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PEROXIDE-INHIBITED DECONTAMINATION SOLUTIONS FOR CARBON STEEL AND OTHER METALS IN THE GAS-COOLED REACTOR PROGRAM: PROGRESS REPORT, NOVEMBER 1959-JULY 1962

A. B. Meservey

OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

A search for solutions suitable for dissolving uranium dioxide powder or lumps and yet noncorrosive enough to be used for decontaminating the carbon steel EGCR charge and service machines resulted in the development of buffered oxalate solutions of controlled temperature and pH, with hydrogen peroxide added to act as corrosion inhibitor, UO_2 oxidizer, and decontamination aid. Hydrogen peroxide acts either as a corrosion promoter or inhibitor, depending on factors such as its concentration, the ratio to other ingredients, acidity, temperature, the presence of complexing agents, and the ferric ion content of the solution.

In general, oxalate-peroxide solutions for fission product decontamination from metal surfaces were superior to more conventional decontaminating solutions and had attractively low corrosion rates on carbon steel (less than 0.01 mil/hr). Solution instability, initially a serious drawback, was largely overcome. Of nearly a hundred formulations studied, the one having the best combination of long life, low corrosivity, high solvency for UO_2, decontamination power, safety, and ease of waste disposal was an aqueous solution of 0.4 $\underline{M}$ oxalic acid, 0.16 $\underline{M}$ ammonium citrate, and 0.34 $\underline{M}$ H_2O_2, adjusted to pH 4.00 with ammonium hydroxide and used at 85 to 95°C. Similar solutions at lower pH, with increased H_2O_2 concentration to maintain noncorrosiveness, were successful decontaminants at 60°C when contact times were increased to several hours. Contaminated stainless steels heated to 500°C in helium resisted decontamination in noncorrosive reagents.

Oxalate-peroxide solutions are currently recommended as UO_2 solvents and as general decontaminants for mild steel and aluminum surfaces in the GCR program, and for stainless steels which have not been strongly heated while contaminated. These solutions may also find application in the decontamination of metals used in the aqueous reprocessing of radioactive nuclear fuels. The work is continuing.

1.0 INTRODUCTION

1.1 Scope and Summary

This progress report begins with a brief general discussion of the metals decontamination problem, particularly with regard to carbon steel surfaces contaminated from the gas phase with volatile fission products and with irradiated UO_2 dust. The failure of detergents to remove ultrafine irradiated UO_2 dust from laboratory specimens led to a search for noncorrosive UO_2 solvents. Noncorrosive carbonate-peroxide mixtures dissolved the dust, but did not dissolve UO_2 lumps such as would result from broken fuel elements. The carbonate solution was unstable, and also redeposited some of the fission products, making follow-up reagents necessary for decontamination. Oxalate-peroxide was much superior as a UO_2 solvent, and was an excellent single-solution noncorrosive decontaminant but needed to be buffered against a rise in pH to maintain its decontaminating properties. Both the buffers and the oxalate reacted with the peroxide, the reaction being catalyzed by ferric ion introduced by the very slight corrosion of the steel. Hydrogen peroxide acted as a corrosion inhibitor on carbon steel (when it was above a certain minimum concentration, which depended on pH, temperature, and buffer concentration) but promoted corrosion in slightly acidic solution when its concentration fell below the minimum value. It therefore became necessary to develop "fail-safe" solutions that decomposed as slowly as possible, with a controlled and gradual rise in pH, so that the solutions never entered a corrosive phase as the peroxide concentration decreased. The decontamination effectiveness of these solutions, whose corrosion rates on carbon steel at elevated temperatures were less than 0.01 mil/hr, compared well with those of many other types of decontamination solutions.

Hydrogen peroxide was also effective as a corrosion inhibitor in several mineral acids, including hydrofluoric acid mixtures. No suitable noncorrosive methods were found for the decontamination of laboratory-contaminated stainless steel coupons baked at 500°C in helium, although oxalate-peroxide solutions were effective on baked carbon steel and aluminum, similarly contaminated. The decontamination of several stainless steel samples from gas-cooled loops in nuclear reactors was successful in oxalate-peroxide, however. The work is continuing.

1.2 Decontamination Viewed as Metal Cleaning

The art of metal decontamination is simply the art of metal cleaning carried almost to its ultimate degree of perfection. Contamination on metals consists of foreign matter on the metal surface, more or less strongly held, depending on the surface condition of the metal when the contamination occurred (i.e., oxide-coated or bare, dirty or clean, rough or smooth), the surface temperature, the physical and chemical state of the contaminant (ionic, molecular, small or large aggregates), the concentration of the contaminant, the nature of the solvent if any (gaseous, liquid, or solid), the chemical reactivity of the metal and contaminant for each other, the adhesive or surface forces operating between the metal and its contaminant, and factors operating subsequent to contamination (or during decontamination) which change some of these conditions or relations (e.g., further oxidation or reduction of metal surface, abrasion, decay of nuclide to another element, dirt overlay, change in chemical state of contaminant, etc.). When to this complex picture we add the requirement that the degree of cleanness demanded in the decontamination of metals from a large proportion of the elements in the periodic table, and their compounds, must often be thousands of times better than the requirements for industrial metal cleaning, without substantial corrosion, the magnitude of the problem becomes fully realized.

1.3 Specialization of Decontamination Methods

Metal decontamination problems are commonly not attacked from the standpoint of improving existing cleaning methods. Instead, partly because of the great diversity of the problems, the recent practice has been to tailor a method or reagent to remove the contamination under specialized conditions tolerable to the situation. These tailored methods are finding their greatest popularity in the low-corrosion decontamination of the several types of nuclear reactors. General decontamination methods for metals developed before the era of specialized methods depended rather more heavily on surface removal by strong acids, such as nitric and hydrofluoric acid, sometimes with an attempt also to complex the released contaminants to prevent redeposition. Strong acids are particularly unsuitable for low-corrosion decontamination of carbon steels but do find application with more resistant stainless steels. Several recent reviews and status reports are available on the decontamination of metals.[1-7]

1.4 Decontaminating the Experimental Gas-Cooled Reactor

One of the specialized decontamination problems undertaken at Oak Ridge National Laboratory was for the purpose of permitting direct maintenance on certain components of the Experimental Gas-Cooled Reactor (EGCR), then under construction at Oak Ridge.[8] Of particular interest were the charge and service machines, to be used while the reactor was at power, and which therefore would be partially exposed to the pressurized circulating helium coolant at 1050°F. The insides of these huge and complex machines were expected to become contaminated with irradiated UO_2 dust from defective fuel elements, volatile fission products and their daughters, other dusts such as graphite with adsorbed fission products, thoria and protactinium with their daughters if thorium was used in the fuel, and possibly lumps of UO_2 from fuel elements broken in the machines during handling.

Fortunately, exposure to the contaminated helium at 1050°F would be minimized during operation by pumping purified and cooled helium into the charge and service machines, at temperatures of 350 and 125°F and flow rates of 4200 and 1250 lb/hr respectively, with discharge through the connecting openings into the reactor core.

1.5 Requirements of EGCR Decontamination Solutions, and Purposes of this Report

The requirements of a decontamination solution for the EGCR charge and service machines were that it be effective as a heated spray, that it be essentially noncorrosive to the carbon steel which comprised the bulk of the machines, and that it dissolve both powdered and sintered uranium dioxide at a practical rate. Other desirable characteristics were that it be relatively easy to prepare and use, that it should not be overly expensive, and that it should not present unusual waste-disposal problems.

These requirements seemed to be well satisfied with mixtures of ammonium oxalate and hydrogen peroxide, with additives such as ammonium citrate or acetate to buffer the solutions at a chosen pH and retard peroxide decomposition. Carbonate-peroxide solutions were useful in dissolving finely divided UO_2 dust, but not lumps, and they needed follow-up reagents for complete decontamination. Therefore little work was done with this reagent. A description of the development and present status of peroxide reagents is one object of this report.

A second purpose of this report is to describe the present status of the development of improved reagents (buffered oxalate-peroxide, acid fluoride solutions inhibited with peroxide, etc.) for the decontamination of stainless steel and other alloy components of the EGCR, such as found in in-pile loops, mainstream blowers, and heat exchangers. Here UO_2 solvents might not be required, and somewhat more corrosive solutions could be used than would be permissible for the charge and service machines.

The decontamination studies which were begun initially for the EGCR are applicable also to the Pebble Bed Reactor (PBR), which will probably have spherical fuel elements clad in graphite. The PBR will doubtless have much more severe decontamination problems than the EGCR.

1.6 Acknowledgment

Analytical services for this work were provided by G. R. Wilson and J. H. Cooper of the Analytical Division, ORNL. Loop samples from the LITR were furnished by E. S. Collins of the General Electric Company, and samples from the Brookhaven loop by Nuclear Science and Engineering Company. Other gas-contaminated samples were provided by J. L. Scott of the ORNL Metals and Ceramics Division and R. M. Carroll of the Solid State Physics Division. The work was directed by D. E. Ferguson.

2.0 DEVELOPMENT OF REAGENTS AND METHODS

The necessary first step in the decontamination of the EGCR charge and service machines was assumed to be the removal of finely divided uranium dioxide powder, preferably by detergent action. If detergents failed, noncorrosive solvents would have to be developed, and ideally these should also be suitable for dissolving lumps of sintered UO_2 weighing up to 40 g. The next step would be the removal of volatile fission products and those that had been deposited, if any, from the solution which had dissolved the uranium dioxide. These topics will be discussed in the order mentioned.

2.1 Detergent Removal of UO_2 Dust

Steam cleaning, with detergents aspirated into the steam jet, failed as a practical method for the removal of UO_2 dust from steel. The conditions were intentionally made rigorous, to simulate the worst conditions that might be encountered in the charge and service machines. First, about 0.2 g of ultrafine UO_2 dust was prepared by sifting 2 g through a 325-mesh screen, suspending it in water in a 2-liter graduated cylinder, allowing it to settle several hours, siphoning off the top suspension containing the fines, and evaporating this suspension to dryness. About 100 mg of this powder was sealed in an aluminum capsule, and irradiated for 1 hr in the Oak Ridge Reactor in a thermal neutron flux of 1×10^{14}. After several hours of cooling, the capsule was opened and the irradiated UO_2 was shaken dry with small threaded bolts of carbon steel and stainless steel. The bolts were then tapped on a hard surface to jar off any loose powder, and the gamma activity was measured in a well-type gamma scintillation counter. The bolts were mounted at varying distances from a steam jet and subjected to 5 min of blasting with steam and detergent mixtures at pressures up to 10 lb/in.^{2} In three washes of 5 min each, the best removal of oxide was 72%, as measured by comparison of final to initial gamma activity, corresponding to a "decontamination factor" (DF, ratio of initial to final activity) of only 3.6. Dry air blasting was even less successful as a dust remover, resulting in only a 12% decrease. It was concluded that the only sure way of removing ultrafine irradiated UO_2 dust from rough metal surfaces, when deposited dry, was by means of a solvent.

2.2 Solubility of UO_2 in Carbonate-Peroxide

A peroxide-carbonate-bicarbonate mixture was effective as a noncorrosive solvent for UO_2 dust, but failed as a solvent for slugs of sintered UO_2. Carbonate complexes ot hexavalent uranium have been known for many years. In the early days of the Manhattan Project, Warf[9] found that UO_2 was soluble in a sodium peroxide solution, and Kraus[10] listed quantitative data for the solubility of UO_2 powder in sodium peroxide, hydrogen peroxide plus potassium or ammonium carbonate, and hydrogen peroxide plus ammonium oxalate. In 1958, Mendel,[11] in a study of noncorrosive reagents for the decontamination of carbon steel, found that 0.25 $\underline{M}$ Na_2CO_3–0.25 $\underline{M}$ $NaHCO_3$–1.0 $\underline{M}$ H_2O_2 dissolved -325 mesh UO_2 (<44 microns) in less than an hour, and particles as large as 150 microns in 3 hr. The speed of dissolution at 24°C was about the same as that at 60°C, because the increased decomposition rate of peroxide balanced the increased solution rate of UO_2 with rise in temperature. This mixture was the most promising one tested by Mendel. Other uranium complexers studied were Versene, sulfate, citrate, and sulfamic acid, together with oxidizers from the group comprising periodate, dichromate, bromine, permanganate, persulfate, and peroxide.

At Oak Ridge National Laboratory qualitative tests showed that -325-mesh high-fired UO_2 would dissolve in Mendel's carbonate-peroxide reagent in about 30 min when warmed. Uranium dioxide which had not been strongly ignited dissolved in less than 3 min. "Ultrafine" UO_2 prepared by the water classification method previously described dissolved in a few seconds. A sintered slug of UO_2 weighing 39 g placed in an even more concentrated carbonate-bicarbonate-peroxide solution than Mendel's reagent dissolved at a rate of only 0.2 g/hr at 40 to 70°C, however, showing the impracticality of usage for dissolving slugs from broken fuel elements. The corrosion rate of carbonate-peroxide solutions on carbon steel at 70°C was less than 0.001 mil/hr.

2.3 Carbonate-Peroxide as a Decontaminant

Carbonate-peroxide redeposited some fission products from solution, and was too unstable for large scale use. Carbon steel and stainless steel bolts contaminated with irradiated ultrafine UO_2 as previously described were jetted for 20 min with steam into which was aspirated Mendel's reagent. The decontamination factor (DF) on the bolt about an inch in front of the jet was about 325, and on the bolt about 3 in. away was 75. Bolts farther away had much lower decontamination factors. The activity remaining on the bolts was identified by gamma scintillation spectrometry to be chiefly tellurium-132. The tellurium had been deposited after the UO_2 dissolved, as confirmed by another test in which irradiated UO_2 was dissolved in Mendel's reagent in a beaker, pieces of steel were added, and the steel became contaminated with Te^{132}. Had the UO_2 been irradiated longer, in order to bring the fission product concentrations more nearly to their equilibrium ratios, there would very likely have been other identifiable deposits also.

When 1-hr irradiated UO_2 had been cooled five weeks, thus becoming nearly free of 77-hr Te^{132}, the activity remaining on dust-contaminated bolts sprayed with steam and Mendel's reagent (with 0.25 $\underline{M}$ sodium citrate added), as shown by gamma spectrometry, was about 90% Ce^{141} and 10% Ru^{103}. Deposition of ruthenium from Mendel's reagent was confirmed when eight clean steel pieces (0.005 x 0.5 x 1 in.) were soaked for 1 hr at room temperature in 50 ml of the reagent containing 1 millicurie of added Ru^{106}. After four washes in hot water all the pieces read between 100 and 140 mr/hr (beta-gamma) on a portable Geiger counter at standardized geometry. A control solution of carbonate without peroxide contaminated two other steel pieces to only 15 and 16 mr/hr under identical conditions. When mild steel was contaminated with pure Ce-Pr^{144} by a drying and baking method, the decontamination factor after 20 min in Mendel's reagent at 80°C was only 2, in contrast with decontamination factors of 15,000 and 3,000 after 20 min of boiling with inhibited oxalic and phosphoric acids. Similarly poor results were obtained with Zr-Nb^{95} and Ba-La^{140}. In preliminary tests, the effectiveness of carbonate-peroxide on decontaminating UO_2-dusted metal bolts in a steam jet was somewhat improved by the inclusion of 0.25 $\underline{M}$ sodium citrate in the formula, but in tests with pure fission products, those not removed by Mendel's reagent resisted the modified reagent also.

A further disadvantage of carbonate-peroxide, besides its inability to dissolve UO_2 slugs and its deposition of fission products such as tellurium, ruthenium, and cerium from solution, was its short life. At 90°C, the peroxide was completely decomposed in 0.75 min. At 70°C, the half-life was 1.0 min; at 60°, 2.5 min; and at 55°, 5.5 min. Thus, in a steam jet, the peroxide life might well be too brief for use in such large-scale equipment as the charge and service machines. In a liquid spray at not over 60°C, however, the reagent would doubtless dissolve fine UO_2 dust blown into the machines by the circulating helium, without corroding the carbon steel components. A suitable follow-up reagent or reagents would be necessary for removing fission products deposited from solution, and other fission products not removed by the carbonate-peroxide. Such a procedure was initially recommended for decontaminating the EGCR charge and service machines[13] and is described below.

2.4 Follow-up Reagents for Carbonate-Peroxide

A 10% aqueous solution of Turco 4518, a proprietary mixture containing inhibited oxalic acid, at 80 to 100°C showed desirable properties as a follow-up reagent for carbonate-peroxide mixtures.[12,13] In steam-jet spraying tests after carbonate-peroxide, additional decontamination was as high as a factor of 10. Pure tellurium and ruthenium deposited onto carbon steel from carbonate-peroxide solutions were removed in a few minutes at 100°C by factors of 15 and 65, respectively. $Ba\text{-}La^{140}$ similarly deposited was removed by a factor of 360 in 30 min of boiling. $Zr\text{-}Nb^{95}$ was particularly well removed from steel, by factors of several thousand, due to the oxalate content of the mixture. The corrosion rate of a boiling 10% aqueous solution of Turco 4518, measured by overnight weight loss, was only 0.003 mil/hr on carbon steel, but an undesirable yellow film, probably composed of ferrous oxalate, formed on the metal. Uranium dioxide was not soluble in the reagent.

Several other reagents were investigated briefly, with fair to moderate success, as follow-up solutions for carbonate-peroxide. Attention soon turned, however, to a more promising method for decontaminating the charge and service machines. This was with oxalate-peroxide reagents, which form the subject of the following sections.

2.5 Oxalate-Peroxide Mixtures as Solvents for UO_2

Oxalate-peroxide was a superior solvent for UO_2. It was reported in the early days of the Manhattan Project that 10% H_2O_2 with 10% ammonium oxalate dissolved 35% of a standard UO_2 powder in 2 min at 25°C, in comparison with 10% H_2O_2-10% K_2CO_3, which dissolved 46% at 25°C and 83% at 35°C in the same length of time.[10] Even peroxide with ammonium carbonate dissolved 69% of the oxide at 25°C. Five percent sodium peroxide at 45°C dissolved only 17% of the oxide. It was concluded that H_2O_2-carbonate reagents were the most effective solutions for dissolving UO_2. Unfortunately, as we have seen, carbonate-peroxide was an ineffective solvent for high-fired or sintered UO_2 of the EGCR type except when it was in very finely powdered form. Trials with oxalate-peroxide, however, established that such a mixture was relatively stable to heat, compared with carbonate-peroxide, and that the heated reagent was much superior to carbonate-peroxide as a solvent for UO_2. For example, in initial 30-min trials, a 39-g, sintered UO_2 slug suspended in a mixture 0.3 M in sodium oxalate and 1 M in H_2O_2 dissolved at rates from 3%/hr at 60° to 17%/hr at 100°C, with a maximum corrosion rate on carbon steel of 0.003 mil/hr.

A disadvantage of the oxalate-peroxide mixture was that the pH of the heated solution slowly rose due to consumption of the hydrogen ion in the oxidation of oxalate by the peroxide, followed by rapid decomposition of the peroxide when the solution approached neutrality:

$$\text{In acid solution, } H_2O_2 + C_2O_4^{=} + 2H^+ \longrightarrow 2H_2O + 2CO_2; \qquad (1)$$

$$\text{neutral or basic solution, } 2H_2O_2 \longrightarrow 2H_2O + O_2 \, . \qquad (2)$$

When 0.3 M sodium or ammonium oxalate with 1 M H_2O_2 was held at 95°C in the presence of mild steel, the initial pH of about 6.4 rose typically in 30 to 45 min to about 7.0. Here the decomposition of H_2O_2 to water and oxygen began to dominate, with increasing oxygen evolution that ceased in a few minutes when the peroxide was exhausted.

It had earlier been shown that mixtures of oxalic acid and hydrogen peroxide were very good solvents for UO_2 as well as superior fission-product decontaminants but that they dissolved carbon steel rapidly and hence would be unsuitable for the EGCR charge and service machines.[13] It therefore seemed that the UO_2 dissolution properties of oxalate salts with hydrogen peroxide would not suffer, and in fact would probably be enhanced, if the pH of the mixture were lowered in order to increase its stability by providing more acid reserve. Increased acidity should also improve the decontamination properties, if any, since many fission products require some acidity for dissolution. An obvious disadvantage of lowering the pH would be to increase the corrosion on carbon steel. An idea of the extent of this increase, as well as effects on the solubility of UO_2, was gained in a simple preliminary test, results of which are shown in Table 1. Note that UO_2 is soluble in the pH range of 2 to 9,

Table 1. Five-Minute Solubility of -325 Mesh UO_2 in 0.3 M Oxalate–1.0 M H_2O_2

pH	Temperature (°C)	UO_2 Dissolved (%)	Corrosion (mils/hr)
2	70	95.5	0.028
3	70	98.5	0.004
4	80	99.7	0.005
5	80	96.0	0.001
6	80	88.9	<0.001
7	80	82.8	0.002
8	80	78.8	
9	80	65.0	
10	80	1.2	

with solubility increasing at lower pH. Here 1-g portions of a test lot of -325-mesh "high-fired" UO_2, similar to that used for preparing sintered UO_2 pellets for the EGCR, were agitated 5 min in 100 ml of 0.3 $\underline{M}$ NaC_2O_4–1 $\underline{M}$ H_2O_2 at 70 and 80°C, promptly filtered and washed, dried and weighed. The pH of the solutions ranged from 2 to 10. Mild-steel corrosion by 1-hr weight loss measurements in separate tests increased at lower pH, but not as much as had been expected. The corrosion effect in peroxide solutions later turned out to be complex, and will be discussed in other sections of this report. Uranium dioxide solubility also increased with increasing concentrations of either oxalate or peroxide, but these relationships also were not extensively studied; the solubility rate was already adequate for the purpose. For example, with one of the formulas tested later in the program (0.3 $\underline{M}$ ammonium oxalate with 0.3 $\underline{M}$ ammonium acetate and 1.0 $\underline{M}$ hydrogen peroxide at pH 4.5 and 95°C), a 39-g EGCR slug dissolved completely in only 2.5 hr. Ultrafine UO_2 such as might be carried by circulating helium dissolved instantly. Problems with the use of oxalate-peroxide did not therefore center around its solubility for UO_2 but took the form of testing and developing its decontaminating properties, increasing its useful life, and maintaining its corrosive qualities within acceptable limits. These subjects are treated in the following sections.

2.6 Some Initial Comparisons of Oxalate-Peroxide Mixtures with Other Decontamination Solutions

In extensive tests, oxalate-peroxide preparations compared very favorably with other miscellaneous decontamination reagents in the removal of fission products from carbon steels and stainless steels, and even protactinium from titanium. The first test series, shown in Table 2, was made with 0.3 $\underline{M}$ sodium oxalate–1 $\underline{M}$ H_2O_2 at pH 5.0.

Table 2. Results of Decontamination of Type 347 Stainless Steel and Mild Steel by Oxalate-Peroxide vs H_2O at pH 5, 20 min at 95°C

Fission Product	Decontamination Factors			
	347 SS		Mild Steel	
	Ox-H_2O_2	H_2O	Ox-H_2O_2	H_2O
Ce^{144}-Pr^{144}	6.3×10^3	4.7	350	1.0
Cs^{137}-Ba^{137}	2.6×10^4	5.7×10^3	2.3×10^4	2.2×10^3
Ru^{106}-Rh^{106}	345	7	7.5	1.1
Y^{91}	3.4×10^4	34	44	1.1
I^{131}	5×10^3	530	2.4×10^3	240
Sr^{90}-Y^{90}	1.1×10^4	4.1	200	2.1
Zr^{95}-Nb^{95}	$>2 \times 10^4$	34	$>2 \times 10^4$	1.1
Mo^{99}	1.4×10^4	1.8×10^3	2.7×10^4	14
Ba-La^{140}	2.1×10^4	7.5	91	2.9
Mo^{99} (heated)	1.1×10^4	780	3.1×10^4	4.5
Ba-La^{140} (heated)	8.3×10^3	1.9	150	1.6

In the control group, water was adjusted to pH 5.0 with sulfuric acid. Stainless and mild steel coupons in duplicate were contaminated for the tests by room temperature drying-on of neutralized solutions of individual fission products. Molybdenum and barium-lanthanum coupons were prepared also by heating the contaminated steels on a hot plate until a blue color formed on the carbon steel. Treatment was for 20 min at 95°C, with hand agitation. All carbon steels after oxalate-peroxide treatment were clean, in contrast to the rusted appearance of the controls.

Titanium coupons were contaminated to 1.0-4.5 r/hr, chiefly with Pa^{233}, with some $Zr-Nb^{95}$ and minor amounts of $Ru-Rh^{106}$, by immersion in aqueous feed solutions of the Darex process. As shown in Table 3, decontamination by oxalate-peroxide at pH 5.0 at 95°C compared favorably with that of several other reagents. The corrosion by 5% oxalic acid and by 10% Turco 4518 was 0.17 mil/hr vs less than 0.05 mil/hr by the oxalate-peroxide. Thus, in the event that thorium was used in the EGCR fuel, protactinium decontamination by oxalate-peroxide reagents seemed possible.

Table 3. Decontamination of Darex Titanium

Sample	Reagent	Treatment	Beta-Gamma DF
1	Turco 4501-A, 10%	Boil 30 min	1.4
2	Citric acid, 10%	Boil 30 min	1.1
3	Turco 4518, 10%	Boil 30 min	1.4×10^3
4	$KMnO_4$ 2%, NaOH 2%	Boil 30 min	1.2
1, retreat	Turco 4518, 10%	Boil 30 min	460
2, retreat	Turco 4518, 10%	Boil 30 min	900
4, retreat	Turco 4518, 10%	Boil 30 min	1.0×10^4[a]
5	Oxalic acid, 5%	Boil 30 min	115
5, retreat	Oxalic acid, 5%	Boil 1.5 hr	500 (total)
6	$Na_2C_2O_4$, 0.3 $\underline{M}$; H_2O_2, 1.0 $\underline{M}$; pH 5.0	95°C, 20 min	135
6, retreat	Reagent 6, maintained at pH 5.0 with $H_2C_2O_4$	95°C, 40 min	5.2×10^3 (total)
7	H_2O, pH 5.0 with H_2SO_4	95°C, 20 min	1.0

[a] Gamma scan by scintillation spectrometer showed marked lowering of the $Ru-Rh^{106}$ peak, the result of a $KMnO_4$ pretreatment.

In decontamination testing preceding the trials with oxalate-peroxide, the most difficult fission product to remove from carbon steel had been ruthenium. Alkaline permanganate, proposed in 1953 by Wilson,[14] proved generally effective for increasing the degree of ruthenium decontamination when used as a pretreatment on mild steel surfaces, and its use was proposed for the EGCR service machine if required.[13] Cerium behavior toward permanganate was similar to that of ruthenium. The peroxide oxidizer in oxalate-peroxide reagents was also beneficial to ruthenium decontamination, in all probability lessening the need for an alkaline permanganate pretreatment for strongly bound ruthenium, as will be shown (Secs. 2.8.5 and 2.8.7.4). These decontamination tests led to initial proposals for the decontamination of the charge and service machines, which form the subject of the next section.

2.7 Decontamination of EGCR and PBR: Initial Proposals

The method first proposed for decontaminating the EGCR charge and service machines was with carbonate-peroxide followed by Turco 4518, an inhibited proprietary mixture containing oxalic acid.[12] A second method, based on oxalate-peroxide, was later proposed.[15] In brief, the method featured first steam-jet spraying with hot detergent solution to remove water soluble contamination and wash away as much dust as possible. After a rinse, the surfaces were to be steam sprayed with 4% (0.3 M) sodium oxalate–3% (1.0 M) H_2O_2–0.7% (0.056 M) oxalic acid at pH 5.0 for several minutes, rinsed, and resprayed until the drain-line activity dropped to about 10% of its peak value. If ruthenium and/or cerium were prominent remaining activities, as shown by a gamma scan with a scintillation gamma spectrometer, the machine would be similarly sprayed with a 2% NaOH–2% $KMnO_4$ mixture, followed if necessary after a rinse, by 10% Turco 4518. Broken pieces of UO_2 slugs would be dissolved by digesting them for several hours in oxalate-peroxide whose pH was maintained at 4.5 to 5.0 by periodic additions of oxalic acid.

In October 1960, an essentially similar proposal was made for decontaminating components of the Pebble Bed Reactor,[16] except that oxalate-peroxide instead of Turco 4518 was recommended as a follow-up for alkaline permanganate.

2.8 Further Decontamination Tests with Oxalate-Peroxides, and Comparisons with Other Reagents

After the above proposals were made for decontaminating EGCR and PBR components, interest continued in further evaluation of oxalate-peroxide reagents in comparison with other decontaminants, and in developing the reagents for optimum usage. A status report with limited distribution appeared in December 1960.[17] Expanded excerpts from this report will be made the subjects of the following sections.

2.8.1 Decontamination of Mixed Fission Products from Stainless Steel with Acidic Peroxides

Because of favorable British statements concerning dilute sulfuric acid as a decontaminant for stainless steel, several mixtures of H_2SO_4 (0.3 N) were compared with similar oxalic acid preparations and with nitric acid, as shown in Table 4. Oxalic acid with peroxide was superior to sulfuric with peroxide. Coupons of 347 stainless steel were contaminated by the drying and baking on of an acid solution of

Table 4. Results of Decontamination of Type 347 Stainless Steel from Mixed Fission Products

Aqueous solutions, 95°C, 20-min agitation

Reagent	Beta-Gamma DF	Corrosion (mil/hr)
Water	2.4	
H_2SO_4, 0.3 $\underline{N}$	94	0.016
H_2SO_4, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2	319	0.001
H_2SO_4, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 0.12 $\underline{M}$ NaF	332	0.002
H_2SO_4, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 0.12 $\underline{M}$ NaF + 0.16 $\underline{M}$ oxalic acid	491	0.002
H_2SO_4, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 0.16 $\underline{M}$ oxalic acid	238	0.003
H_2SO_4, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 1% Versene (EDTA)	263	
HNO_3, 0.3 $\underline{N}$	123	
$H_2C_2O_4$, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2	1472	0.001
$H_2C_2O_4$, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 0.12 $\underline{M}$ NaF	825	0.002
$H_2C_2O_4$, 0.3 $\underline{N}$ + 1 $\underline{M}$ H_2O_2 + 1% Versene (EDTA)	1216	

mixed fission products, using a laboratory hot plate turned to the "low" range. They were then partially decontaminated by immersion in the test reagent for 20 min at 95°C. Triplicate samples were used throughout. One-hour corrosion tests in duplicate were also run where appropriate. Decontamination was limited by ruthenium and niobium, with H_2O_2 and fluoride aiding niobium removal. Sulfuric acid discolored the steel. Peroxide made the acid less corrosive, even when fluoride was included, and left a bright surface.

2.8.2 Decontamination of Ruthenium and Zirconium-Niobium from Type 347 Stainless Steel with Acid Mixtures

Oxalic acid preparations were excellent niobium decontaminants (Table 5). Since many common reagents remove the bulk of fission product activity from stainless steel but fail to remove all of the ruthenium and niobium, a series of comparisons was made between decontamination reagents using only these two nuclides. As with the mixed fission products, triplicate samples were contaminated by the drying and baking of a drop of solution (1 mc/ml) onto the steel, and decontamination was at 95°C for 20 min in agitated aqueous solution. Peroxide and fluoride additions to several acids

Table 5. Results of Decontamination of Ruthenium and Niobium from Type 347 Stainless Steel

Reagent	Decontamination Factors	
	Ru^{106}	$Zr\text{-}Nb^{95}$
H_2SO_4, 0.3 N	2.3	65
H_2SO_4, 0.3 N + 0.3 M H_2O_2	3.0	4.4×10^3
H_2SO_4, 0.3 N + 0.12 M NaF (corrosion 0.016 mil/hr)	2.8	1.1×10^4
H_2SO_4, 0.3 N + 0.12 M NaF + 0.3 M H_2O_2	3.3	$>1.3 \times 10^4$
HNO_3, 0.3 N	1.1	1.6
HNO_3, 0.3 N + 0.3 M H_2O_2		$>7 \times 10^3$
HNO_3, conc.		22
HNO_3, DF peak between 3 and 6 M		175
Citric acid, 0.3 N	1.3	73
Citric acid, 0.3 N + 0.3 M H_2O_2	1.3	7.0×10^3
Citric acid, 0.3 N + 0.12 M NaF	2.0	7.6×10^3
Citric acid, 0.3 N + 0.12 M NaF + 0.3 M H_2O_2	2.9	$>7.6 \times 10^3$
Tartaric acid, 0.3 N	1.2	790
Tartaric acid, 0.3 N + 0.3 M H_2O_2	1.5	4.1×10^3
Tartaric acid, 0.3 N + 0.12 M NaF	1.8	$>7.6 \times 10^3$
Tartaric acid, 0.3 N + 0.12 M NaF + 0.3 M H_2O_2	2.6	5.1×10^3
Oxalic acid, 0.3 N	2.7	$>8.0 \times 10^3$
Oxalic acid, 0.3 N + 0.3 M H_2O_2	2.8	$>9.8 \times 10^3$
Oxalic acid, 0.3 N + 0.12 M NaF	5.5	$>1.4 \times 10^4$
Oxalic acid, 0.3 N + 0.12 M NaF + 0.3 M H_2O_2	4.6	$>1.0 \times 10^4$
$KMnO_4$, 2% + 2% NaOH	10	
Turco 4518, 10% (contains oxalic acid)	1.5	7.8×10^3
Radiac wash (contains EDTA)	1.2	6.6

increased their effect on niobium. Alkaline permanganate, as has been known for several years (ref 14), was more effective on ruthenium than many other reagents. Baking the steel on a hot plate in this manner until a blue color formed was too severe a treatment to permit good ruthenium decontamination with any of the reagents, however.

2.8.3 Decontamination of Ruthenium from Type 347 Stainless Steel Following Alkaline Permanganate Treatment

Coupons of type 347 stainless steel contaminated with Ru^{106} in the manner described above were agitated with 2% $KMnO_4$ + 2% NaOH for 20 min at 95°C, rinsed with hot water, dried, and monitored. They were then treated in the same way with several other reagents in order to compare efficiencies for ruthenium removal after the $KMnO_4$ pretreatment, as shown in Table 6. Oxalic acid mixtures were superior to sulfuric and nitric acids, but further tests at other concentrations need to be made. The decontamination figures are averages of 3 coupons each.

Table 6. Results of Decontamination of Type 347 Stainless Steel from Ruthenium Following $KMnO_4$-NaOH Pretreatment

Reagent	Ruthenium DF
Oxalic acid, 0.5 $\underline{M}$	89
Oxalic acid, 0.5 $\underline{M}$ + 0.3 $\underline{M}$ H_2O_2	138
Oxalic acid, 0.5 $\underline{M}$ + 0.3 $\underline{M}$ H_2O_2 + 0.12 $\underline{M}$ NaF	233
Oxalic acid, 0.5 $\underline{M}$ + 0.12 $\underline{M}$ NaF	97
H_2SO_4, 0.3 $\underline{N}$	5
H_2SO_4, 0.3 $\underline{N}$ + 0.3 $\underline{M}$ H_2O_2	48
H_2SO_4, 0.3 $\underline{N}$ + 0.3 $\underline{M}$ H_2O_2 + 0.12 $\underline{M}$ NaF	51
H_2SO_4, 0.3 $\underline{N}$ + 0.12 $\underline{M}$ NaF	7
HNO_3, 0.3 $\underline{N}$	2.3
HNO_3, 3 $\underline{N}$	39
Radiac wash, 17%	11
Turco 4518, 2%	57

Table 7. One-Step Decontamination of Gas-Loop Piping

Reagent	Gamma DF		Ruthenium DF		I^{131} DF		Ce^{141} DF	
	A(1)	B(2)	A	B	A(3)	B	A	B
4% $Na_2C_2O_4$–3% H_2O_2, pH 5	66	26	97	55	134	32	140	(32)
10% Turco 4518	14	11	20	6	(19)	23	27	(11)
2% Turco 4518	10	7	8	4	(18)	15	18	(9)
4.5 $\underline{M}$ HNO_3	39	28	126	58	(31)	31	154	(33)
4.5 $\underline{M}$ HNO_3 + 3% H_2O_2	65	30	134	89	(76)	33	120	(36)
50% Deoxidine 170 (inhibited H_3PO_4)	27	10	31	14	(21)	14	56	(16)
100% Turco 4501A (130°C)	19	27	37	31	(35)	82	22	(32)
2.2% Turco 4324	10	9	11	22	(21)	7	18	(11)
3.7% Turco 4306-B	6	4	4	3	(15)	9	(16)	(4)
25% Turco 4512 (inhibited H_3PO_4)	30	9	37	8	(30)	21	(82)	(10)
H_2O	1.9							

Notes

(1) Pipe type A: Ce^{141} and Ru^{103}, Ru^{106} prominent.

(2) Pipe type B: I^{131} and Ru^{103}, Ru^{106} prominent.

(3) Parenthetical numbers: DF minimum, not certain, due to disappearance of gamma peak during decontamination.

2.8.4 Decontamination of Gas Piping from LITR Loop

Gas loop piping of type 347 stainless steel, contaminated with Ce^{141}, Ru^{103}, Ru^{106}, and I^{131} from heated air after it had been passed over unclad UO_2 in the Low Intensity Test Reactor (LITR) was decontamination tested with several reagents in 20-min treatments at 95°C. The pipe specimens were kindly furnished by General Electric Co. personnel at Oak Ridge National Laboratory. As shown in Table 7, oxalate-peroxide at pH 5, which has such a low corrosion rate that it can be used on mild steel, compared favorably with 4.5 $\underline{M}$ HNO_3-peroxide. Oxalate-peroxide treated steel had a clean, bright appearance. The generally low decontamination factors are to be expected because of the low activities of the samples, less than 1 mr/hr each. Decontamination of the fission products on pipe types A and B in the table were estimated by comparison of peak heights on gamma scan charts. Overall gamma decontamination was measured by gamma counting in a well-type-detector scintillation counter.

The effect of alkaline permanganate on the piping, followed by other reagents, was also studied for comparative purposes. Eight sections were agitated 20 min with 2% NaOH–2% $KMnO_4$ at 95°C. The average ruthenium DF was 8.9 ± 2.7 (95% $L.E._x$), the I^{131} DF was 11.3 ± 3.5, and the gross-gamma DF 6.6 ± 0.9. Further decontamination was then tested in eight reagents, as shown in Table 8. Only one pipe sample

Table 8. Results of Decontamination of Gas-Loop Piping After $KMnO_4$ Pretreatment

Reagent Used After $KMnO_4$-NaOH Pretreatment	Ruthenium DF		I^{131} DF		Gamma DF	
	R(1)	T(2)	R	T	R	T
$Na_2C_2O_4$ 4%, H_2O_2 3%, pH 5	3.9	35	2.7	29	3.5	21
$Na_2C_2O_4$ 4%, H_2O_2 3%, pH 4	5.0	50	3.1	36	3.3	23
$H_2C_2O_4$ 0.5 $\underline{M}$, H_2O_2 3%	6.5	60	4.5	50	5.5	39
HNO_3 4.5 $\underline{M}$	9.5	88	6.0	66	6.0	40
HNO_3 4.5 $\underline{M}$ + H_2O_2 3%	9.7	85	3.6	51	5.2	34
Turco 4512, 25%	5.3	44	5.9	65	4.2	30
Turco 4518, 10%	1.4	12	2.4	29	2.1	14
Deoxidine 170, 25%	5.0	38	5.0	45	4.0	25

Notes

R = decontamination by the reagent.
T = total decontamination (reagent DF x $KMnO_4$ DF).

was used for each reagent. Nitric acid with H_2O_2 gave the best ruthenium DF. The worst was with Turco 4518. Oxalate-peroxides at lowered pH, and inhibited H_3PO_4, had intermediate effects.

2.8.5 Steam-Spray Tests with Oxalate-Peroxide

Decontamination by oxalate-peroxide in a steam spray was successful. The steam-spraying tests mentioned previously in connection with carbonate-peroxide were made in a brass chamber, using an ordinary laboratory-sink aspirator as a steam jet with initially unregulated pressures of 3 to 10 $lb/in.^2$ of steam. Brass was rapidly corroded by oxalate-peroxide in steam, and the peroxide was quickly decomposed. A new jet apparatus was constructed of a 2-ft section of 2-in. ID Pyrex pipe, with several glass condensers (water cooled) on one end and a stainless steel aspirator-jet held with a rubber stopper and connected to a regulated-pressure steam supply at the other. The assembly was nearly horizontal and slanted slightly downward toward the exit end for drainage. Steel coupons (1 x 0.25 x 0.005 in.) or opened and flattened pipe pieces, contaminated on one side with fission products, were suitably supported facing the steam jet. The flow rate of steam at 15 $lb/in.^2$ was such as to condense about 400 ml of water per minute, and the optimum flow rate of the aspirated decontamination solution was normally adjusted to 25 ml/min.

For each test, which lasted 20 min, one coupon was mounted 2 in. in front of the steam jet and the other 24 in., at the far end of the pipe. Decontamination was usually higher on the sample nearer the jet, showing the value of high velocity impingement. Some results on low-activity ruthenium removal from stainless steel gas-loop piping are shown in Table 9A. Ruthenium removal was almost complete with weakly to strongly acidic peroxide, and peroxide imparted a bright finish. The background count was about 250 counts/min and was subtracted from the sample counting rates. The corrosion rate of 3 $\underline{N}$ H_2SO_4 + 1 $\underline{M}$ H_2O_2, which decontaminated the stainless steel so well, was less than 0.001 mil/hr at 95°C.

Test 12, in Table 9B, was at a much higher activity level than those on gas-loop piping. Here, a basic Ru^{106} solution was baked onto carbon steel at 300 to 500°C in order to produce a stubborn deposit. This was done in a nitrogen atmosphere to prevent oxide formation on the steel. The alkaline permanganate treatment, as in several of the other listed tests, did not live up to expectations as a most outstanding ruthenium decontaminant. Again the oxalate-peroxide solution was quite effective. Control tests 13 and 14, with only water aspirated into the steam, showed the ineffectiveness of wet steam alone on ruthenium-contaminated coupons prepared in this manner.

Many other steam-and-reagent spray tests on ruthenium were made, but for the sake of brevity are not listed. When dark oxide coatings were produced on carbon steel coupons by strongly heating in air after contamination, the decontamination factors in a variety of low-corrosion reagents were less than 10. These dark oxide coatings were soluble in inhibited phosphoric acids such as Turco 4512, and thinner coatings in various oxalate-peroxide formulas, as will be pointed out.

Table 9A. Ruthenium Decontamination from Stainless Steel Gas-Loop Piping by Steam Spray Using Various Reagents

20 min spray at 15 lb/in.^{2}

Test	Aspirated Reagent	Gamma Counts per Min Before	Gamma Counts per Min After	Gamma DF	Appearance
1	0.3 M $Na_2C_2O_4$ + 1 M H_2O_2, pH 4.0	(a) 2.00 x 10^4 (b) 2.17 x 10^4	460 1199	43 18	
2	0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2, pH 4.0	(a) 2.26 x 10^4 (b) 2.43 x 10^4	409 610	55 40	
3	0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2 + 0.044 M $(NH_4)_2$ cit., pH 4.0	(a) 1.73 x 10^4 (b) 1.74 x 10^4	424 566	41 31	
4	2% NaOH + 2% $KMnO_4$	(a) 1.84 x 10^4 (b) 1.36 x 10^4	1291 1539	14 9	Dingy, yellow Dingy, yellow
4, Retreated	5% (NH_4) citrate	(a) 1291 (b) 1539	583 371	2.3 (32) 4.1 (37)	Brighter Brighter
5	4.5 M HNO_3 + 1 M H_2O_2	(a) 7.24 x 10^3 (b) 1.05 x 10^4	315 233	23 45	Much brightened Much brightened
6	0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2 + 0.5% Tergitol No. 4	(a) 4.76 x 10^3 (b) 6.78 x 10^3	141 478	34 14	Much brightened Much brightened
7	4.5 M HNO_3 + 1 M H_2O_2 + 0.5% Tergitol No. 4	(a) 9.17 x 10^3 (b) 7.35 x 10^3	209 144	44 51	Very bright Very bright
8	2% NaOH + 2% $KMnO_4$	(a) 1.69 x 10^4 (b) 1.71 x 10^4			Dark film Dark film
8, Retreated	3 N H_2SO_4		282 964	60 18	Corroded Corroded
9	2% NaOH + 2% $KMnO_4$	(a) 1.80 x 10^4 (b) 1.51 x 10^4			Dark film Dark film
9, Retreated	0.3 N H_2SO_4		1389 2511	13 6	Corroded Corroded
10	2% NaOH + 2% $KMnO_4$	(a) 2.53 x 10^3 (b) 4.83 x 10^3	1.45 x 10^3 3.24 x 10^3	1.7 1.5	Dark film Dark film
10, Retreated	3 N H_2SO_4 + 1 M H_2O_2	(a) 1.45 x 10^3 (b) 3.24 x 10^3	77 115	19 (33) 28 (42)	Bright Bright
11	3 N H_2SO_4 + 1 M H_2O_2	(a) 5.21 x 10^3 (b) 4.86 x 10^3	92 170	57 29	Brilliant Brilliant

Table 9B. Ruthenium Decontamination from Steel Coupons by Steam Spray: Comparison of Alkaline Permanganate, Oxalate-Peroxide, and Water

20 min steam spray at 15 lb/in.^{2}

Test	Steel Type	Aspirated Reagent	Gamma Counts per Min		Gamma DF	Appearance
			Before	After		
12	Carbon	2% NaOH + 2% $KMnO_4$	(a) 2.04×10^6 (b) 1.38×10^6	6.3×10^4 6.9×10^5	33 2	Dark film Dark film
12, Retreated		0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2, pH 4.0	(a) 6.3×10^4 (b) 6.9×10^5	552 2.85×10^4	114 (3.7×10^3) 24 (48)	Clean Clean
13	347 SS	H_2O	(a) 90 mr/hr (b) 82 mr/hr	65 mr/hr 66 mr/hr	1.4 1.2	Dull Dull
14	Carbon	H_2O	(a) 71 mr/hr (b) 150 mr/hr	28 mr/hr 140 mr/hr	2.5 1.1	Dark, rusted Dark, rusted

Table 9C. Zr-Nb^{95} Decontamination from Steel Coupons: Comparison of Oxalate-Peroxide, Turco 4518, and Water

20 min steam spray at 15 lb/in.^{2}

Test	Steel Type	Aspirated Reagent	Gamma Counts per Min		Gamma DF (c)	Appearance
			Before	After		
15	Carbon	0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2, pH 4.5	(a) 4.10×10^6 (b) 7.24×10^6	557 7.87×10^4	7.4×10^3 92	Nearly clean Half clean
16	347 SS	0.3 M $(NH_4)_2C_2O_4$ + 1 M H_2O_2, pH 4.5	(a) 2.70×10^6 (b) 3.15×10^6	342 930	7.9×10^3 3.4×10^3	Bright Bright
17	Carbon	Turco 4518, 10% soln.	(a) 7.87×10^6 (b) 5.67×10^6	2.75×10^3 6.60×10^5	2.9×10^3 8.6	Partly clean Dingy
18	347 SS	Turco 4518, 10% soln.	(a) 4.41×10^6 (b) 6.30×10^6	828 5.45×10^3	5.3×10^3 1.2×10^3	Clean Clean
19	Carbon	H_2O	(a) 160 mr/hr (b) 150 mr/hr	1 mr/hr 150 mr/hr	160 1	Rusted Rusted
20	347 SS	H_2O	(a) 220 mr/hr (b) 110 mr/hr	18 mr/hr 66 mr/hr	12 1.7	Dull Dull

(a) Sample 2 in. from steam jet.

(b) Sample 24 in. from steam jet.

(c) Gamma DF = gamma decontamination factor (initial count/min)/(final counts/min).

Oxalate-peroxide aspirated into a steam jet was at least as effective on Zr-Nb^{95} as was a strongly acid proprietary oxalic acid mixture, as shown in Table 9C. The peroxide mixture produced a brighter finish. Wet steam alone, at a 2-in. impingement distance, decontaminated carbon steel by a factor of 160 and stainless steel by a factor of 12 (tests 19 and 20), but was useless at a 24-in. distance.

2.8.6 Decontamination of Gas Piping from Brookhaven Loop[19]

During January and February of 1961, a stainless steel low-pressure helium loop was operated in the Brookhaven Graphite Reactor to test fuel balls of the type proposed for the Pebble Bed Reactor. Considerable air inleakage occurred during operation. Sections of the contaminated loop piping after shutdown were sent to ORNL for fission product and uranium analysis and decontamination testing. Seven out-of-pile sections were cut into smaller pieces, each about 1/4 x 1 in., and three months after shutdown they were successfully decontaminated with oxalate-peroxide.

Table 10 shows the results of the standard 20-min test at 95°C, in which samples

Table 10. Decontamination of BNL Loop Samples in Oxalate-Citrate-Peroxide

20-min immersion, 95°C, pH 4.0

	Scintillation Gamma counts/min		Gamma
	Before Decon.	After Decon.	DF
		Group 1	
1a	3.40×10^6	2.84×10^4	120
1b	4.58×10^5	1.98×10^4	23
2a	2.98×10^5	3.20×10^3	93
2b	1.83×10^5	4.23×10^3	43
3a	3.10×10^5	2.26×10^4	14
3b	4.54×10^5	2.25×10^4	20
4a	2.22×10^6	2.42×10^4	92
4b	3.75×10^6	3.60×10^4	104
		Group 2	
5a	1.55×10^5	1.24×10^3	125
5b	1.70×10^5	869	196
6a	1.17×10^4	1.34×10^3	9
6b	5.76×10^3	353	16
6c	6.57×10^3	179	37
6d	2.90×10^4	1.85×10^3	16
7a	4.99×10^4	1.62×10^3	31
7b	3.15×10^4	5.20×10^3	6
		Avg.	59

Group 1: Cerium, ruthenium, and zirconium-niobium prominent.
Group 2: Spectrum of mixed fission products.

were agitated with 0.3 M ammonium oxalate—0.1 M ammonium citrate—0.1 M oxalic acid—0.35 M H_2O_2 (pH 4.0). By gamma scan on a scintillation spectrometer, group 1 displayed prominent peaks at about 0.13, 0.47, and 0.72 Mev, corresponding to Ce^{141}, $Ce-Pr^{144}$, Ru^{103}, Ru^{106}, and $Zr-Nb^{95}$. Group 2 had a broader spectrum of assorted fission products. The total gamma counting rate of each sample before and after decontamination is given, the ratio providing the decontamination factor. The average DF was 59.

The residual fission products after the above 20-min treatment were very strongly bound to the steel, but oxalate-peroxide rated at least as well in their further removal as did stronger reagents. For example, sample 1a was boiled 20 min in 2% $KMnO_4$-2% NaOH, but the additional gamma DF was only 1.36. A second 20-min in oxalate-peroxide at 95°C added a DF of 3.25. Sample 3a was then treated for 20 min at 95°C in 3 M HNO_3-0.5 M H_2O_2, which gave an additional DF of only 1.64. A treatment of 3 more hours at 95°C in oxalate-peroxide for all of the specimens listed in Table 10 (except samples 6) produced a further average DF of only 2.4.

Liquid-impingement decontamination results with oxalate-peroxide were better than those from simple immersion in the same formula, as shown in Table 11. The

Table 11. Decontamination of BNL Loop Samples in Oxalate-Citrate-Peroxide, 3-hr Impingement[a] by Liquid Spray

	Scintillation Gamma counts/min		Gamma
	Before Decon.	After Decon.	DF
	Group 1		
1c[b]	2.93×10^5	1.66×10^3	177
1d[b]	1.91×10^6	2.38×10^3	803
2c	1.78×10^5	604	294
2d	2.03×10^5	1.20×10^3	169
3c	2.19×10^5	8.90×10^3	25
4c	2.66×10^6	1.24×10^4	215
4d	1.08×10^6	8.88×10^3	122
	Group 2		
5c	5.54×10^4	1.17×10^3	39
5d	5.78×10^4	195	296
6c	2.21×10^4	569	39
6d	3.91×10^5	1.34×10^3	292
7c	3.44×10^4	760	45
7d	3.33×10^4	136	245

[a] 1 hr at 55 to 95°C, and 2 hr at 95.

[b] "C" samples were in the top rack (avg DF = 119), and "d" samples were in the bottom rack (avg DF = 321), close to the impinger.

impingement device was a G-E Mobile Maid dishwasher, modified by the removal of all internal brass fittings, the addition of heat insulation, and the optional disconnection of the timer motor. The average DF in 3 hr was 212, the top-rack average being 119 and the bottom rack average 321. During the 3-hr test, the pH of the solution rose from 4.0 to 4.5, and the H_2O_2 concentration dropped from 0.35 to 0.22 M, showing that considerable improvement in solution stability had been made over the first oxalate-peroxide formula recommended for the EGCR charge and service machines.

The lack of samples prevented further extensive decontamination testing. A 10-min boil in water, however, decontaminated a fresh portion of pipe sample 1 by a factor of 2.3 and pipe sample 3 by a factor of 4.0.

2.8.7 Decontamination Comparisons: Oxalate-Peroxide vs Other Reagents[20]

In a special study, summarized in Table 12, an oxalate-peroxide-citrate formula compared well with five more-corrosive reagents in decontamination tests on Ce^{144}, $Eu^{152,154}$, Am^{241}, Ru^{106}, Cs^{137}, and I^{131}.[20] Metals tested included carbon steel, aluminum, and types 302 and 347 stainless steels. (Comparisons with several other reagents under different circumstances are discussed in Secs. 2.8.1 through 2.8.5.) In this special study, the six reagents in which contaminated coupons were agitated for 20 min at 95°C were:

(1) 0.3 $\underline{M}$ H_2SO_4–0.1 $\underline{M}$ $H_2C_2O_4$–0.05% 1-phenyl-2-thiourea[5]

(2) 1 $\underline{M}$ HNO_3

(3) 1 $\underline{M}$ HNO_3-0.1 $\underline{M}$ NaF

(4) 1 $\underline{M}$ HNO_3–0.1 $\underline{M}$ NaF–1 $\underline{M}$ H_2O_2

(5) 0.3 $\underline{M}$ $(NH_4)_2C_2O_4$–0.1 $\underline{M}$ $(NH_4)_2HC_6H_5O_7$–0.1 $\underline{M}$ $H_2C_2O_4$ (pH 4.0)

(6) Solution 5 with 0.35 $\underline{M}$ H_2O_2

The several nuclides studied will be considered separately in the following sections.

2.8.7.1 Cerium. – All six reagents decontaminated metals from cerium quite well. Metal coupons were cut to 1 x 1/4 in. from 0.005-in. shim stock and degreased in acetone. A drop of concentrated NH_4OH was then placed on each coupon, and two drops of $Ce\text{-}Pr^{144}$ in 1 $\underline{N}$ HCl (1 mc/ml) were added. After 6 hr of drying, the cerium was bound strongly enough that 15-min of boiling in distilled water (two coupons of each metal) removed an average of only about 10% of the 1 to 2 r/hr of beta-gamma activity. In scouting tests, two coupons of each metal were then agitated for 20 min at 95°C in each of the six decontaminating solutions. Decontamination factors, judged by portable survey meters, were several hundred to several thousand. Other contaminated coupons were then heated in helium at 100°C for 1 hr in order

Table 12. Gamma Decontamination Factors of Five Decontamination Solutions[20]

Contaminated coupons agitated 20 min with reagent at 95 ± 1°C

Contaminant	Type of Metal	0.3 $\underline{M}$ H_2SO_4, 0.1 $\underline{M}$ $H_2C_2O_4$, 0.05% phenylthiourea[5]	1 $\underline{M}$ HNO_3	1 $\underline{M}$ HNO_3, 0.1 $\underline{M}$ NaF	1 $\underline{M}$ HNO_3, 0.1 $\underline{M}$ NaF, 1 $\underline{M}$ H_2O_2	0.3 $\underline{M}$ $(NH_4)_2C_2O_4$, 0.1 $\underline{M}$ $H_2C_2O_4$, 0.1 $\underline{M}$ $(NH_4)_2H$ Cit.	0.3 $\underline{M}$ $(NH_4)_2C_2O_4$, 0.1 $\underline{M}$ $H_2C_2O_4$, 0.1 $\underline{M}$ $(NH_4)_2H$ Cit., 0.35 $\underline{M}$ H_2O_2
$Ce\text{-}Pr^{144}$	CS[a]	950				320	310
	Al	1.1×10^3	700	36	2.7×10^3	690	695
	347	1.7×10^3	3.1×10^3	1.3×10^3	890	8.3×10^3	1.2×10^3
	302	3.2×10^3	1.1×10^3	220	570	530	600
$Eu^{152,154}$	CS	24, 9[b]				104, 16	15, 15
	Al	405, 100	76, 480	180, 380	6.2×10^3, 2.9×10^3	225, 450	105, 295
	347	345, 130	42, 24	105, 27	39, 24	150, 43	67, 185
	302	155, 84	53, 59	25, 96	23, 22	100, 42	55, 130
Am^{241}	347	35	23	635	127	48	80
$Ru\text{-}Rh^{106}$	Al	11, 10[b]	36, 31			22, 10	40, 60
	347	19, 11	36, 12	34, 14	120, 120	9, 7	59, 41
	302	22, 18	69	78, 41	660, 480	23, 17	119, 90
Cs^{137}	347						1.6×10^3
I^{131}	Al	8				6	6
	347	5	5	9	11	3	31
	302	4	5	5	11	4	7

[a] CS = carbon steel, type A-109.

[b] First DF is for unbaked samples, second DF for samples baked in helium.

to more nearly approach EGCR conditions, gamma counted through a lead absorber in a well-type scintillation counter, and decontaminated as before. Results for all solutions were quite good, as shown in Table 12. The figures are for only one coupon each, except for carbon steel (CS), which are an average of two. Further work, featuring higher helium baking temperatures and possibly cerium volatilization, needs to be done (see also Sec. 2.8.12).

The apparent effect of fluoride in lowering the gamma DF of cerium (Table 12, HNO_3 vs HNO_3-NaF) was rechecked with duplicate samples, this time after heating the coupons to 300°C in helium. The gamma DF's, 1 M HNO_3 without vs with 0.1 M NaF, were: aluminum, 1020 vs 270 (corroded); type 347 stainless steel, 105 vs 700; type 302 stainless steel, 305 vs 640. Hence the fluoride effect was probably not significant.

Ammoniacal peroxide (1 M NH_4OH-1 M H_2O_2) was also rather effective on cerium in 20 min at 95°C. Average DF's of duplicate samples were: carbon steel 160, aluminum 230, type 347 stainless steel, 1.3×10^3; and type 302 stainless steel, 360. Basic peroxide is too unstable for use at such elevated temperatures, however.

2.8.7.2 Europium. – Oxalate-citrate-peroxide was as good as the other reagents on europium. Metal coupons were contaminated with $Eu^{152,154}$ in the same way as with cerium (Sec. 2.8.7.1). After being air dried, the beta-gamma activities of the coupons were 200 to 600 mr/hr. Decontamination of two coupons of each metal by 20 min of boiling in distilled water was by average factors of 2.2 for carbon steel, 16 for aluminum, 11 for type 347 stainless steel, and 7 for type 302 stainless steel. This was considerably superior to that experienced for cerium. Some of the remaining coupons were then baked in helium for 30 min at 100°C, and some were not baked. One or two coupons of each baked metal and one or two of the unbaked metal were then agitated in each reagent for 20 min at 95°C. Scintillation gamma counts before and after decontamination were used to compute the DF's, which ranged from 9 to 6000 (Table 12). Aluminum coupons were badly corroded by the fluoride solutions. Europium decontamination was poorer than for cerium. More data are needed for statistically significant differences.

When europium-contaminated coupons were boiled 10 min in 2% $KMnO_4$-5% NaOH, water washed, and placed in oxalate-citrate-peroxide at 95°C for 20 min, the gamma DF for carbon steel was 11, for type 347 stainless steel, 32, and for type 302 stainless steel, 57, showing no improvement over the oxalate reagent alone.

2.8.7.3 Americium. – Oxalate-peroxide results were second only to those from acidic fluorides. Am^{241}-contaminated coupons of type 347 stainless steel, 3/4 x 3/4 x 0.005 in., were prepared by boiling the coupons in a nitric acid solution of the actinide, then washing them in hot water until no alpha count could be transferred to dry filter paper when the paper was rubbed on the dry steel. All coupons then had alpha activities (on one side) of 1000 to 3000 counts/min. Decontamination tests were successful in all six reagents when duplicate coupons were agitated with the reagents for 20 min at 95°C (Table 12). The highest DF of 635 was obtained in the corrosive acid fluoride solution. The lowest DF, 23, resulted from the treatment in 1 M HNO_3. The oxalate-peroxide DF of 80 was exceeded only by the ones in the fluoride reagents. Final alpha activities ranged from an average of 2 counts/min (HNO_3-NaF) to 85 (with 1 M HNO_3). Considerable more work with americium is planned.

2.8.7.4 Ruthenium. – Acid peroxide was again demonstrated to be an effective ruthenium decontaminant. Coupons of aluminum and of types 302 and 347 stainless steels were contaminated with trivalent Ru^{106} (in equilibrium with its daughter Rh^{106}) in HCl solution in the same manner as with cerium (Sec 2.8.7.1). The average gamma activity per coupon was about 8 x 10^5 counts/min. Duplicate coupons were used for each of the six decontamination solutions. One group of coupons was decontaminated after simple air drying, and the other was first baked at 110°C in helium for 1 hr. As shown in Table 12, the addition of H_2O_2 to both the oxalate mixture and the nitric acid mixture significantly increased ruthenium decontamination. Noncorrosive oxalate-peroxide was second in effectiveness only to the nitric acid-fluoride-peroxide mixture (119 vs 660 for unbaked type 302 stainless steel). The fluoride-peroxide mixture was noncorrosive to stainless steel (Sec 2.8.11), but highly corrosive to carbon steel. The trend toward the increased tenacity of ruthenium in adhering to metals when baked in helium was evident in all solutions.

2.8.7.5 Cesium. – Elemental Cs^{137}, carrier-free, was decontaminated from stainless steel by factors of about 2 x 10^3 by oxalate-peroxide after deposition on the metal from high temperature helium. The cesium vapor was produced by drying 10 mc of Cs^{137} as the chloride in HCl solution in a porcelain boat, covering the dry residue with metallic calcium, and heating for 90 min in a stream of helium at 750°C in a quartz tube. The helium was then led through a spiral winding of 0.005-in. type 347 stainless steel sheet in an unheated portion of the tube. Nine samples with gamma activities of about 2 x 10^6 counts/min were then cut from the spiral. The average DF of three of these after 20 min at 95°C in oxalate-citrate-peroxide was 1.6 x 10^3 (Table 12). Three more were similarly treated in 0.4 M ammonium oxalate–0.1 M acetic acid–0.5 M H_2O_2 (pH = 4.0), with an average DF of 1.8 x 10^3. The remaining three had an average DF of 230 when treated for 20 min in distilled water at 95°C. Other metals need to be tested in the same way and the relative effectiveness of other reagents measured.

2.8.7.6 Iodine. – A method was found by which carrier-free I^{131} could be volatilized, transported in high-temperature helium, and deposited on various metals. Iodine so deposited was more difficult to decontaminate than that put on by the aqueous method previously described for other fission products. The best decontaminant was a hot solution of KOH or NaOH. Oxalate-peroxide reagents rated well in the study, however.

The first method tried for volatilizing I^{131} was to place 1 ml of basic sulfite solution, containing 5 mc of I^{131} as the iodide, in a porcelain boat. A few drops of

30% H_2O_2 were then added to oxidize the iodide to elemental iodine. The boat was placed in a quartz tube in a tube furnace and heated to 400°C in a stream of helium, whose flow rate was about 200 ml/min. The helium was passed over metal coupons placed in an extension of the tube outside the furnace. Heating was continued for 1 hr. The samples were then removed and gamma counted. The counting rates averaged about 3×10^6 counts/min per coupon (1 x 0.25 x 0.005 in.). Six coupons each of aluminum and types 302 and 347 stainless steel were boiled in distilled water for 10 min, dried in air, and again gamma counted. The aluminum was apparently decontaminated quite uniformly, by a factor of 12 ± 1 (95% confidence interval of the average), but it was later shown that nearly all the decontamination was due to volatilization of the iodine in air over a period of one to two days; therefore, the decontamination in boiling water was less than a factor of 2. The hot-water DF for type 302 stainless steel, also including the DF due to volatilization, was 36 ± 6, which was significantly better than for aluminum, and the DF for type 347 stainless steel was 14 ± 9, which was not significantly better, but with significantly worse precision than for aluminum. The coupons were then treated with the six reagents for 20 min at 95°C, but the apparent additional DF's of 2 to 18 were later found to be in error due to the high activities of the empty counting tubes resulting from the volatilization of the iodine from the metals and deposition on the walls of the tubes. This mention of these early difficulties may serve to warn other workers who also deal with elemental iodine in contamination experiments.

A second method for volatilizing elemental I^{131} in helium was identical to the first, except that the mixture of iodide and sulfite with H_2O_2 was dried in air or helium at room temperature before the iodine residue was heated. Thus no steam was generated in the tube furnace. Six coupons each, of the three metals contaminated by gaseous I^{131} to about 5×10^5 counts/min, were allowed to stand overnight and then were boiled in water for 10 min, as before. Unboiled controls had an evaporation DF of 10 to 14, as in the first test. There was no further significant DF on aluminum by water, but the DF in water on the two stainless steels was 2. One sample of each metal was then treated for 20 min at 95°C in the six reagents (Table 12). The highest DF, 31, for type 347 stainless steel in oxalate-citrate-peroxide, was partly due to an unusually low DF of only 3.6 on that coupon from evaporation and the 10 min of boiling in water. The next highest DF, 11, was in the powerful decontaminant mixture of nitric acid, fluoride, and hydrogen peroxide. Other DF's were only 3 to 9, as shown.

These rather poor results for the decontamination of iodine were cause for concern, since iodine could well be one of the major volatile fission products released into the coolant of a gas-cooled reactor. Many other decontamination solutions were tested on the adherent iodine residue remaining on metals after initial aging and water decontamination (Table 13). In this test series, strong bases were best for I^{131} on carbon steel and stainless steel, with DF's up to 1.4×10^3 from 20 min of boiling in 30% KOH. Aluminum was best decontaminated by several 20-min treatments at 95°C in oxalate-citrate-peroxide at pH 4.0, with DF's up to 4×10^3. The failure of alkaline permanganate as an I^{131} decontaminant was interesting (DF 3 to 6), as also was the comparative success with reducing agents (DF up to 1000 with $CrSO_4$).

Table 13. Other Decontamination Results on Vapor-Deposited I^{131}

Reagent	Conditions	Gamma Decontamination Factor			
		Carbon Steel	Al	347 SS	302 SS
5% H_2O_2 + 5% NaOH	20 min, 40°C	14-17	50-135	15-54	10-68
2% $KMnO_4$ + 5% NaOH	20 min, boil	4		3	5-6
0.4 M $CrSO_4$, ~0.1 M H_2SO_4	20 min, 80°C	18-32	2-1000	30-60	60-300
Turco 4501-A	20 min, boil	24-670		11-80	240-380
0.1 M NaN_3 + 0.1 M $Na_2S_2O_3$	20 min, 80°C	27	4	3	35
~0.5% "Fab" detergent	20 min, boil	1.1	4	3	4
0.4 M $CrSO_4$, ~0.1 M H_2SO_4 + 0.01 M KI	20 min, 80°C	120	440		
10% Turco 4501-A	20 min, boil	20			22-106
30% KOH	20 min, boil	1.4×10^3			28-500
3% KOH	20 min, boil	23			14-120
30% KOH + 20% triethanolamine	20 min, boil	27			70-90
30% KOH + 20% triethanolamine, 10% solution	20 min, boil	11			23-73
0.1 M Na_2SO_3 + 2% NaOH	20 min, 95°C	38			13
0.1 M $NaHSO_3$ + 0.1 M $H_2C_2O_4$	20 min, 95°C	8	690		3
0.3 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ + 0.1 M $(NH_4)_2H$ cit. + 0.35 M H_2O_2	(a) 10 min, 95°C		840		
	(b) 20 min, 95°C	14	100-470		9
	(c) 20 min, 95°C, 3 treatments, fresh solutions		3300-4000		

Still a third method used for producing carrier-free fission product iodine was the heating of neutron-irradiated tellurium. For this test, 70 mg of TeO_2 was neutron irradiated for 24 hr in a quartz ampoule at a thermal neutron flux of 2×10^{14} and then cooled four days. The oxide was transferred to a porcelain boat and heated at 900°C in a tube furnace for about 24 hr, at a helium flow rate of 250 cc/min. A second furnace, downstream from the first, was held at 450°C, and the exit end of the quartz heating tube was at 50°C. Twenty coupons each of type A-109 carbon steel, aluminum, and types 347 and 302 stainless steel were positioned from the boat all the way downstream to the cool end of the tube. From scintillation gamma scanning it was found that almost all the activity present in the 50-300°C region was from I^{131}, and some tellurium activity was present, in addition to I^{131}, in the 400-800°C region.

In scouting tests of decontamination by isotopic exchange, four different iodine solvents containing cold iodine removed varying proportions of iodine from metal samples from the tube furnace. Iodine-131 decontamination, estimated from comparing the 0.36-Mev gamma peaks on scintillation gamma spectrum charts, varied from 2.0 on type 302 stainless steel in the 850°C region (20 min at 95°C in aqueous 0.1 M KI-0.01 M I_2) to 30 on carbon steel in the 50°C region (20 min at 46°C in carbon disulphide containing 0.1 M I_2). There was only a rough correlation between furnace-zone temperature and the I^{131} decontamination factor. The other decontamination reagents were 0.1 M I_2 in ethanol and in toluene. One hour of boiling in water resulted in an I^{131} DF of 29 on a type 302 stainless steel sample whose initial gamma counting rate of 1.4×10^5 counts/min on the 0.36-Mev peak was higher than the average of 6×10^4. The lowest DF's (1.3 and 2) were on the stainless steel samples with the lowest peak heights (about 5×10^3), in the iodine-CS_2 and iodine-H_2O reagents respectively. Thus, although more work needs to be done on this problem, it is clear that isotopic exchange of I^{131} on metal surfaces with cold iodine in solution did not produce dramatic results.

In still another iodine decontamination test series, 12 mc of carrier-free I^{131} were vaporized from a dried peroxide-sulfite residue at 500°C and led by helium through spirals of type A-109 carbon steel, aluminum, and type 347 stainless steel. The spirals were then washed in hot water and cut into coupons, 1 x 0.25 x 0.005 in. In 3 hr at 95°C, the I^{131} was removed from ten coupons of carbon steel by factors of 136 ± 25 with 0.4 M oxalate–0.1 M acetate–0.5 M H_2O_2 (pH 4.0), 96 ± 28 with 10% Turco 4518, 23 ± 10 with 3% NaOH, and 25 ± 4 with distilled water. Initial activities were about 10^5 counts/min/sample. From aluminum, the DF was 710 ± 240 with oxalate-peroxide when the initial activity exceeded 5×10^6, and only 75 when the initial activity was less than 1×10^6. With distilled water, the average aluminum DF from I^{131} with ten coupons was 8 ± 3. With type 347 stainless steel, whose average gross-gamma activity per coupon was about 2×10^4 counts/min, a series of one to four treatments of five coupons each in oxalate-acetate-peroxide, each treatment being for 20 min at 95°C, showed increasing decontamination with increased time. With one treatment, the average DF was 7 ± 2, with two it was 17 ± 3, with three it was 23 ± 17, and with four, 31 ± 11. The precisions were computed as 95% confidence belts. Decay and evaporation were allowed for by running suitable controls.

In view of the difficulties associated with the decontamination of metals from a small but stubborn fraction of the I^{131} on the metal surfaces, Lawson proposed that an investigation be made of the practicability of precoating the metal surfaces with cold iodine before exposure.[20] This idea has not yet been tested.

2.8.8 Oxalate-Peroxide Impingement Tests on Synthetically Applied Fission Products

The liquid spraying of oxalate-peroxide decontamination solutions in the charge and service machines was simulated by the use of the modified household dishwasher described in Sec 2.8.6. Most of the DF's were in the range of 10^3 to 10^5 (Table 14). Fifty-four coupons of carbon steel, type 347 stainless steel, and aluminum (2 x 0.25 x 0.005 in.) were contaminated with pure fission products and with mixed fission products by first wetting one side of each coupon with ammonium hydroxide and then spreading several drops of the fission product solution (about 1 mc/ml) on the wet surface. The surfaces were dried in air, and the coupons then baked in air on a hot plate until the metal changed color slightly. The coupons were then cooled, rinsed vigorously in hot water to remove loose and soluble contamination and dried again in air. Since the gamma activities, which were as high as 6×10^7 counts/min/coupon, were too high for standard gamma counting equipment, the beta-gamma activities were measured with a portable "Cutie-Pie" type of radiation meter, with a range of 5 to 10,000 mr/hr. For this measurement, the instrument was carefully zeroed and the geometry of measurement standardized. A suitable conversion factor, derived from cross checks between the Cutie-Pie and the gamma scintillation counter made at lower levels of activity, was used to convert each Cutie-Pie reading to estimated gamma-count-per-minute values, with an accuracy of ±10%.

The contaminated coupons were then mounted in the top and bottom racks of the dishwasher and washed for 30 min as the temperature in the machine rose from 75 to 95°C, followed by 1 hr at 95°C. The solution used was 0.4 M $(NH_4)_2C_2O_4$ + 0.36 M H_2O_2 at pH 4.1, except for the last two fission products listed in Table 14, when 0.1 M ammonium citrate was also included. The coupons were then rinsed, dried in air, and gamma counted on a scintillation gamma counter. The high DF for I^{131} applied to the metals by the liquid method was in some contrast to the lower values obtained when the iodine was deposited from the gas phase (Sec 2.8.7.6).

2.8.9 Oxalate-Peroxide Derusting and Decontamination of Miscellaneous Tools

The derusting and fission product decontamination of miscellaneous hand tools of carbon steel was easily accomplished either by immersion in or impingement by an aqueous solution of 0.4 M ammonium oxalate—0.2 M ammonium acetate—0.5 M hydrogen peroxide—0.1% Tergitol nonionic NPX at 90 to 95°C, at pH 4.0 to 4.3, for 30 min to 2 hr. Although iron rust promoted the conversion of H_2O_2 to H_2O and O_2, its rapid dissolution and the complexing of the ferric ion by the oxalate, together with the buffering action of the acetate, combined to prolong peroxide life. Corrosion was substantially prevented by the inhibitive effect of the peroxide, to be discussed later (Sec 2.9). Aluminum and stainless steel tools and small machinery were also decon-

Table 14. Decontamination in Dishwasher by Oxalate-Peroxide to Simulate Solution Spraying in EGCR Service Machine

Fission Product	Avg. Initial β-γ Activity (mr/hr)	Metal Coupon	Decontamination Factor	
			Top Location	Bottom Location
Ru^{106}	36	Carbon steel	730	1.7×10^4
		Type 347 SS	32	420
		Aluminum	1.8×10^4	1.1×10^4
Zr^{95}-Nb^{95}	72	Carbon steel	2.5×10^4	2.3×10^5
		Type 347 SS	1.9×10^4	3.3×10^3
		Aluminum	2.7×10^4	130
Sr^{90}	460	Carbon steel	3.9×10^5	9.0×10^4
		Type 347 SS	3.7×10^4	1.1×10^5
		Aluminum	5.3×10^4	1.9×10^5
Cs^{137}	31	Carbon steel	1.2×10^5	4.9×10^3
		Type 347 SS	8.6×10^3	120
		Aluminum	3.7×10^4	6.5×10^3
Y^{91}	60	Carbon steel	3.3×10^3	2.0×10^4
		Type 347 SS	2.8×10^3	7.5×10^3
		Aluminum	2.4×10^3	3.2×10^4
Ce^{144}	1030	Carbon steel	8.5×10^5	2.5×10^5
		Type 347 SS	1.7×10^5	9.6×10^4
		Aluminum	2.4×10^4	1.8×10^5
Mixed fission products	93	Carbon steel	6.6×10^4	1.8×10^4
		Type 347 SS	5.9×10^3	2.3×10^3
		Aluminum	7.1×10^4	1.7×10^5
I^{131}[a]	185	Carbon steel	520	980
		Type 347 SS	2.0×10^3	5.1×10^3
		Aluminum	1.6×10^4	1.6×10^4
Ba^{140}-La^{140}[a]	1600	Carbon steel	8.8×10^4	2.1×10^4
		Type 347 SS	2.9×10^4	1.5×10^4
		Aluminum	2.7×10^5	2.1×10^5

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[a] Formula contained 0.1 M citrate.

taminated to background levels by the reagent. Initial beta-gamma activities were as high as 100 mr/hr.

2.8.10 Decontamination with Oxalate-Peroxide at 60°C vs 95°C

An oxalate-peroxide mixture at 60°C and pH 2.5 was as effective a decontaminant for carbon steel as the same mixture at 95°C and pH 4.5, when 2 to 10 times the contact time was used (Table 15). The solution was 0.4 $\underline{M}$ $(NH_4)_2C_2O_4$ + 0.2 $\underline{M}$ $NH_4C_2H_3O_2$ + 0.5 $\underline{M}$ H_2O_2. It was prepared from a mixture of the acids and peroxide, the pH being raised to either 2.5 or 4.5 with ammonium hydroxide. Contaminated coupons were prepared by first boiling them in an aqueous detergent solution until the absence of "water break" to ensure a clean surface, dipping them in carrier-free fission product solutions at 1 mc/ml, pH about 5, draining, and drying and baking at moderately high temperature as indicated. The coupons were then rinsed well in hot water to remove water-soluble contaminants, and the gamma activity measured either by portable instruments under standardized geometry or by scintillation gamma counting. Five numbered coupons were then placed in each of the two solutions in each test series and agitated for the first time period shown (Table 15). The coupons were then removed, rinsed, dried in air, and the activities again measured. The same coupons were returned to solution for the second time period, etc., until the end of each test. The gamma DF figures in Table 15 are the averages for the five coupons in each case. Precision estimates are not quoted because each coupon followed its own decontamination curve, often diverging from the others with increased time, so that precisions computed on each average DF would tend to give an unduly pessimistic estimate of the precision of comparison between the efficiencies of the two solutions.

Heating of ruthenium residues with slight oxidation was necessary in order to make the element tenacious enough to demonstrate decontamination differences. The water-control DF of only 1.1 in 30 min illustrates the degree of bonding to the steel. Overheating caused difficulties, however. After test series 5, a group of five additional $Ru\text{-}Rh^{106}$ contaminated coupons, badly oxidized by heating to 500°C in helium containing some oxygen, was decontaminated by a factor of only 1.6 after 1.5 hr in the oxalate-acetate-peroxide at pH 4.0 and 60°C. The DF after 6 hr at 60°C in 2% NaOH-2% $KMnO_4$ was an additional 3.1, and, after 5.5 hr in a final treatment in the peroxide reagent at pH 2.5 and 60°C, it was only 2.1 more.

The effectiveness of oxalate-peroxide on $Zr\text{-}Nb^{95}$ was again illustrated in test series 6 (Table 15), with a DF of 2.6×10^5 after 2 hr at 95°C. Another group of five $Zr\text{-}Nb^{95}$ coupons was boiled 2 hr with 10% Turco 4512, an inhibited phosphoric acid proprietary mixture, which removed the blue oxide film, yielding an average DF of 2×10^3. The same coupons were then treated 2 hr at pH 4.5 in oxalate-peroxide at 95°C, with an average additional DF of 51. The average activity was then only 39% over the low background of the scintillation counter.

Tenaciously adherent $Ce\text{-}Pr^{144}$ that was baked onto the steel was also removed about as well in 2 hr at 60°C as it was in 15 min at 95°C (test series 7-9, Table 15).

Table 15. Decontamination of Carbon Steel with an Oxalate-Peroxide Formula at 60°C (pH 2.5) vs 95°C (pH 4.5) (0.4 $\underline{M}$ $(NH_4)_2C_2O_4$ + 0.20 $\underline{M}$ $NH_4C_2H_3O_2$ + 0.5 $\underline{M}$ H_2O_2)

Test Series	Fission Product	Initial Activity (counts/min)	Decontamination Time (hr)	Gamma DF		Remarks
				60°C	95°C	
1	$Ru\text{-}Rh^{106}$	4×10^5	0.5	>200		Coupons dried under heat lamp
2	$Ru\text{-}Rh^{106}$	2×10^5	0.5	16		Baked 15 min in He, 100°C
			1.0	130		
			1.5	>200		
3	$Ru\text{-}Rh^{106}$	$3\text{-}6 \times 10^5$	0.5	20	28	Baked 15 min in He, 150°C; trace of bluing of steel
			1.0	27	37	
			1.5	33		
			2.5	43		
			3.5	52		
			4.5	59		
			6.5	76		
			22.5	96		
4	$Ru\text{-}Rh^{106}$	6×10^5	0.5		1.1	Baked 15 min in He, 150°C (distilled H_2O control)
5	$Ru\text{-}Rh^{106}$	$3\text{-}6 \times 10^5$	0.5	43	169	Baked 15 min in He, 150°C
			1.0	77	249	
			2.0	145	343	
			3.0	267	417	
			4.0	295	478	
6	$Zr\text{-}Nb^{95}$	6×10^6- 1.1×10^7	0.25	192	903	Baked 15 min in He, 200°C
			0.50	374	5.7×10^3	
			1.0	1.4×10^3	4.9×10^4	
			2.0	1.1×10^4	2.6×10^5	
7	$Ce\text{-}Pr^{144}$	$3\text{-}6 \times 10^5$	0.25	>200	>200	Not baked
8	$Ce\text{-}Pr^{144}$	$1\text{-}4 \times 10^5$	2.0	23		Baked until blue, 15 min in He, 200°C
9	$Ce\text{-}Pr^{144}$	2×10^5	0.25	4.4	>100	Baked 15 min in He, 150°C
			2.0	>100		
10	Y^{91}	4×10^5	0.5		1.5×10^5	Baked 15 min in He, 200°C
			2.0	1.1×10^3		
11	$Ba\text{-}La^{140}$	$1\text{-}3 \times 10^6$	0.25	37	55	Rinsed after drying, then baked 30 min 650°C in O_2-free He. No bluing of metal.
			0.50	53	106	
			1.0	84	323	
			2.0	142	788	

A good comparison similarly was obtained with Y^{91} (series 10). Before the Ba-La^{140} series 11 was run at 650°C, a slight oxygen inleakage through the walls of rubber tubing into the helium was corrected. Before being baked, the contaminated coupons were rinsed in hot water to remove soluble chloride. When four times the decontamination contact time was used, the decontamination of Ba-La^{140} at 60°C was approximately as effective as that at 95°C. (For other decontamination tests after baking in helium at high temperature, see Sec 2.8.12).

2.8.11 Plutonium Decontamination with Fluoride Mixtures[21]

Acid fluoride solutions, with corrosion inhibited by hydrogen peroxide, were the most effective decontaminants tested for plutonium on stainless steel. This work is reported here because of the possible occurrence of transuranics in the EGCR experimental loops. Coupons of type 347 stainless steel contaminated with about 4×10^5 alpha disintegrations per minute of tenaciously adherent Pu^{239} were cut from the wall liner of the 3019 Pilot Plant cell which had sustained a plutonium release incident and had repeatedly been sprayed and flushed with various decontaminating solutions.[22,23] The coupons were boiled 20 min in a detergent solution to remove loose contamination, washed in distilled water, dried, and alpha counted to obtain initial readings. They were then suspended in several decontamination solutions at room temperature for 30 min (Table 16), washed, dried, and recounted. They were

Table 16. Decontamination of Type 347 Stainless Steel from Plutonium[21]

Solution	30-min DF	
	25°C	95°C
0.1 $\underline{M}$ $KMnO_4$, pH 3.5, 7, and 10	1.0-1.2	1.0-1.3
0.1 $\underline{M}$ Ce^{4+} in 1 $\underline{M}$ H_2SO_4	1	32
1 $\underline{M}$ $H_2C_2O_4$	1	1
1 $\underline{M}$ $H_2C_2O_4$ + 1 $\underline{M}$ HNO_3	1	1
0.4 $\underline{M}$ $H_2C_2O_4$ + 1 $\underline{M}$ H_2O_2		1.2
0.4 $\underline{M}$ $H_2C_2O_4$ + 1 $\underline{M}$ H_2O_2 + 0.1 $\underline{M}$ NaF		122
5 $\underline{M}$ H_3PO_4	1	1
25% H_2SO_4	180	360 (3 min)
1 $\underline{M}$ HNO_3 + 1 $\underline{M}$ NaF	1.5	280
0.3 $\underline{M}$ H_2SO_4 + 1 $\underline{M}$ H_2O_2		1.2
0.3 $\underline{M}$ H_2SO_4 + 1 $\underline{M}$ H_2O_2 + 0.1 $\underline{M}$ NaF		170
10% Turco 4501A	1	1
100% Turco 4501A		1.1
10% Turco 4306B	1.1	7.7
10% Turco 4518	1.0	1.2
10% Turco 4324	1	1

then resuspended in fresh solutions at 90 to 100°C for 30 min, washed, dried, and counted as before. The best decontamination factor at room temperature of 180 was in 25% H_2SO_4, which corroded the steel prohibitively. Nitric acid with fluoride was excellent at 95°C, but it also was too corrosive. Oxalic and sulfuric acids with fluoride, and with corrosion inhibited by peroxide, gave favorable DF's of 122 and 170 in 30 min at 95°C (Table 16).

In a further study of plutonium decontamination vs temperature, in 0.1 M NaF + 1 M H_2O_2 with 1 M HNO_3, 0.3 M H_2SO_4, or 0.4 M $H_2C_2O_4$, in 30 min at 50°C, decontamination was by factors of only 4.9, 1.4, and 1.1 respectively. In 30 min at 90°C, however, the DF's were 2.9×10^3, 1.7×10^3, and 1.2×10^3. Prolonged time at 50°C partially made up for poorer performance at the lower temperature. In 90 min at 50°C in the nitric acid-peroxide-fluoride the plutonium DF was 320.

The corrosion rate of the nitric acid mixture at 70°C on type 347 stainless steel was 0.004 mil/hr; on Incoloy, 0.003; Ni-o-nel, 0.002; Hastelloy C, 0.030; and Hastelloy F, 0.012 mil/hr.

2.8.12 Deleterious Effect of 500°C Baking on Subsequent Decontamination from Fission Products

When stainless steels were contaminated to 100-400 mr/hr with carrier-free Zr-Nb^{95}, Ce^{144}, Ba-La^{140}, or Ru-Rh^{106} in nonacid solutions, dried, baked at 500°C in oxygen-free helium, rinsed in hot water, and then treated with decontaminating reagents, results were poor. Type 347 stainless steel had decontamination factors from Zr-Nb^{95} of only 1.5 to 5 in 20 min at 95°C, and scarcely higher in 3-1/2 hr, with oxalate-peroxide reagents containing citrate and acetate buffers, with and without fluoride (Sec 2.10). The same low results were obtained with type 302 stainless steel, showing that they were not caused by isotopic exchange with the columbium stabilizer. Poor Zr-Nb^{95} results were also not caused by chloride residues, since the contaminating solution was composed of oxalate salts. Boiling Turco 4501, normally quite effective on Zr-Nb^{95}, produced additional decontamination factors of only 1.1 to 1.2. Equally poor results on stainless steels were obtained with cerium, barium-lanthanum, and ruthenium when treated for 20 min with oxalate-peroxide, but chloride residues not removed before baking may have contributed to this. Carbon steel decontamination factors were somewhat better, being 20 to 40 in 20 min and 250 to 320 in 3-1/2 hr for Zr-Nb^{95}, 17 in 20 min for Ce^{144}, 10 to 38 for Ba-La^{140}, and about 3 for Ru-Rh^{106} in 20 min. Baked aluminum had decontamination factors of 3×10^3 in 20 min for Zr-Nb^{95}, 700 to 1×10^4 for Ba-La^{140}, 60 to 100 for Ce^{144}, and 20 to 110 for Ru-Rh^{106}. The higher decontamination factors for aluminum were partly due to the higher corrosion rate of fluoride on aluminum than on steels. Baking at lower temperatures did not fix the fission products as firmly to the metals as at 500°C, as described previously (Sec 2.8.10). Evidently difficulties may be encountered in decontaminating metals run at high temperatures in gas-cooled reactors, such as heat exchangers and blowers, although rather good results were obtained on Brookhaven loop samples (Sec 2.8.6). This problem will be further investigated.

2.9 Corrosion Inhibition and Promotion by Hydrogen Peroxide in Decontamination Solutions:[24] The Probability that Peroxide May Be a Controllable Corrosion Inhibitor

Under chosen conditions of concentration, acidity, temperature, and formulation with other ingredients, hydrogen peroxide becomes either a corrosion inhibitor or a corrosion promoter for carbon steel. These conditions are now becoming known with enough confidence to permit the safe recommendation of peroxide-containing solutions for use in plant-scale decontamination. The study of the corrosion behavior of peroxide mixtures has been closely connected with the development of improved decontamination performance and longer effective life of the solutions. Corrosion rates of many of the solutions have already been given in this report. Specific studies of the corrosion behavior of peroxide solutions on several metals will now be given as functions of the conditions listed above.

The passivation and increased corrosion of carbon steel by different concentrations of hydrogen peroxide in oxalic acid have been known for several years. In 1952 Marshall,[25] in connection with the development of a chemical polishing method for mild steel, noted that stainless steel was passivated by a solution of 2.5% oxalic acid–1.3% hydrogen peroxide–0.01% sulfuric acid at room temperature. Hickling and Rostron,[26] in an extension of Marshall's work, observed that as the hydrogen peroxide concentration was increased in a solution of oxalic acid at room temperature, the solution became more corrosive to mild steel, then, less corrosive, with a polishing action, and finally at higher concentrations, it passivated the steel. For example, in 0.3 $\underline{M}$ $H_2C_2O_4$, metal filming and slight attack began at about 0.05 $\underline{M}$ H_2O_2. At 0.2 $\underline{M}$ H_2O_2 the metal became clean and attack was rapid. There was a polishing action between 0.3 and 1.0 $\underline{M}$ H_2O_2, and attack ceased above 1.0 $\underline{M}$ H_2O_2. In the region of beginning attack the electrical potential of the metal vs a calomel electrode was about -300 mv; during rapid attack it was approximately zero; during polishing it oscillated between about +200 and +500 mv; and, in the passive region, it was steady at about +600 mv.

The study of the passivation of carbon steel by hydrogen peroxide in oxalate salt solutions at elevated temperature, in the present ORNL work, may in part be considered a further development of the work of Marshall, Hickling, and Rostron.[25,26] Their electrode-potential method, slightly modified, was a useful tool in the evaluation of the peroxide concentration necessary to maintain corrosion passivity with various formulations and temperatures. Although Schumb *et al.*[18] warn that the inhibitive behavior of hydrogen peroxide on iron surfaces is capricious and should not lead to consideration of its use in practice, it now appears that safe use can be made of this property in oxalate formulations at controlled temperature and pH for decontamination purposes.

Figure 1 illustrates the types of corrosion curves which were experimentally determined on several metals in different oxalate formulas as the peroxide concentration was increased from zero to about 1 $\underline{M}$ at pH 4.0, 4.5, and 5.0. The illustration is for type 1020 carbon steel in 0.3 $\underline{M}$ ammonium oxalate at pH 4.0, 95°C, and

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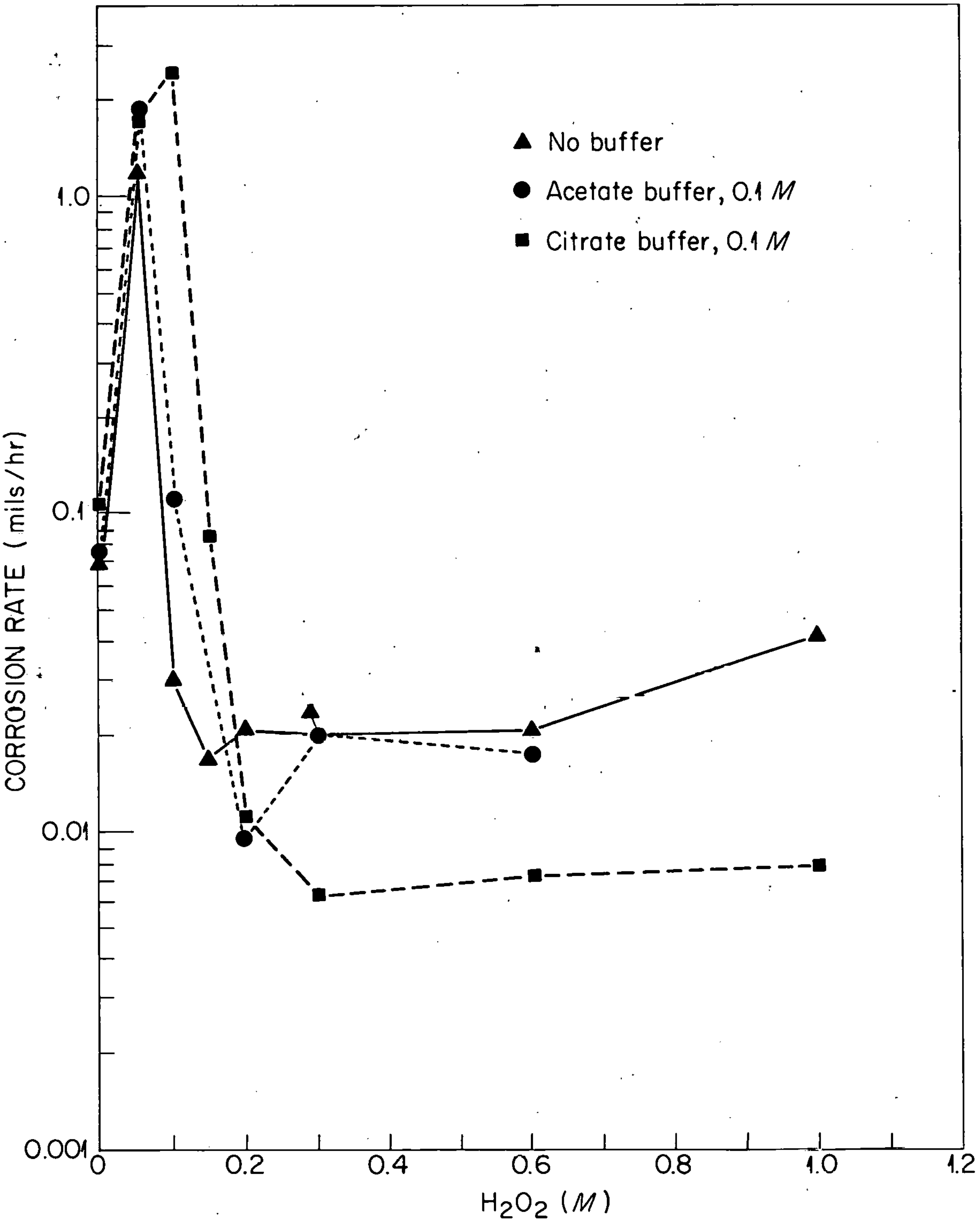

Fig. 1. Effect of H_2O_2 concentration and buffers on corrosion of type 1020 carbon steel in 0.3 M ammonium oxalate at pH 4.0, 95°C.

also in the same formula buffered with 0.1 M acetate and citrate. The pronounced increase in corrosion to about 2 mils/hr at about 0.1 M H_2O_2 corresponds to the corrosive region observed by Hickling and Rostron in oxalic acid-H_2O_2 at room temperature. During plant decontamination operations on carbon steel, an excursion into this region, perhaps caused by a decrease in peroxide concentration from some higher passivating value, could prove quite damaging to steel surfaces. Fortunately, the height of the corrosion peak decreased and its location receded toward zero H_2O_2 as the pH was raised. Advantage was taken of this property by developing long-lived "fail-safe" solutions, as described in Sec 2.10, which rose in pH at a rate which kept pace with the H_2O_2 decrease, so that the corrosive region was avoided.

Corrosion rates vs H_2O_2 concentrations, run by the method illustrated by Fig. 1, were less than 0.001 mil/hr at 0.05 M H_2O_2 and above for types 302 and 347 stainless steels, Inconel, and Zircaloy-2. Ball bearings of high carbon steel had a corrosion rate of 1.6 mil/hr at pH 5.1 and 95°C in oxalate-citrate without peroxide, but the location and extent of the corrosion peak at low peroxide concentrations have not yet been determined. At pH 4.0, the bearings were in the passive region at 0.33 M H_2O_2, however, with a corrosion rate of 0.01 mil/hr.

The corrosion curve data for four other metals in oxalate-acetate solutions at H_2O_2 concentrations of 0, 0.05, and 0.50 M at pH 4.0 and 95°C are summarized in Table 17. Aluminum shows a modest maximum of 0.075 mil/hr, followed by a drop to 0.048 mil/hr, which is a higher corrosion rate in 0.50 M H_2O_2 than in the peroxide-free solution. Type 440C stainless steel and Croloy 2-1/4 show corrosion inhibition without a maximum, but maxima could occur somewhere in the region between 0.00 and 0.05 M H_2O_2, which was not studied. Titanium corrosion increased with increasing peroxide concentration, but 0.007 mil/hr at 0.50 M H_2O_2 should not be a prohibitive rate for decontamination work.

Table 17. Corrosion Rates of Four Metals in 0.3 M Oxalate—0.1 M Acetate—Peroxide Solutions at pH 4.0, 95°C

H_2O_2	Corrosion Rate (mils/hr)			
(M)	Al	440C Steel	Ti	Croloy 2-1/4
0.00	0.013	0.60	0.00001	0.010
0.05	0.075	0.075	0.0008	0.00008
0.50	0.048	0.004	0.007	0.00002

The experimental method of determining the corrosion rates of metal by weight loss, as a function of the peroxide concentration (Fig. 1), was laborious. A preferred method which was adopted was the determination of the peroxide concentration which induced passivity, as shown by the electrode-potential method.[26] The metal was sanded clean, dipped into the solution under test, and connected to one terminal of a Beckman model G pH meter, set for millivolt readings. The other terminal was connected to a standard calomel electrode in a small beaker of the solution at room temperature, which was electrically continuous, via a liquid bridge, with the heated solution. The peroxide concentration in the solution was periodically raised by adding from a buret a mixture containing the same concentrations of oxalate and other salts as in the test solution, but with a relatively high concentration of peroxide. The H_2O_2 concentration was followed analytically by the iodometric method.[18] When the metal was still in the phase of being rapidly corroded, it was withdrawn from solution after each millivolt reading was taken, in order to prevent unnecessary contamination of the solution with metal ions while a new temperature or peroxide concentration was being established. Polishing the metal with sandpaper before replacing it in the solution and measuring the new potential prevented false passivity points that might have resulted from invisible oxide coatings, especially when redetermining the passivity point by decreasing the peroxide concentration after passivity had been reached. The effects of ferric ion concentration on corrosion rates in oxalate-peroxide solutions have not yet been studied, but they are suspected to be significant.

By the electrode potential method it was found that solutions in a wide variety of conditions of temperature and pH could be adjusted in H_2O_2 concentration to a point where a chosen carbon steel was actively corroded when the liquid impinged against it, but it became passive when impingement ceased. For example, a solution of 0.4 $\underline{M}$ oxalate–0.2 $\underline{M}$ acetate–0.7 $\underline{M}$ H_2O_2 at pH 2.0 and at room temperature corroded carbon steel at 5 mils/hr when agitated and at 0.02 mil/hr when not agitated. This type of solution might be excellent for the decontamination of large machinery by the hand scrub method, since corrosion would occur only under the brush. It might also be of value in the selective removal of thin layers of metal for other purposes, such as in the preparation of metal blanks for astronomical mirrors.

The determination of corrosive and passive conditions will be discussed further in connection with the development of "fail-safe" solutions of long life and low corrosivity, in Sec 2.10.

2.10 "Fail Safe" Oxalate-Peroxide Decontamination Solutions of Low Corrosivity and Long Life

2.10.1 Introduction

It has been pointed out in Sec 2.5 that the useful life of 0.3 $\underline{M}$ sodium or ammonium oxalate with 1 $\underline{M}$ H_2O_2 at 95°C in the presence of mild steel was less than 1 hr. This short life would be inconvenient for many types of decontamination operations. Subsequent evaluation of over 100 different formula mixtures resulted in lengthening the useful low-corrosive life to as much as 36 hr at 95°C in the presence of limited amounts of carbon steel, or to 12 hr in the presence of steel plus 100 ppm of ferric ion, the most destructive catalyst likely to be encountered in gas-cooled reactor decontamination. This improvement resulted from the empirical optimization of pH, peroxide concentration, and buffer choice and concentration in an aqueous solution of 0.4 M ammonium oxalate. This solution was almost saturated with oxalate at room temperature, thus providing the highest concentration convenient to mix in the cold, for maximum decontamination effectiveness and UO_2 dissolving power. The establishment of optimum values for other ingredients will be discussed in the following sections.

In all of the oxalate-peroxide formulation work, the peroxide composition was periodically determined on 1-ml samples by the iodometric method.[18] Oxalate analyses, when necessary, were made by the permanganate method, with suitable corrections for the peroxide. The pH readings were made with a Beckman model G pH meter, using electrodes immersed in the reaction flask in the earlier work, and later for increased reliability using miniature electrodes in small samples at room temperature.

2.10.2 Effects of pH, Ferric Ions, and EDTA

The useful life, decontamination effectiveness, and corrosive properties of oxalate-peroxide solutions are heavily dependent on pH. It was pointed out in Sec 2.5 that hydrogen ion is consumed in the oxidation of oxalate by hydrogen peroxide, thus raising the pH at an ever increasing rate and eventually resulting in rapid peroxide loss through autodecomposition. Both reactions are catalyzed by ferric ions, and the catalysis is more rapid at higher pH. The decontamination of carbon steel will result in some iron pickup. Providing enough acid reserve to prevent the pH from rising into the rapid-catalysis range is thus required for extended life. Hydrogen peroxide is most stable at a pH of about 4. At lower pH, not only is more H_2O_2 required for metal passivity, but carbon steel corrosion is more vigorous when in the corrosive range, and also the Fe^{3+}-catalyzed oxidation of oxalate by H_2O_2 is more rapid. In early development work, temporary stabilization of pH between 4 and 5 was accomplished by adding oxalic acid from time to time. This method was superseded by that of using buffers adequate to maintain the pH in the noncorrosive region as peroxide became depleted, as will be discussed later.

The interrelation of the oxidative power of H_2O_2 with pH and ferric ions in oxalate solution is not well understood, so no attempt will be made here to discuss any theories.[18] A few examples will serve to illustrate the interesting behaviors encountered.

1. In an early experiment, a solution 0.1 M in ammonium oxalate and 0.33 M in H_2O_2 was heated to 95°C, the pH being continuously monitored with a pH meter. The pH rose from 5.50 to 5.70 in 30 min and remained constant for the next 30 min. Ferric ion (100 ppm) as ferric sulfate was then added. Evolution of CO_2 then began, and the pH rose in 20 min to 6.40, with increasing frothing from CO_2 and destruction of the peroxide.

2. The experiment was repeated, with the Fe^{3+} in the solution from the beginning. Foaming took place as CO_2 was evolved. The pH rose to 6.50 in only 30 min.

3. When 0.4 $\underline{M}$ ammonium oxalate with about 0.15 $\underline{M}$ H_2O_2 at 95°C was made slightly basic with ammonia, no appreciable decomposition occurred in 15 min. When 25 ppm of Fe^{3+} was added, gas evolution began. The peroxide was then increased to 0.3 $\underline{M}$, and gas evolution increased. It increased still further when the Fe^{3+} content was doubled. When 0.07 $\underline{M}$ ammonium citrate was added and the solution again made basic with ammonia, foaming was still vigorous. The gas was chiefly CO_2, since it extinguished match flames inserted into the flask, but also contained some O_2. The oxygen could be demonstrated at the top of a reflux condenser by the glowing-splint test, after the CO_2 had been condensed on the cold walls as $(NH_4)_2CO_3$. There was enough oxygen to even explode mildly with the NH_3 vapors, after it was allowed to build up for a few minutes in a closed space and then ignited with a match. (In plant practice, purging off-gas lines with air would prevent the deposition of $(NH_4)_2CO_3$, which might result in the enrichment of oxygen to hazardous levels in gaseous ammonia.)

4. The quantitative effect of various concentrations of iron on peroxide life was demonstrated by means of four solutions, each 0.4 $\underline{M}$ in oxalate, 0.5 $\underline{M}$ in H_2O_2, and 0.2 $\underline{M}$ in citrate, at pH 4.5, 95°C. One solution contained no Fe^{3+}, one 10 ppm, one 100 ppm, and one 1000 ppm, added as ferric citrate. The solutions were stirred under reflux and their life behaviors noted. In 21 hr at 95°C, with no Fe^{3+} the pH was 4.6 and the H_2O_2 0.47 $\underline{M}$, showing great stability. With 10 ppm of Fe^{3+}, the pH was 5.75 and the H_2O_2 0.285 $\underline{M}$. With 100 ppm, in only 5 hr the pH had risen to 8.1, and the H_2O_2 had decomposed to 0.005 $\underline{M}$. With 1000 ppm, in 35 min the solution became basic, with complete decomposition of the peroxide.

5. Instead of prolonging peroxide life by inactivating ferric ion, versene (EDTA) promoted vigorous decomposition of the peroxide in the presence of 100 ppm of Fe^{3+}. For example, when 30% H_2O_2 (to make the solution 0.33 $\underline{M}$ in H_2O_2) was added to a solution of 0.1 $\underline{M}$ ammonium oxalate with 100 ppm of Fe^{3+} and 0.31% Versene at 95°C and pH 5.40, there was almost violent gassing, and the pH rose in 3 min to 6.60, with complete decomposition of the H_2O_2. (The composition of the gas was not determined.) When the same test was run without the Fe^{3+}, at a pH of 5.24, the pH did not rise for 50 min, at which time the Fe^{3+} was added. The pH then rose much more slowly in 1-1/2 hr to 5.80. It was reasoned that the peroxide had probably destroyed the Versene before the Fe^{3+} was added (a slight drop in pH of 0.15 during the initial 15 min had been noted), but a subsequent test seemed to disprove this. In a 0.31% Versene-0.33 $\underline{M}$ H_2O_2 solution without iron or oxalate, the adjusted pH held steady for 5 min at 3.86 at 95 ± 2°C, without visible reaction, but when 100 ppm of Fe^{3+} was added, vigorous foaming began. In 3 min the pH rose to 4.83, and the flask contents a few seconds afterward were violently ejected. The pH of the liquid remnant afterward was 7.70. In still another test, H_2O_2 (sufficient to make the solution to 0.3 $\underline{M}$) was added to 0.3 $\underline{M}$ oxalate—100 ppm Fe^{3+}—0.31% Versene at pH 4.50 and 95°C. This time, there was vigorous foaming, the pH rising in 8 min to 5.10, and in another hour to 6.10, with the H_2O_2 down to 0.028 $\underline{M}$. In a control test without the Versene the pH rose gradually to 6.10 in over 3 hr, and the solution still contained 0.20 $\underline{M}$ H_2O_2. No further work was done with Versene as an Fe^{3+} sequesterant in oxalate-peroxide formulas.

2.10.3 Effects of Peroxide Stabilizers

In the optimum oxalate-peroxide decontamination formulas as of July 1962, no stabilizers other than citrate and acetate are needed or used. There is doubtless a small amount of organic stabilizer in the laboratory reagent grade 30% H_2O_2, but this may not survive in the presence of oxalate and ferric ion in hot solution. Further work needs to be done in this field. The disappointing results on EDTA as a stabilizer, described in Sec 2.10.2(5), discouraged extensive further efforts along the lines of the complexing of impurities, but a number of life tests nevertheless were run with 8-hydroxyquinoline and sodium pyrophosphate as stabilizers. When 8-hydroxyquinoline (100 ppm) was added to 0.25 M oxalate-0.25 M H_2O_2 at 95°C and pH 4.5, the useful life was extended for about an hour (from 3 hr to 4), when no Fe^{3+} was added. The effect of 100 ppm of pyrophosphate was even less, and 1% pyrophosphate with 100 ppm of Fe^{3+} in another formula had little if any stabilizing effect.

2.10.4 Effects of Citrate on Solution Life and Corrosion Properties

The effects of ammonium citrate in oxalate-peroxide solutions containing ferric ions and carbon steel were so varied as to suggest complex and unknown mechanisms. Since it was not within the scope of the present work to investigate these mechanisms, only behavior was studied, and this study was confined to usage in peroxide decontamination solutions. To summarize, citrate can be quite beneficial as a buffer and life extender in oxalate-peroxide solutions, and can even reduce corrosion, but its presence in slightly acid solutions can greatly increase corrosion if its concentration or that of the acid is too high or if the peroxide concentration is too low. The best oxalate-citrate formula developed was 0.4 M oxalate—0.16 M citrate—0.34 M H_2O_2, pH 4.0, with a useful low-corrosive life of 12 hr at 95°C in the presence of 100 ppm of Fe^{3+}, and 36 hr in the presence of steel surfaces without added Fe^{3+}.

The buffering effect of citrate was first observed when 0.1 M citrate was mixed with 0.4 M oxalate-0.34 M H_2O_2 at pH 4.00 and 95°C. To promote decomposition, 36 in.^{2} of carbon steel surface in the form of 0.005-in. shim stock was suspended in the 800 ml of solution, and 100 ppm of Fe^{3+} was included. The useful life of the solution was 6 hr, at which time the pH had gradually risen to 5.8 and the H_2O_2 had decreased to 0.05 M. The corrosion rate on the steel by the weight-loss method was 0.0030 mil/hr during the first 3 hr and 0.0011 mil/hr during the last 3 hr. In a control life-and-corrosion test without citrate, the useful life was only 3 hr, the pH rising rather steeply to 6.40 and the H_2O_2 dropping to 0.03 M during the third hour. The corrosion rate was 0.015 mil/hr during the first hour and 0.0034 mil/hr during the last 2 hr.

Hopes for the use of citrate as a buffer were dimmed by the next test, with 0.30 M oxalate—0.22 M citrate—0.32 M H_2O_2 and the former iron surface and Fe^{3+} content. After 2-1/2 hr, vigorous decomposition and considerable metal attack occurred, with holes through the 0.005-in. steel at several points. It did not seem possible that citrate would ever be safe enough to use in oxalate-peroxide decontamination solutions for carbon steel.

Several other tests also showed citrate in oxalate-peroxide solutions to be potentially corrosive to carbon steel. For example, 0.4 M citrate with 0.4 M oxalate, 0.4 M H_2O_2, and 100 ppm of Fe^{3+}, at pH 4.0 and 95°C, did not corrode flat coupons of carbon steel excessively (0.003 mil/hr), but attacked 0.005-in. shim stock, when it was bent upon itself so as to make a narrow crevice, at rates of 8 to 24 mils/hr.

Some of the paradoxical behavior of citrate was explained when a carbon-steel passivity curve was run by the electrode-potential method. The corrosion threshold, here defined as the minimum H_2O_2 concentration necessary to induce passivity on carbon steel in oxalate-peroxide, was radically altered by citrate. At only 75°C and pH 4.0, when the ammonium citrate concentration in 0.4 M ammonium oxalate was increased from zero to 0.4 M, the peroxide necessary to induce passivation increased from 0.13 to about 0.7 M. Thus at 0.4 M H_2O_2-0.4 M citrate, the solution at 95°C was virtually at the corrosion threshold, and coupons containing crevices were readily attacked, while flat coupons were not. Corrosion threshold curves at 95°C at the pH's of interest have not yet been run.

It was obvious that if citrate were to be used as a buffer in oxalate-peroxide, the concentration should be minimized because of its effect on the corrosion threshold. Fortunately, in a series of life tests with the citrate varied from 0.05 to 0.18 M in 0.4 M oxalate—0.34 M H_2O_2—100 ppm Fe^{3+} at pH 4.00 and 95°C, the optimum citrate concentration of 0.16 M for longest life was also well within the passivating region. In this formula, the corrosion rate on carbon steel at 95°C was 0.0030 mil/hr for the first hour, 0.0015 mil/hr for the next 3 hr, and 0.00038 mil/hr for the next 7 hr. As the peroxide concentration went from about 0.005 M to zero, a corrosion peak of 0.11 mil/hr occurred, the pH by now having risen to between 6 and 7. After complete peroxide decomposition, the corrosion rate dropped to about 0.03 mil/hr. The metal surfaces remained bright and clean for 12 hr, and then turned dull. Crevice- and stress-corrosion samples of type A-109 carbon steel showed no pitting or cracking, even after the peroxide had failed. The peak corrosion rate lasted less than an hour. The total useful and noncorrosive life of this iron-containing solution was thus about 12 hr at 95°C.

The addition of 100 ppm of Fe^{3+} (as the oxalate or citrate) to oxalate-peroxide formulas for life and corrosion testing was an arbitrary but standardized measure designed to approximate severe conditions of iron pickup in large-scale usage. When no Fe^{3+} was added to the above 0.4 M oxalate—0.34 M H_2O_2—0.16 M citrate formula, starting at pH 4.00 and 95°C, but with 4 in.^{2} of mild steel corrosion surface in 800 ml of solution, the useful low-corrosive life of the solution was 36 hr at 95°C (under a reflux condenser) plus 130 hr at room temperature in overnight periods and one weekend. The 4 in.^{2} of steel in 800 ml simulated the steel-area-to-volume ratio of a storage tank of several hundred gallons. There was a gradual accumulation of Fe^{3+} in solution from corrosion of the steel test coupons. The initial corrosion rate of 0.0023 mil/hr gradually decreased to about 0.0003 mil/hr as the pH rose. During the 36th hour, when the H_2O_2 was 0.002 to 0.001 M and the pH about 8, the corrosion rate went through a peak of 0.16 mil/hr, after which it decreased to 0.06 mil/hr in the absence of peroxide. When 40 in.^{2} of mild steel was heated with this same formula, the life was decreased to 12 hr at 95°C, with three overnight periods at room temperature. The corrosion-rate dependence on H_2O_2 concentration and pH was similar to the test with 4 in.^{2} of steel. Halving the oxalate concentration in the presence of 100 ppm of Fe^{3+} did not shorten solution life (12 hr 95°C), but halving the citrate did decrease life (10 hr 95°C). In one test with 0.3 M citrate and 0.33 M H_2O_2 at pH 4.00, with 100 ppm of Fe^{3+} but without oxalate, the life was only 4 hr. Life and corrosion testing of citrate-peroxide solutions without oxalate were not carefully investigated, but preliminary results were unattractive.

2.10.5 Effects of Glycolate

Ammonium glycolate was effective as a buffer in oxalate-peroxide solutions, but in some ways was less desirable than citrate. The corrosion threshold was lowered by glycolate, as was the case with citrate. When ammonium glycolate solution at pH 4.00 was added to 0.4 M oxalate at pH 4.00, 95°C, in increments sufficient to increase the solution concentration 0.05 M at a time, the H_2O_2 molarity necessary to preserve carbon steel passivity rose linearly from 0.13 M at zero glycolate to 0.80 M at 1.05 M glycolate.

The buffering effect of 0.16 M glycolate in 0.4 M oxalate-0.34 M H_2O_2 with 100 ppm of Fe^{3+} at pH 4.0 and 95°C was quite pronounced. The pH of this solution rose to 5.0, and the H_2O_2 decreased to 0.12 M in 7 hr, showing a probability of perhaps 2 hr more of useful life, while a control without glycolate became basic, and the H_2O_2 concentration fell sharply in less than 5 hr.

The importance of the H_2O_2-glycolate ratio was shown by a series of four life tests in 0.4 M oxalate-100 ppm Fe^{3+} at pH 4.0, 95°C. The tests were with 0.16 and 1.00 M glycolate, each with 0.34 and 1.00 M H_2O_2. With 0.16 M glycolate, the 0.33 M-H_2O_2 test had a useful life of over 5 hr, and the 1 M-H_2O_2 test a life of about 2 hr. With 1 M glycolate, the pH was very stable, being 4.04 in 4 hr, but 0.34 M H_2O_2 decreased to 0.02 M in only 2 hr and the solution was doubtless in the corrosive region. With 1 M H_2O_2 and 1 M glycolate, the pH rose to 4.8, and the H_2O_2 decreased to 0.02 M in about 4 hr. In both of the 1 M glycolate solutions a voluminous white precipitate soon formed. Other ratios of glycolate to peroxide were not studied, and extensive corrosion tests with a wide range of formulas were not made. The peak corrosion region present at about 0.1 M H_2O_2 at pH 4.0 (Sec 2.9, Fig. 1) was not present at pH 4.5 and 5.0 in 0.1 M glycolate–0.3 M oxalate–peroxide solutions, as it was with citrate. The peak was doubtless present, but of lesser severity, and was missed by the experimental method then prevailing of adding H_2O_2 to the solution in 0.05 M increments and observing corrosion by weight loss. Corrosion rates of carbon steels and other metals in glycolate-oxalate-peroxide were not more severe than in solutions buffered with citrate or acetate.

2.10.6 Effects of Acetate

Ayres, Perrigo, and their co-workers at Hanford showed that acetates were effective buffers for oxalate-peroxide solutions.[27] Acetate buffers in oxalate-peroxide were also studied by Seefeldt, Vogler, and Tyler at Argonne.[28] At ORNL, the life of 0.4 M oxalate–0.34 M H_2O_2–100 ppm Fe^{3+} at pH 4.0 and 95°C was not extended by 0.1 to 0.8 M acetate addition as much as had been experienced with 0.16 M citrate. With acetate concentrations of 0.1, 0.2, 0.4, and 0.8 M the peroxide was exhausted after about 8 hr at 95°C and two overnight periods at room temperature. The pH stability increased with increasing acetate, but low pH resulted in an earlier loss of corrosion passivity on carbon steel. The corrosion rate at failure was also higher when the pH was lower. For example, with 0.8 M acetate after 6 hr the solution became corrosive at 0.1 M H_2O_2, pH 4.38, at a rate of 1.6 mils/hr during the peak rate, and 0.25 mil/hr after the peak rate. With 0.1 M acetate, however, after 7-3/4 hr the solution became corrosive at 0.003 M H_2O_2, pH 7.55, and the peak rate was only 0.13 mil/hr, followed by a rate of 0.07 mil/hr.

The electrode-potential method showed that more H_2O_2 was required for carbon steel corrosion passivity when acetate was present in oxalate-peroxide solutions, as was also the case for citrate and glycolate (Secs 2.10.4 and 2.10.5). In a cursory test, the minimum amount of H_2O_2 required in 0.4 M ammonium oxalate at pH 4.0, 95°C, was 0.12 M without acetate, 0.45 M with 0.25 M acetate, and 0.63 M with 0.6 to 1.0 M acetate.

The addition of 0.2 M ammonium acetate to the previous optimum 0.4 M oxalate–0.16 M citrate–0.34 M peroxide formula at pH 4.0 and 95°C, containing 100 ppm of Fe^{3+} as a peroxide-destruction catalyst, lengthened the low-corrosion life almost 50%, from 12 to 17.5 hr. The corrosion rate on carbon steel during this life was 0.002 mil/hr. When the H_2O_2 had decreased to about 0.03 M, in 17.5 hr, corrosion occurred for about 45 min at about 0.14 mil/hr (pH 4.8) and then decreased to about 0.09 mil/hr. Other formula combinations which had shorter lives were: 0.1 acetate-0.16 citrate (14 hr), 0.1 acetate-0.08 citrate (12.5 hr), and 0.2 acetate-0.08 citrate (16 hr). Stress- and crevice-corrosion samples of the one type of steel tested did not show abnormal attack, but the margin of corrosion safety may have been too narrow for practicality in solutions containing 0.2 M acetate and 0.16 M citrate with 0.34 M H_2O_2. (The narrowness of this margin was later confirmed.) Steel in acetate-containing solutions did not have as bright a surface as in non-acetate solutions.

One drawback to the usage of acetate as a buffer in oxalate-peroxide solutions was the severe rusting of carbon steel exposed to the acetic acid vapor above the liquid level of the solution. This rusting was not materially lessened by the use of slowly hydrolyzing glyceryl triacetate (triacetin) instead of acetate. In spray decontamination, with the metal surfaces intermittently wetted with the peroxide-containing solution, the inhibitive properties prevailed, however, and corrosion was low. This was shown in a 2-1/2 hr spray dishwasher test with 0.4 M oxalate–0.5 M H_2O_2–0.2 M acetate–0.05% Tergitol nonionic NPX at pH 4.0, the temperature being 75 to 95°C for 0.5 hr and 95°C for 2 hr. Total corrosion to carbon steel was 0.015 ± 0.002 mil, with no rusting. The coupons were resprayed for 5 min and then allowed to stand in the closed machine in the vapor space above the liquid level for 1 hr. Vertical steel surfaces still showed no rust, but horizontal, poorly drained surfaces were slightly rusted. A 10-min rinse in the machine with water at 80°C afterward caused considerably more rust than had the decontamination solution. When citrate was used instead of acetate, corrosion was slightly less (0.011 mil total) and rusting after rinsing was also somewhat less. Aluminum (type 1100) was corroded 0.17 mil by the acetate and 0.22 mil by the citrate washes. The type X8001 aluminum figures were 0.20 and 0.26 mil, respectively.

The use of acetate with peroxide in decontamination formulas raised the question of whether peracetic acid is formed. Vapors of this acid are explosive if strongly heated.[29] No peracetic acid was produced, however, when a solution of 0.3 M acetate–0.3 M oxalate–1 M H_2O_2 at pH 4.5 was boiled to dryness. The ceric sulfate analytical method was used.[30,29] When 600 ml of 1 M acetic acid-2 M H_2O_2 was boiled to dryness, the first 200 ml of condensate contained 0.3%, the second 0.08%, and the third 0.04% peracetic acid. Similarly, from a mixture of 50 ml of glacial acetic acid with 50 ml of 30% H_2O_2, the first distillate contained 1.1%, the second 0.45%, and the third 0.26% peracetic acid. It was concluded that peracetic acid formation would not be a safety hazard in the use or disposal of oxalate-acetate-peroxide decontamination solutions of the type studied.

2.10.7 Effects of Fluoride and Aluminum Ions in Oxalate-Peroxide Formulas

Fluoride ion is an excellent decontaminant for several fission products and transuranics, but its corrosivity to metals has been a drawback to wide usage. The inhibition of fluoride corrosivity by H_2O_2 was studied by the electrode-potential method, and fluoride was safely added to oxalate-peroxide formulas. The electrode potentials of carbon steel, types 304 and 347 stainless, and types 1100 and X8001 aluminum were observed vs an H_2O_2 concentration from 0 to 3 M, in a solution of 0.05 M NaF in 0.4 M ammonium oxalate-0.2 M ammonium acetate at pH 4.0, 95°C. At zero H_2O_2, potentials (vs the calomel electrode) were, in the above order, -705, -545, -535, -960, and -855 millivolts, all indicating corrosivity. At 0.11 M H_2O_2 the stainless steels became passive at about +180 mv. At 0.3 M H_2O_2 the carbon steel entered the oscillating phase at about +35 mv associated with brightening, and at 0.6 M H_2O_2 it became passive at about +245 mv. The aluminum potential was still -500 mv at 3 M H_2O_2. Fifteen-minute corrosion rates taken at 3 M H_2O_2 were the following in mils/hr: carbon steel, 0.012; stainless steels (very bright), 0.003 and 0.006; and aluminums, 1.8. In a similar run with 0.2 M NaF, the stainless steels went passive at 0.12 M H_2O_2 and the carbon steel at 1.1 M H_2O_2.

The extent of corrosion reduction of fluoride by Al^{3+} was also measured. In 0.4 M oxalate–0.2 M acetate–0.2 M fluoride without H_2O_2, at 95°C and pH 4.0, types 304 and 347 stainless steels were active at -300 mv, but when 0.2 M Al^{3+} was added as the nitrate the steels became passive at about +200 mv. Carbon steel became passive at 0.38 M H_2O_2 in the mixture, instead of the 1.1 M H_2O_2 required when no Al^{3+} was added. When 1 M H_2O_2 was used in the oxalate-acetate-fluoride solution, without Al^{3+}, the corrosion rate on aluminum was 6 to 9 mils/hr; with 0.067 M Al^{3+} it was 2.1 mils/hr; and with 0.2 M Al^{3+} it was 0.27 mil/hr.

The tendency toward corrosion was greater when 0.16 M citrate was added to the oxalate-acetate-fluoride-aluminum formula. When peroxide was added, the stainless steels became passive at 0.1 M H_2O_2 and the carbon steel at 0.4 M H_2O_2. The aluminums remained active even at 1 M H_2O_2. Corrosion rates at 1 M H_2O_2 in mils/hr were 0.012 for carbon steel, 0.003 for type 304 stainless steel, 0.000 for type 347, and 0.66 and 0.63 for types 1100 and X8001 aluminums, respectively. The stainless steels acquired a very bright finish during the tests.

Aluminum ion was so effective a corrosion inhibitor for fluoride on steel surfaces that 0.05 M F^- and Al^{3+} could be added to the optimum oxalate-peroxide formula without the need for increasing the peroxide, although the useful life of the solution was somewhat shortened. When 0.05 M F^- and 0.05 M Al^{3+} were added to 0.4 M oxalate–0.16 M citrate–0.34 M H_2O_2–100 ppm Fe^{3+} at pH 4.0 and 95°C, the noncorrosive life toward carbon steel was 6.5 hr. Addition of 0.1 M acetate lengthened the life to 11 hr, and 0.2 M acetate to 11.5 hr. In the 0.2 M acetate solution, corrosion to carbon steel during the first 11.5 hr was less than 0.001 mil/hr. During a short corrosion peak thereafter it was 0.15 mil/hr, and after the peak, when the H_2O_2 was all decomposed, at pH 5.4, the corrosion was 0.09 mil/hr.

The margins of safety in peroxide concentration which prevent the excursion of the solutions into the corrosive region have not yet been determined in the formulas containing fluoride, nor in citrate-acetate mixtures.

2.10.8 Long-Lived Formulas for 60°C Decontamination

The development of long-lived "fail-safe" oxalate-peroxide formulas for use at 60°C was successful (Sec 2.8.10). The fundamental mixture, to which additions were made, was 0.4 M ammonium oxalate–1.0 M H_2O_2–100 ppm Fe^{3+} at pH 2.50 and 60°C. The preferred citrate concentration was 0.1 M. With no citrate, in 79 hr the H_2O_2 had fallen to 0.005 M, and the pH had risen to 7.95; but, with 0.1 M citrate, the H_2O_2 was still 0.7 M and the pH 4.19. With 0.47 M citrate, carbon steel was rapidly corroded. In the 0.1 M citrate solution, initial corrosion to carbon steel was about 0.001 mil/hr, and this rate decreased with time. There was no stress-corrosion cracking or crevice corrosion. The initial corrosion rate on types 1100 and X8001 aluminum in the 0.1 M citrate formula was about 0.02 mil/hr, and the final rate was about 0.01 mil/hr.

A very stable and low-corrosive oxalate-peroxide formula containing fluoride was found. In 144 hr at 60°C, a mixture consisting of 0.4 M oxalate–0.1 M citrate–0.2 M acetate–1 M H_2O_2–0.05 M F^-–0.05 M Al^{3+}, initially at pH 2.5, with 100 ppm of Fe^{3+} added to decrease life, still contained 0.7 M H_2O_2 at pH 4.24. Corrosion on carbon steel and aluminum during the first hour were 0.006 and 0.44 mil, and during the 127th hour they were less than 0.001 and 0.1 mil, respectively. After 144 hr in a similar mixture without acetate, the H_2O_2 was 0.05 $\underline{M}$ and the pH 7.5. Without citrate, the H_2O_2 was again 0.05 $\underline{M}$, and the pH 6.4. Without citrate, fluoride, and aluminum, the life ended also at about 144 hr but with the aluminum corrosion a twentieth of that when F^- was present.

2.10.9 Effects in Boiling Oxalate-Peroxide Solutions

Boiling oxalate-peroxide solutions deteriorated considerably more rapidly than solutions held at 95 ± 1°C. Boiling was done in glass, under reflux, with several square inches of carbon steel corrosion specimens in each 800-ml batch. All solutions originally contained 0.4 $\underline{M}$ oxalate and 0.34 $\underline{M}$ H_2O_2, with 100 ppm of Fe^{3+} as a peroxide-destruction promoter, and had been adjusted to pH 4.00 ± 0.01 from the acid mixtures with ammonium hydroxide. A solution buffered with 0.16 $\underline{M}$ citrate lasted 3 hr; one with 0.2 $\underline{M}$ acetate lasted slightly over 3 hr; one with both buffers lasted 45 min; and one with both buffers plus 0.05 $\underline{M}$ fluoride and Al^{3+} lasted 55 min. The short lifetimes in the mixed buffers may have been due to operating too close to the corrosion threshold, followed by excursion into the corrosive region, excessive iron dissolution, and increased catalysis. The tendency toward shorter solution life at elevated temperature may in part account for the early failure of oxalate peroxide solutions in circulating loops, as reported from Hanford.[27] The very long lives and reasonably good decontaminating properties of the solutions at 60°C (Secs 2.8.10 and 2.10.8) indicate that temperatures intermediate between 60 and 95°C may prove to be optimum for safe and effective usage. These studies are continuing.

3.0 CONCLUSIONS AND RECOMMENDATIONS

An aqueous decontamination solution whose corrosion rate is less than 0.01 mil/hr has been developed and is proposed as a general-purpose fission product decontaminant for carbon steel. The solution also dissolves UO_2 powder and sintered lumps rapidly and therefore seems suitable for the decontamination of the EGCR charge and service machines, which are made of carbon steel.

The optimum composition so far determined for use at 85 to 95°C is 0.40 $\underline{M}$ oxalate and 0.16 $\underline{M}$ citrate at pH 4.0, with 0.34 $\underline{M}$ H_2O_2 as a corrosion inhibitor, uranium oxidizer, and oxidant for some of the fission products.

The value of 0.4 $\underline{M}$ for the oxalate concentration is not critical, but ensures an oxalate-saturated solution at room temperature. The concentrations of 0.16 $\underline{M}$ for citrate and 0.34 $\underline{M}$ for hydrogen peroxide are more critical, closely approaching an apparent optimum citrate:peroxide molar ratio of 1:2. A higher citrate concentration decreases the corrosion safety factor at fixed peroxide concentration, and lower citrate concentration lessens the buffering action and hence shortens the effective life of the solution. Increased peroxide concentration shortens solution life by hastening the oxidation of the oxalate and citrate, and decreased peroxide concentration lessens the corrosion safety factor. Below the passivating concentration, which varies with conditions, the peroxide becomes a corrosion promoter.

The initial pH of 4.0 is approximately the pH at which hydrogen peroxide is the most stable. It provides adequate acid reserve without excessively increasing the danger from corrosion and without greatly increasing the rate of oxidation of the organic components by the peroxide. As the decontamination of a carbon steel surface proceeds, the ferric ion introduced by the corrosion rate of 0.001 to 0.01 mil/hr catalyzes this oxidation, which consumes hydrogen ions and peroxide. The pH then rises as the peroxide concentration drops, so that less peroxide is required for maintaining passivity at the higher pH, and the solution does not become corrosive.

Ferrous metal surfaces in the solution remain bright, or even increase in brightness, as long as enough peroxide is present to maintain passivity, but they become somewhat dulled by corrosion if the peroxide drops below the passivating concentration. The surfaces may become filmed with insoluble ferrous oxalate when peroxide is very low or absent, so that soluble ferric oxalate is not formed. The normal mode of usage for decontamination is only within the passive region. In plant practice, occasional measurement of pH and peroxide concentration would guard against misoperation.

Decontamination at lower temperatures, such as 60°C, can be effected with oxalate-peroxide solutions at lower pH (e.g., 2.5) if the peroxide is increased to about 1 $\underline{M}$ to prevent corrosion and 2 to 4 times the contact time of 95°C solutions is used. The solution life at 60°C is several times that at 95°C.

Fluoride may be safely added to oxalate-peroxide preparations, the added corrosion tendency being curtailed either by aluminum ions or increased peroxide. Fluoride aids in the decontamination of metal surfaces from plutonium, americium, and some of the fission products.

Oxalate-peroxide solutions may be prepared which are corrosive (e.g., 5 mils/hr) to carbon steel at room temperature when agitated and low-corrosive (e.g., 0.02 mil/hr) when not agitated. Such solutions may find use in decontamination by hand scrubbing and in the selective removal of thin layers of metal (e.g., in the preparation of curved surfaces on metal blanks for astronomical mirrors).

In the waste disposal of oxalate-peroxide decontaminating solutions, when prepared with ammonium salts, only heating is required to decompose and volatilize the components, leaving a trace residue of fission products and iron oxide.

The disadvantages of oxalate-peroxide decontaminating solutions for carbon steel include the likelihood of corrosiveness or short life if incorrectly prepared. Provision should be made in large-scale operations for analytically following the rise in pH and the decrease in H_2O_2 content so that the solution may be modified or dumped if the corrosive region is unexpectedly approached. The noncorrosive solution has so far been ineffective for the decontamination of stainless steel which was laboratory contaminated in aqueous solution with fission products and then baked at 500°C in helium that contained a trace of hydrogen. (There is hope for successful decontamination in solutions with corrosion rates on stainless steel of about 0.01 mil/hr). The useful lives of the oxalate-peroxide solutions are limited, ranging from as little as a few hours to as long as a few days, depending on the amount of iron dissolved from surfaces, the pH, and the temperature.

Since the technology of oxalate-peroxide solutions is not yet fully developed, large-scale usage without preliminary experience is not encouraged. The outlook for future use, however, is optimistic. The developmental work is continuing.

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