminary data are: 100% H_2SO_4 at 150 C, 0.02 mils/day; 90% H_2SO_4 , 10% HNO_3 at 125 C, 0.4 mils/day; and 75% H_3PO_3 at 120 C, about 4 mils/day.

DECONTAMINATION OF 2 N REACTOR STEAM GENERATORS (AP Iarrick and RD Weed)

The activity levels at N Reactor, which have been gradually increasing since startup, are still low enough that they do not complicate routine operation. The readings at the insulated piping surface are generally less than 15 mr/hr, because most of the activity is shielded by the piping and insulation. However, it was desired to decontaminate 2 steam generators to facilitate inspection and repair. On March 15, the steam generators were decontaminated using an APSUL procedure: alkaline permanganate (18,3) at 105 C for 2 hours, water rinse, dilute sulfamic acid* rinse, concentrated (9%) sulfamic acid* at 70 C for 2 hrs, and water rinse. Even though a great deal of thought and planning had gone into the decontamination, inadequate design of some parts of the system resulted in off-standard conditions. Leakage caused excessive

*Proprietary

dilution of the reagents. The diluted reagents were not efficient and the decontamination factors were low, ranging from 1.6 as measured on the secondary side of one exchanger to 9.0 as measured on the outside of pipes and valves. The film and activity in general were effectively removed from carbon steel surfaces and only partially removed from stainless steel surfaces. These results again show that it is necessary to use the correct conditions if activity is to be removed effectively.

Additional examinations of several pieces of tubing removed from the steam generators revealed that partial cleaning and film removal had occurred; the film was a reddish-brown color instead of the normal black color. In areas of the tubes near the tube sheet, the film had been removed; in areas further from the tube sheet (between baffle 2 and 3) the film was partially stripped; still further removed from the tube sheet (between baffle 4 and 5) the film appeared to have only changed color from black to reddish-brown.

Coupons of several alloys were installed in the turret of the 2A steam generator to monitor the corrosion during the decontamination. Total corrosion penetrations are given in Table IV.

TABLE IV

Decontamination Corrosion Measurements

<u>Alloy</u>	<u>Penetration, mils</u>
A212 Carbon Steel	0.4
Al06 Carbon Steel	0.3
Stellited A212 CS.	0.02
440-A Stainless Steel	0.3
416 Stainless Steel	0.3
440-C Stainless Steel	1.3
A212 CS welded to 304 SS	0.2
304 Stainless Steel	0.01
316 Stainless Steel	0.02
Haynes 25	0.004
17-4 PH Stainless Steel	0.05
304 SS Steam generator tubing	0.02

Some pitting was noted on the A212 CS, 440-A SS, 416 SS, and 440-C SS. There was no cracking on stressed U-bend samples of 304 SS.

A carbon steel corrosion probe installed in the temporary piping during the decontamination to continuously measure the corrosion gave a total penetration of 0.6 mils, which agrees with the above coupon data. Most of the corrosion occurred during the dilute acid step. In future decontaminations, it will be desirable to add some inhibitor to the dilute acid rinse.

The major isotopes found were Sb^{124} , Fe^{59} , Mn^{54} , Zr-Nb^{95} , Cr^{51} , Co^{60} , Ru^{103} , Ce^{141} , and Zn^{65} . The total amount of each isotope present was significantly reduced by the decontamination; however, some isotopes were more effectively removed than others. The Fe^{59} composed 20 to 50% of the total activity after the decontamination while Mn^{54} , Cr^{51} , Co^{60} and Zr-Nb^{95} each composed 10 to 20% of the total activity.

Analyses of the radiochemical data from the liquid samples which were taken periodically during the decontamination show that a total of two curies of activity was removed. Considerable Cr^{51} , Mn^{54} , Fe^{59} , Co^{60} and Zn^{65} and small amounts of Sb^{124} , Ru^{103} and Zr-Nb^{95} were removed during the alkaline permanganate step. Large amounts of Cr^{51} , Mn^{54} , Fe^{59} , and Co^{60} and small amounts of Ce^{141} , Ru^{103} , and Zr-Nb^{95} were removed during the acid steps.