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LABORATORY INVESTIGATION OF DECONTAMINATING SOLUTIONS FOR PRIMARY
LOOP DECONTAMINATION IN THE NEW PRODUCTION REACTOR

by

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PRELIMINARY REPORT

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I. INTRODUCTION

An investigation of methods for decontaminating the primary loop of the New Production Reactor (NPR) is described. The decontamination problem is unusual because both carbon steel and stainless steel are used in the loop.

The Coolant System's Development Operation is investigating possible NPR decontamination procedures in test loops. Preliminary beaker scale testing of several potential decontaminating solutions was done by the Development and Corrosion Operation. The latter work is described in this report.

II. OBJECTIVE

The purpose of this document is to describe the laboratory testing of candidate decontaminating solutions for the New Production Reactor. The solutions were evaluated on the basis of (1) ability to decontaminate, and (2) corrosivity.

III. SUMMARY AND CONCLUSIONS

A. Decontamination factors ranging from fifty to several thousand were obtained with several different combinations of cleaning solutions. In general, fission product activity was removed to a lower residual level than was activated corrosion product activity, and carbon steel was easier to decontaminate than was stainless steel.

B. It was necessary to completely remove the oxide film from the metal surfaces to obtain adequate activated corrosion product decontamination. The best techniques found for this purpose were two-step processes. These consisted of treatment with alkaline permanganate solution, followed by treatment with an acidic solution. Several acids, both mineral and organic, were found satisfactory for the second treatment.

C. Descaling procedures were also satisfactory for decontaminating fission product and uranium dioxide contamination. However, nearly complete removal of this type contamination was achieved in some cases without descaling. Uranium dioxide was dissolved and more than ninety-seven per cent of the fission product contamination was removed by treatment with a non-corrosive solution containing hydrogen peroxide and sodium carbonate, plus buffering, complexing, and wetting agents.

D. Average carbon steel corrosion rates were estimated to be 0.15 - 0.25 mils per decontamination when the descaling decontamination techniques were used. Local attack in some areas of the loop may exceed these rates because of galvanic and other effects.

IV. EXPERIMENTAL PROCEDURE

A. General

The metal specimens used for decontamination testing were circular wafers approximately 1.5 inches in diameter and 0.125 inches thick. Metals studied

were 302 and 304-L stainless steel, A245-52T Grade A carbon steel, and Zircaloy-2. The surfaces had to be contaminated with representative radioactivity prior to the decontamination tests. The two general types of contamination expected in the NPR loop-activated corrosion products and fission products were studied in separate experiments.

B. Preparation of Activated Corrosion Product Contaminated Surfaces

Coupons contaminated with activated corrosion products were obtained by exposing test wafers in the KER recirculating in-pile loops. In most cases the wafers were in the loop, at temperature, for about thirty days. Conditions of water quality, pH, and temperature duplicated those planned for the NPR. The in-pile portion of the KER loops is Zircaloy-2. The out-of-pile portion is carbon steel in KER-1 (where most of the coupons were exposed) and stainless steel in the other loops (where the remainder of the coupons were exposed).

The exposure in the loops covered the wafers with an adherent black oxide film which was radioactive due to incorporated activated crud. Exposed wafers were rinsed with water and maintained in an air-dried condition in desiccators until decontamination tests were performed.

C. Preparation of Fission Product Contaminated Surfaces

The contamination resulting from a fuel element failure was simulated in the following manner. First, the test wafers were coated with oxide films which were non-radioactive but otherwise typical of those expected on NPR loop components. The oxide films were obtained by exposure of wafers to pH 10 water at 300 C in Elmo-5, an out-of-pile recirculating loop.

The oxidized wafers were then contaminated with uranium dioxide and fission products in the laboratory. Irradiated uranium metal (total exposure ranged from 7×10^{17} to 2×10^{19} nvt) was reacted with water in an autoclave also containing the oxide-coated test wafers. The autoclave was heated to 195 C and held at this temperature 15 to 60 minutes, depending upon the age of the irradiated uranium. After the autoclave reached temperature, agitation was supplied by a magnetically driven Teflon-covered stirring bar. Following contamination, the wafers were rinsed with water and acetone. Gamma activity of the individual wafers ranged from 3 to 10 mr/hr depending upon the age of the uranium. Carbon steel surfaces adsorbed, on the average, about 10 per cent more activity than did stainless steel surfaces.

D. Decontaminating Procedure

The relative effectiveness of candidate decontaminating procedures was determined by immersing contaminated wafers in the test solutions at chosen standard conditions. Glass equipment was used. Flow of solutions past contaminated surfaces was simulated by rotating the wafers in the solutions. A solution velocity, past the contaminated metal surface, of about one foot per second was approximated in this manner. Two ratios of decontaminating solution volume to contaminated surface area were used, 1000 ml/40 sq cm during the early part of the program, and 50 ml/40 sq cm during more recent studies.

Decontamination efficiency was evaluated by the decrease in gamma activity. A gross gamma count of the activity on the wafers was made with a gamma scintillation counter before and after each decontamination treatment. Decontamination factors (gross gamma activity before decontamination/gross gamma activity after decontamination) were then calculated.

Individual isotopes were also studied by means of the gamma spectrometer.

3. Corrosion Testing

Corrosion tests, to have validity for this system, must take account of many factors, such as galvanic and crevice corrosion, erosion, previous history of the surface, and dissolved iron and oxygen. Although expected corrosion in the NPR loop can best be determined in loop tests (as is being done by the Coolant Systems Development Operation), it was also desirable to compare the corrosivity of the decontaminating agents in the laboratory concurrently with the decontamination tests.

A standard technique for laboratory determination of corrosivity was adopted. Galvanic coupling and dynamic conditions were used. Variations in either of these factors caused important changes in corrosion rate. For instance, in 0.5 M dibasic ammonium citrate -0.01 M ethylene diamine tetra-acetic acid at 90 C, carbon steel corrosion increased from 0.04 mils/hr, when not coupled, to 0.085 mils/hr when coupled to stainless steel with surface area 1.3 times that of the carbon steel. When coupled to stainless steel with a surface area 55 times its own, carbon steel corroded at a rate of 0.322 mils/hr. Mild agitation was used while determining these rates. The magnitude of erosion effects was estimated in separate experiments. An uncoupled carbon steel specimen corroded at a rate of 0.032 mils/hr in stagnant 0.5 M dibasic ammonium citrate -0.01 M ethylene diamine tetra-acetic acid at 90 C. When mounted on a rotating shaft, spinning at a rate calculated to give an average linear velocity of 9.8 ft/sec, a similar carbon steel specimen corroded at 0.080 mils/hr.

The corrosion rates given in this document were obtained by rotating test coupons on a shaft at a calculated average linear velocity of 7.5 ft/sec. The coupons were coupled to stainless steel plates of equal area spaced 0.125 inch from each side of the specimen. No attempt was made to exclude air, but a blanket of relatively stable water vapor shielded the solution.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The majority of the decontamination tests made in this study concerned modifications of the APACE process. The APACE process (Alkaline Permanganate-Ammonium Citrate-Ethylene diamine tetraacetic acid) utilizes two treatments in sequence. Alkaline permanganate conditions the oxide film on stainless and carbon steels so that it may be dissolved, or loosened, and flushed away with ammonium citrate. The APACE process was known to be a promising decontamination technique (1). A literature review did not uncover any other chemical method of decontamination which appeared promising for a mixed system of carbon and stainless steel.

A. Conditioning the Oxide Film Prior to Descaling

In most cases it will be necessary to completely remove the oxide film from the surface of concern to achieve good decontamination. It should be noted that descaling, in itself, does not assure good decontamination. For instance, hydrochloric acid, although an excellent descaling agent, is a relatively poor decontaminating agent.

The APACE process utilizes a treatment with alkaline permanganate to condition oxide scales for subsequent removal with acidic solutions. Several solutions were tested as replacements for, or for use in addition to, the alkaline permanganate pretreatment. Results obtained with these solutions are given in Table I. Decontamination factors obtained by use of the pretreating solution alone and obtained by use of the pretreating solution followed by a treatment in dibasic ammonium citrate are shown. The advantage of scale conditioning can be seen by comparing lines 1 and 3 in Table I. Treatment with dibasic ammonium citrate alone was somewhat effective for removal of fission products and removed some activated corrosion products from carbon steel. However, the same treatment was more effective by factors of from 16 to over 100 when preceded by an alkaline permanganate pretreatment. It should be noted that only small decontamination factors were achieved with alkaline permanganate alone. An additional treatment with an acidic solution was necessary to remove the oxide scale and achieve good decontamination.

1. FCA-1 Process

A proprietary formulation, FCA-1*, is designed for a three-step cleaning process which utilizes two successive conditioning treatments, FCA-1 and alkaline permanganate. The process originally called for a final treatment with nitric acid. Nitric acid is excessively corrosive to carbon steel; therefore, ammonium citrate was substituted. As can be seen in Table I, the use of FCA-1 as the first step resulted in slightly better decontamination than was obtained with the APACE process. However, the improvement was not large, and does not warrant the use of the expensive FCA-1 solution in the NPR, where very large volumes are needed. A modification of FCA-1, designated FCA-1A, was tested and found less effective than FCA-1.

2. INCA Process

The INCA process, developed by the General Electric Company Aircraft Gas Turbine Division for engine cleaning, involves a scale conditioning treatment with the INCA solution followed by an acid treatment: INCA solution was tested and found to be definitely less effective than alkaline permanganate as a first step in decontamination processes. For instance, comparison tests were

* Proprietary formulations are designated by code numbers in this document. The code is available from T. F. Demmitt, Hanford Laboratories Operation, or G. E. Neibaur, Coolant Systems Development Operation.

made using pretreatments of INCA, two hours at 110 C, and alkaline permanganate (0.23 M potassium permanganate - 5.4 M sodium hydroxide), two hours at 95 C. The pretreatments were followed in both cases by treatment with 10 volume per cent Phos-1 for two hours at 60 C. Overall decontamination factors of 23.6 and 10,000 were obtained for stainless steel, using INCA and alkaline permanganate pretreatments, respectively. Corresponding carbon steel decontamination factors were 32 and 2670. Wafers contaminated with fission products and uranium dioxide were used for these tests.

The INCA solution was also evaluated as a substitute for FCA-1 in a three-step process, using alkaline permanganate as the second step, and ammonium citrate as the third step. As can be seen in Table I, the advantage over using a single alkaline permanganate pretreatment was not large. The INCA solution was also tested at higher temperatures, 135 and 190 C. These tests were made in a rocking autoclave. Alkaline permanganate and ammonium citrate treatments were again used as the second and third steps of the decontamination procedure. For wafers contaminated with activated corrosion products, stainless steel decontamination factors were 130 at both 135 and 190 C; corresponding carbon steel decontamination factors were 980 and 256. Thus carbon steel decontamination was actually decreased at the higher temperature. A similar effect was noted several times during these studies. Decontamination often decreased when the carbon steel corrosion rate became large. This was attributed to the formation of a film of corrosion products which retained activity. Carbon steel corrosion during the INCA process was prohibitively severe at the elevated temperatures:

<u>Temperature of INCA Step, deg C</u>	<u>Mils Penetration During Total Process</u>	
	<u>Stainless Steel</u>	<u>Carbon Steel</u>
110	0.016	0.249
135	0.014	0.580
190	0.038	1.404

3. Other Descaling Tests

Two solutions shown to be capable of dissolving uranium dioxide were tested as film conditioning agents. The solutions contained 0.25 M sodium carbonate - 0.25 M sodium bicarbonate and either 0.25 M potassium permanganate or 0.5 N hydrogen peroxide. In both cases stainless steel was only partially descaled. Thus, while fairly adequate fission product decontamination was obtained, activated corrosion product decontamination was unsatisfactory (somewhat different experimental procedures were used for these tests so the results are not included in Table I).

One acidic solution containing 0.75 M CrO_3 - 0.5 M HNO_3 was compared with the alkaline pretreatments. Stainless steel was not descaled and, as can be seen

in Table I, the decontamination achieved was inferior to that obtained with the APACE process.

4. Alkaline Permanganate

It was concluded that the single alkaline permanganate pretreatment of the APACE process was better than any of the alternates tested. It was more economical than processes tested which used two pretreatments and more effective than any which used a single pretreatment.

The composition of the alkaline permanganate solution used in this work was generally 0.23 M potassium permanganate - 5.4 M sodium hydroxide. A few decontamination tests were made in which the composition was varied. Sodium hydroxide concentration was decreased to 1.0 M without seriously affecting decontamination; potassium permanganate concentration could not be decreased much below 0.23 M without reducing decontamination. AP-1 is a commercial alkaline permanganate solution. No significant difference was found between the decontamination obtained when this solution was used versus that obtained when laboratory-prepared alkaline permanganate was used.

For best results the alkaline permanganate conditioning treatment should be made at temperatures of 95 C, or higher. When the conditioning treatment was made at 60 C, stainless steel decontamination was definitely reduced. Carbon steel decontamination was not decreased significantly.

A two-hour treatment in the alkaline permanganate solution was used for most of the laboratory tests. However, in some instances, the treatment time was shortened to one hour, and even to ten minutes, without affecting decontamination appreciably.

Corrosion due to the alkaline permanganate treatment is insignificant compared to that caused by the succeeding acidic treatment. The corrosion rate of carbon steel in 0.23 M potassium permanganate-5.4 M sodium hydroxide solution at 95 C was determined to be less than 0.008 mils/hr. Stainless steel corroded at less than 0.001 mils/hr.

B. Film Removal

The decontamination effectiveness of APACE-type procedures depends upon properties of the acidic solution used for descaling or film removal in the second step. Several acidic treatments were compared. In these tests, contaminated wafers were first treated in 0.23 M potassium permanganate - 5.4 M sodium hydroxide for two hours at 95 C (hereafter referred to as the "standard pretreatment"). The wafers were then treated in the acidic solution being evaluated.

1. Ammonium Citrate

In the APACE process the second step involves treatment with an ammonium citrate solution. The optimum concentration appears to be 0.5 M dibasic ammonium citrate. Tests were made to determine the minimum concentration

of ammonium citrate which could be used. The results of these tests are shown in Table II. Although the numbers are somewhat erratic as in all decontamination tests, the trend is definitely toward lower decontamination with decreasing ammonium citrate concentration.

The ammonium citrate solution can be prepared by dissolving dibasic ammonium citrate crystals or by neutralizing citric acid with ammonium hydroxide to a pH of 4.5 - 4.7. Solutions prepared in both ways were equally effective for decontamination. Preparation by neutralization of the acid is more economical. Additional savings can be obtained by neutralizing with sodium rather than ammonium hydroxide. The results of several tests indicated that sodium citrate was as effective for decontamination as ammonium citrate.

Ethylene diamine tetraacetic acid (EDTA) has been added to ammonium citrate to increase ion complexing during decontamination. Tests were made to determine the optimum concentration of EDTA. The concentration was varied from 0.0 to 0.1 M without significantly changing fission product decontamination obtained with 0.5 M ammonium citrate. It was concluded that the complexing action of citrate ion in this solution was sufficient and EDTA could be omitted.

High temperatures are required for maximum decontamination with ammonium citrate. Decreasing the temperature used during ammonium citrate treatment from 90 to 60 C decreased stainless steel decontamination ten-fold; carbon steel decontamination was not changed significantly.

A series of decontamination tests were made to determine the effect of the pH of the citrate solution. The results are shown in Table III. It can be seen that the solution must be on the acid side to obtain good decontamination. At pH 4.5 a grey deposit of corrosion products formed on the surface of carbon steel. The deposit adsorbed some activity and thus inhibited decontamination.

The carbon steel corrosion rate in dibasic ammonium citrate at 90 C was 0.15 - 0.30 mils/hr, when determined using laboratory-simulated loop decontamination conditions. The corrosion rate was increased by the presence of dissolved iron. It is estimated that the iron concentration should not exceed 0.25 g/l; which caused only a twenty per cent increase in corrosion rate. The iron effect could probably be prevented by excluding oxygen from the system.

Decreasing the ammonium citrate concentration to as low as 0.1 M did not lower the corrosion rate appreciably. Raising the pH of the solution reduced corrosion somewhat but, as noted earlier, decontamination was also reduced.

Several corrosion inhibitors were evaluated. In scouting experiments, phenylhydrazine, acridine, n-butylsulfide, 1-ethylquinolium iodide, n-ethyl aniline, thio urea, n-phenyl morpholine, l-erythritol, and 2-mercaptobenzothiozole were tested. All were used at a concentration of 0.5 g/l. Acridine reduced the corrosion rate of carbon steel in 0.5 M ammonium citrate significantly. Thio urea and 2-mercaptobenzothiozole caused some reduction; the others were without effect. Further tests were made with acridine. It was found that pitting attack was accelerated by its use, although overall weight loss was low.

Stannous ion was found to be an excellent corrosion inhibitor. Unfortunately, large reductions in decontamination resulted from its use. When 0.008 M stannous acetate was added to 0.5 M ammonium citrate - 0.01 M EDTA the carbon steel corrosion rate at 90 C was reduced to 0.04 mils/hr. However, when ammonium citrate containing stannous acetate was used in the APACE process, activated corrosion product decontamination factors dropped from 114 to 27 for stainless steel and from 64 to five for carbon steel. It is thought that a layer of tin formed on the surface which reduced corrosion but also interfered with decontamination.

Several corrosion inhibitors were tested which reduced corrosion and did not interfere with decontamination. These were phenylthiourea and the commercial inhibitors, Inhib-1, Inhib-2, and Inhib-4. The use of phenylthiourea and Inhib-4 resulted in the largest decrease in corrosion rate. When used at a concentration of one g/l both reduced the corrosion rate of carbon steel in 0.5 M ammonium citrate to less than 0.10 mil/hr. Neither phenylthiourea nor Inhib-4 interfered significantly with decontamination by the APACE process.

2. Oxalic Acid

Two types of oxalic acid solutions were investigated as the second step of a decontaminating procedure utilizing the standard permanganate pretreatment. Oxal-1 is a proprietary formulation which is principally oxalic acid. It was compared with 0.25 M oxalic acid adjusted to pH 4.5 with sodium hydroxide. Typical fission product decontamination factors obtained when Oxal-1 was used were 150 and 1300, for stainless and carbon steel, respectively. The corresponding decontamination factors were 390 and 1200 when sodium oxalate was used. Decontamination results obtained with oxalic acid solutions were quite erratic. A greenish yellow film, presumed to be ferrous oxalate, was found on many of the coupons after decontamination. The film tended to decrease decontamination.

Uninhibited oxalate solutions produced intergranular corrosion of stainless steel at 90 C, the temperature used for the decontamination tests. No intergranular attack on stainless steel was found when Oxal-1 was used; carbon steel corrosion was also low, approximately 0.03 mils/hr.

3. Other Organic Acids

Lactic and acetic acid were investigated briefly. Substitution of either for ammonium citrate would decrease decontamination costs considerably. The results of the decontamination tests made using these acids were obscured by the presence, on the test wafers used, of silver-110, which is not decontaminated (see Part VI B). However, in these tests, when 0.5 M lactic acid - 0.01 M EDTA was substituted for 0.5 M ammonium citrate - 0.01 M EDTA, decontamination was halved. The reduction in decontamination was greater when acetic acid was used.

Carbon steel corrosion in both lactic and acetic acid was comparable with that in ammonium citrate. When one g/l phenylthiourea was used as a corrosion inhibitor the corrosion rate was reduced to about 0.1 mils/hr. at 90 C.

4. Bisulfate Solutions

A number of proprietary formulations consisting of sodium bisulfate plus unknown quantities of unidentified corrosion inhibitors, complexing agents, and wetting agents were tested. The use of most of these formulations resulted in adequate decontamination factors being obtained if the surfaces were first treated with alkaline permanganate. In general, the formulations were somewhat less corrosive to carbon steel than uninhibited ammonium citrate. Stainless steel corrosion was negligible except for some evidence of intergranular attack above 80 C. The manufacturer's recommended conditions for use are four to 12 oz/gal at 50-60 C.

The results of tests using several bisulfate solutions are shown in Table IV. Bisulf-6, -7, -8, -9, and -10 were also tested. The wafers used for these tests were contaminated with silver-110, which was not removed. Therefore, the results are not directly comparable with those given in Table IV. Estimated comparisons were made, by discounting the silver-110 contribution; it appeared Bisulf's-6 through -10 were slightly less effective than the other bisulfate solutions tested.

Several process variables were investigated. Stainless steel decontamination was reduced a factor of seven when the temperature of the Bisulf-4 treatment was decreased from 60 to 25 C. Carbon steel decontamination was relatively unaffected. These results are similar to those obtained with ammonium citrate.

The results of tests made to investigate the effect of decreasing Bisulf-4 concentration are given in Table V. These results indicate that concentrations as low as 20 grams/liter could be used. Below this concentration inadequate stainless steel decontamination was obtained. Adequate carbon steel decontamination was obtained using only 7.5 g/l Bisulf-4. Carbon steel corrosion was not significantly lower in 7.5 g/l than in 90 g/l Bisulf-4.

It was found that carbon steel corrosion in Bisulf-1 was decreased significantly by partial neutralization with ammonium hydroxide. Decontamination effectiveness was also reduced by this procedure. Addition of 0.05 M citric acid to the solution before neutralization resulted in much less loss in decontaminating effectiveness. The data from these experiments are shown in Table VI.

A substitute for the proprietary bisulfate formulations was prepared in laboratory. Decontamination obtained when using the laboratory formulation was similar to that obtained when using several of the proprietary solutions. The solution had the following composition, 0.75 M ammonium bisulfate - 0.05 M oxalic acid - 0.1 g/l thiourea - 0.4 volume per cent Tween 21. Carbon steel corroded at a rate of 0.14 mils/hr at 60 C in the laboratory formulation. The rate in Bisulf-1 under comparable conditions was 0.10 mils/hr. Substitution of phenylthiourea for thiourea would probably decrease the corrosivity of the laboratory formulation. Such formulations are of interest because of the economies offered; the cost per gallon of the laboratory formulation is estimated at six cents, versus 20-30 cents for the proprietary formulations.

5. Phosphoric Acid

A proprietary cleaner, Phos-1, which is principally phosphoric acid, was investigated as the second step in a decontamination process utilizing the standard permanganate pretreatment for the first step. The solution was tested at 60 and 90 C. Decontamination obtained at 60 C was somewhat lower than that obtained when using bisulfate cleaners at the same temperature.

Second Step, Following Standard Alkaline Permanganate Pretreatment	Decontamination Factor			
	Fission Product Contamination		Activated Corrosion Crud	
	Stainless Steel	Carbon Steel	Stainless Steel	Carbon Steel
10 Vol. % Phos-1, 2 hrs. at 60 C	290	1540	22.6	-
10 Vol. % Phos-1, 2 hrs. at 90 C	10000	2670	57	73

As can be seen, decontamination was considerably improved at 90 C. Carbon steel corrosion rates in 10 volume per cent Phos-1 were determined to be 0.085 mils/hr at 60 C, and 0.114 mils/hr at 90 C.

6. Sulfamic Acid

Lindsay et al developed decontaminating solutions based upon sulfamic acid (2). Their solutions were designed for a one step decontamination process and are not compatible with a mixed carbon and stainless steel system.

The decontamination effectiveness of a solution of 0.05 M sulfamic acid - 0.05 M ferrous ammonium sulfate - 1 gram/liter 2-mercapto-benzothiazole was tested at 60 C when used following the standard permanganate pretreatment. Decontamination factors for activated corrosion products were about a factor of four less than those obtained using the APACE process. The corrosion rate of carbon steel in this solution was 0.05 mils/hr at 60 C.

C. Uranium Dioxide Dissolution

When a fuel element ruptures, uranium dioxide is formed by the reaction of high temperature water with metallic uranium. Most of the fission products present remain associated with the uranium dioxide particles. Thus, to remove debris resulting from rupture of a fuel element it is necessary to dissolve the uranium dioxide.

Uranium dioxide can be dissolved by non-corrosive reagents such as hydrogen peroxide-sodium carbonate-sodium bicarbonate solutions. Potassium permanganate may be substituted for hydrogen peroxide. Hydrogen peroxide was used in most of the tests made in this study. The optimum composition appeared to be 0.25 M hydrogen peroxide-0.25 M sodium carbonate-0.25 M sodium bicarbonate-0.1 M EDTA - 1 g/l 8-hydroxyquinoline - 0.1 g/l sodium lauryl sulfate. Sodium lauryl sulfate and EDTA were added to counteract the tendency of fission products to adsorb on the oxide surfaces. The advantage obtained by using EDTA and sodium lauryl sulfate can be seen by

examining the data in Table VII. Eight hydroxyquinoline was added to increase the stability of hydrogen peroxide in the solution. Another hydrogen peroxide stabilizer, acetanilid, was also tested, as can be seen in Table VIII; it was not as effective as 8-hydroxyquinoline.

Decontamination factors of about 50 were obtained when wafers contaminated with fission products were treated with the peroxide-carbonate formulation.

VI. PROCESS CONSIDERATIONS

The results reported in the previous sections were obtained using standardized procedures designed to compare candidate reagents. Only basic variables such as temperature and chemical composition were considered. In this section investigations of other important factors are described.

A. Decontamination Immediately After a Fuel Element Failure

Uranium cooled from three weeks to three months was used for the fission product decontamination tests described in the previous sections. Two tests were made using short-cooled uranium to determine the behavior of short-lived fission products. A piece of uranium metal weighing about 0.6 gram was irradiated in a pile to a total exposure of 8403×10^{16} nvt. After cooling 24 hours, it was placed in an autoclave with precoated carbon and stainless steel wafers and reacted with pH 10 water at 195 C. The activity on the resulting contaminated wafers was due principally to neptunium-239, tellurium-132, barium-lanthanum-140, and cerium-143. Two procedures were used to decontaminate these wafers, the APACE process and the standard permanganate pretreatment followed by treatment with Bisulf-1. In both cases decontamination was completed within 52 hours after discharge of the uranium from the pile. Overall decontamination obtained was lower, by factors of 10-20 and 5-10, than that usually obtained using the APACE and alkaline permanganate-Bisulf-1 processes, respectively, for removing fission product contamination cooled over thirty days. Over 90 per cent of the activity remaining on the decontaminated wafers was due to tellurium-132. Tellurium-132 has a half-life of about three days.

B. Specific Isotope Behavior

Nearly all of the isotopes encountered in these studies were decontaminated effectively by APACE-type procedures. An exception was tellurium-132, as described above. The other major exceptions were silver-110 and antimony-124.

Silver-110 and antimony-124 were present in the activated corrosion product contamination on most of the wafers exposed in the KER loops during the latter part of this investigation. The presence of silver-110, and perhaps antimony-124 also, is due to the use of silver solder in the loops. The difficulty in decontaminating these isotopes is illustrated by the following data:

Decontamination Procedure	Decontamination Factor					
	Fe^{59}		Sb^{124}		Ag^{110}	
	Stainless Steel	Carbon Steel	Stainless Steel	Carbon Steel	Stainless Steel	Carbon Steel
APACE	87.3	53.3	2.8	1.9	6.2	4.7
Alkaline permanganate- Bisulf-10	39.5	83.4	1.9	5.5	3.0	2.9

Alkaline ammonium citrate, which might be expected to remove silver, was tested. Only slight removal (decontamination factor approximately two) was obtained.

One other example of anomalous isotope behavior was found. In a few tests of the APACE process with fission product contamination, large amounts of iodine-131 remained on the carbon steel wafers after decontamination. Radio autographic examination of the wafers showed that the iodine activity was located only at points which had been covered with red rust rather than normal black oxide film. This was encountered in only a few wafers and is considered an abnormal condition.

C. Effect of Surfaces upon Decontamination

1. Both heat sensitized (one hour at 1250 F, water quench) and non-sensitized stainless steel were used in this work and no significant difference in ease of decontamination was apparent.
2. Zircaloy-2, the third major material of construction in the primary loop of the NPR, was not descaled by the APACE-type decontamination procedures. Consequently very little activated corrosion product decontamination was obtained. Laboratory decontamination factors were typically about two. Fission product decontamination was poor also. In the laboratory tests, fission product decontamination was a factor of ten lower for Zircaloy-2 than for stainless or carbon steel coupons.
3. When freshly descaled surfaces were contaminated with uranium dioxide and fission products they were much more difficult to decontaminate than were oxide-coated surfaces. As an integral oxide film may normally be expected to exist at the time of any fuel element failure in the NPR this effect will not ordinarily be of importance.

D. Effect of Mixing Reagents

Very large volumes of radioactive waste can be generated in decontaminating the NPR. The volume could be decreased by minimizing the flushing done between steps of a decontaminating procedure. If little or no interstep flushing was done, considerable mixing of the two decontaminating solutions would occur. Results of tests made to determine the effects of mixing one-tenth volume of standard alkaline permanganate pretreating solution with

second step solutions are shown in Table IX.

The decontamination then achieved was considerably less than normal, especially for the stainless steel surfaces. A subsequent treatment with the pure second step solution resulted in good overall decontamination.

E. Single Pass Decontamination

Design of the NPR permits once-through flow of decontaminating solutions from front to rear face and to drain as well as recirculation of the solutions.

The solutions which have been discussed from the standpoint of overall loop decontamination are also applicable to once-through use. The choice of solution would depend upon conditions. Flushing with peroxide-carbonate immediately after a fuel element failure may reduce the radiation level to nearly that present before the rupture. If it is desired to lower further the general background radiation level, descaling would be required. This could be done by the usual alternating alkaline permanganate and acidic solutions. One-step acidic treatments could also be used. These would not decontaminate stainless steel. They would decontaminate carbon steel fairly well and might be sufficient because of the high ratio of carbon to stainless steel surface in the system.

VII. OTHER DECONTAMINATION PROCEDURES

The previous sections were devoted to the decontamination processes considered most applicable to the NPR. Other processes which were investigated briefly are discussed below.

A. High Pressure Techniques

The NPR primary loop offers the possibility of using elevated temperatures and pressures not usually available for decontamination applications. Several decontamination runs were made in an autoclave to test this technique. Carbon steel corrosion rates were excessive in all runs. Decontamination was also poor. Deposits, which resulted from either corrosion or decomposition of organic components of the solutions, formed on the surfaces.

B. Foam Cleaning

A technique using foam to clean piping has been developed industrially. The technique offers the advantage that only about one-tenth the normal volume of cleaning solution is required. If decontaminating solutions could be foamed, important reductions in the volume of radioactive wastes would result.

Two decontamination tests were made in which the solutions were foamed by the addition of a foaming agent. The decontamination procedures tested were the APACE process and the alkaline permanganate-bisulf-1 process. Several modifications in solution concentration were used in these tests. Sodium

hydroxide concentration in the alkaline permanganate solution was reduced to one molar in order to obtain a stable foam. The ammonium citrate for the APACE process was used as a 1.5 M solution (three times regular concentration). Increasing the strength of Bisulf-1 by addition of sulfuric acid inhibited foam formation; therefore the regular 90 gram/liter concentration was used. Wafers contaminated with activated corrosion crud were used for the tests. Each solution was foamed past the contaminated wafers at a linear velocity of about one foot per minute for two hours at 25 C. Overall decontamination factors of less than two for both stainless and carbon steel were obtained using the foamed APACE process. Stainless steel decontamination was correspondingly low when the alkaline permanganate Bisulf-1 process was used, but the carbon steel decontamination factor was 32.

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REFERENCES

- (1) Watkins, R. M., A Study of Decontamination Agents for Use in the Yankee Reactor, YAEC-90, November, 1958. (Unclassified)
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TABLE I

COMPARISON OF SCALE CONDITIONING TREATMENTS

Conditioning Treatment	Acid Treatment	Decontamination Factor			
		Fission Products		Corrosion Crud	
		Stainless Steel	Carbon Steel	Stainless Steel	Carbon Steel
None	Citrate	30.5	169	1.0	6.3
Alkaline permanganate	None	16.6	7.8	1.2	1.1
" "	Citrate	1880	2800	100	970
FCA-1	None	47.4	61	1.4	37.7
FCA-1 - Alkaline permanganate	"	(50)	(70)	1.9	54.7
" " "	Citrate	7000	29,000	330	1700
INCA	None	6.3	9.4	1.4	18.0
INCA-Alkaline permanganate	"	17	26	1.8	21.2
" " "	Citrate	>10,000	3,900	290	260
0.75 M CrO_3 - 0.48 M HNO_3	None	19.0	27.0	-	-
	Citrate	170	714	-	-

TABLE IIAPACE PROCESS: EFFECT OF CITRATE CONCENTRATION

<u>Citrate Concentration, M</u>	<u>Fission Product Gross Gamma Decontamination Factor</u>		<u>Carbon Steel Corrosion Rate, mils/hr.</u>
	<u>Stainless Steel</u>	<u>Carbon Steel</u>	
0.1	160	270	0.090
0.2	340	560	0.124
0.3	1,040	350	0.107
0.4	1,200	550	0.116
0.5	>5,000	910	0.156

TABLE IIIAPACE PROCESS: EFFECT OF CITRATE ACIDITY

<u>pH</u>	Fission Product Gross Gamma Decontamination Factor		Carbon Steel Corrosion Rate, mils/hr.
	<u>Stainless Steel</u>	<u>Carbon Steel</u>	
4.5	26,000	2,800	0.167
6.5	4,600	4,400	0.136
7.5	380	160	--
9.0	680	260	0.070

TABLE IV
BISULFATE SOLUTIONS AS DECONTAMINATING AGENTS

<u>Solution</u>	<u>Decontamination Factor</u>			
	<u>Activated Corrosion Products</u>		<u>Fission Products</u>	
	<u>Stainless Steel</u>	<u>Carbon Steel</u>	<u>Stainless Steel</u>	<u>Carbon Steel</u>
0.75 M NaHSO_4	39.7	98.5	21	56
0.75 M NH_4HSO_4 (1)	46.3	261	497	1100
90 g/l Bisulf-1	40.2	1050	990	>5000
90 g/l Bisulf-2	51.5	112	--	--
90 g/l Bisulf-4A	79.5	170	--	--
90 g/l Bisulf-12	91.3	325	2600	540
90 g/l Bisulf-14	39.8	180	430	440

(1) Also contained 0.05 M oxalic acid - 0.1 grams/liter thiourea - 0.4 volume per cent Tween 21.

TABLE V
BISULF-4A: EFFECT OF CONCENTRATION

<u>Concentration g/l</u>	<u>ACTIVATED CORROSION PRODUCT DECONTAMINATION FACTOR</u>	
	<u>Stainless Steel</u>	<u>Carbon Steel</u>
90	80	87
50	66	38
20	84	59
7.5	22	72
2.0	3.6	3.2

TABLE VI

BISULF-1: EFFECT OF ACIDITY

Treatment	pH		Corrosion Rate, mils/hr	Decontamination Factor			
	Orig.	Final		Fission Products		Corrosion Crud	
				Stainless Steel	Carbon Steel	Stainless Steel	Carbon Steel
None	0.7	0.7	0.100	595	804	210	173
NH ₄ OH adjust- ment	1.5	1.5	0.070	-	-	92	3.4
" "	2.5	2.5	0.056	-	-	32.2	1.9
" "	3.5	4.0	0.036	-	-	8.1	1.5
" "	4.5	7.2	0.025	14	19	6.0	2.3
0.05 M citric acid, NH ₄ OH adjustment	4.5	4.5	0.033	450	302	-	-

TABLE VII

EFFECT OF COMPLEXING AND WETTING AGENTS ON FISSION PRODUCT ADSORPTION
FROM 0.25M HYDROGEN PEROXIDE-0.25M SODIUM CARBONATE-0.25M SODIUM BICARBONATE

<u>Complexing or Wetting Agents Added</u>	<u>Solution Activity gamma counts/ min/ml</u>	<u>Fission Product Adsorption⁽¹⁾</u>			
		<u>Stainless Steel</u>		<u>Carbon Steel</u>	
		<u>Oxide Coated</u>	<u>Bare Metal</u>	<u>Oxide Coated</u>	<u>Bare Metal</u>
None	6250	9.65	6.40	12.70	52.4
0.1 M (NH ₄) ₂ H citrate	4948	6.64	4.44	7.61	13.3
0.1 M KCN	4361	3.30	2.90	3.90	3.30
0.1 M EDTA	6301	0.34	0.44	0.56	3.52
0.1 M EDTA - 0.125 g/l Duponal (2)	3796	0.19	0	0.21	0.25
0.01 M EDTA - 0.125 g/l Duponal	3639	3.55	2.14	6.65	1.25

(1) $\frac{\text{Gross gamma activity adsorbed on coupon/sq. cm} \times 100}{\text{Gross gamma activity/ml solution}}$

(2) sodium lauryl sulfate

TABLE VIII

HYDROGEN PEROXIDE STABILIZATION IN 0.25 M SODIUM CARBONATE -
0.25 M SODIUM BICARBONATE AT 25 C

<u>Elapsed Time, min.</u>	<u>No Stabilizer</u>	<u>H₂O₂ Remaining Per Cent Initial Concentration</u>				
		<u>Acetanilid</u>	<u>8-hydroxyquinoline</u>			
		<u>1 g/l</u>	<u>1 g/l</u>	<u>0.5 g/l</u>	<u>0.25 g/l</u>	<u>0.1 g/l</u>
5	84.1	83.5	98.0	96.5	96.5	93.7
15	52.5	60.8	88.2	86.4	88.0	91.0
30	24.4	29.0	81.9	84.2	79.6	80.7
60	1.7	2.4	70.5	76.1	50.0	17.1
90	<1.0	<1.0	61.4	69.9	4.5	1.7
120	-	-	53.4	39.1	-	-

TABLE IX

EFFECT OF INADEQUATE FLUSHING BETWEEN DECONTAMINATION STEPS

<u>Process</u>	<u>Conditions</u>	<u>Fission Product Decontamination Factor</u>	
		<u>Stainless</u>	<u>Carbon</u>
		<u>Steel</u>	<u>Steel</u>
APACE	Normal	>2000	2000
"	10 vol% alkaline permanganate in citrate	28.5	460
"	Same coupons recontacted with pure "	1500	1550
Phos-1	Normal	820	1550
"	10 vol % alkaline permanganate in Phos-1	27.4	575
"	Same coupon recontacted with pure " "	620	2750