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DECONTAMINATION STUDIES FOR N REACTOR

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Corrosion Research and Engineering

CHEMISTRY AND METALLURGY DIVISION

May 22, 1970

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PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

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DECONTAMINATION STUDIES FOR N-REACTOR

INTRODUCTION

Radioactive films that build up on internal surfaces of water-cooled reactor primary systems often increase operational costs and complicate normal maintenance and minor repairs.

The characteristics of the films and, consequently, the type of reagents that will be effective in removing these films will depend on the materials of construction and method of operation of the reactor. Films formed on stainless steel differ materially from those formed on carbon steel. Films formed in boiling water reactors do not resemble those formed in pressurized water reactors.

This paper describes the radioactive films that are formed in pressurized water reactors, the resulting problems, and the procedures that may be used to remove these films and decontaminate the reactor. The discussion is centered principally on problems relating to decontamination of reactors containing carbon steel piping. The use of neutral chelating solutions for cleaning and maintaining cleanliness in a nuclear reactor is discussed in detail.

SUMMARY AND CONCLUSIONS

Inhibited mineral acids can be used to decontaminate nuclear reactors efficiently. Corrosion rates are low, but continued use of inhibited mineral acids may cause accelerated corrosion at weld junctions or at other spots where different materials are galvanically coupled. Other potential dangers result from incomplete rinsing or from destruction or depletion of the inhibitors.

Slightly alkaline solutions containing chelants are used in the fossil fuel industry for cleaning boilers and may be used in a similar fashion to decontaminate nuclear reactors.

A solution of DTPA, citric acid, and hydrazine at pH 8 was used to decontaminate carbon steel with high efficiency and low corrosion rates. At 85 °C, samples were clean in one to two hours, and at 70 °C in about six hours. EDTA, and presumably its homologues, are relatively stable to radiation. In measurements, 10^6 R of gamma radiation decomposed about 2.2 millimoles of EDTA per liter of solution. Hydrazine inhibited the decomposition of EDTA.

Pilot plant experiments in and out of reactor are needed to evaluate these solutions prior to use in a reactor. Tests should be designed to determine optimum pH, concentration, flow rates, contact times, and temperatures.

PROBLEM

During routine operation of water-cooled nuclear reactors, the internal surfaces of the primary piping system becomes covered with an oxide film, essentially heterogeneous in nature and highly radioactive. The radioactivity level increases with time as more and more radioisotopes, either activated corrosion products or fission products from imperfect fuel elements, become an integral part of the film by ion exchange, adsorption, or other physiochemical processes.

It is still a moot point whether the activity level increases continuously with time or tends to reach a plateau. At any rate, the levels are sufficiently high that personnel access must be limited at certain areas. Sometimes this may complicate routine operations and increase costs of maintenance and normal repair to such an extent that decontamination becomes economically attractive or absolutely necessary.

At N Reactor the most critical exposure problems occurred during maintenance on the rear face. Levels were so high the workers were limited to very short working times, and a large number of personnel were required to complete the required operations.¹ The high radiation levels resulted from the films formed on the inner surfaces of the carbon steel nozzles, connectors, and other piping components.

FILM CHARACTERISTICS

The films that are formed on internal piping surfaces are characteristic of the base metal, materials of construction, water quality, and mode of operation. The primary system of the N Reactor, located near Richland, Washington, is constructed essentially of Zircaloy, Inconel, stainless steel, and carbon steel. The pressure tubes and fuel cladding (16% of total surface area) are of Zircaloy, the external piping (16% of total surface area) is of carbon steel, and the heat exchangers (67% of the total surface) were originally of stainless steel, but are being replaced with Inconel.

The films formed on both carbon and stainless steels are jet black. Some of the film is easily removed; in fact a portion of the film rubs off on any surface that touches it. Some workers have attempted to differentiate between the "loose" and "adherent" film, but this appears to be a meaningless distinction, as will be discussed later. Films on carbon steel appear to be thicker and to be composed of a larger amount of material that is easily removed. This so-called loose portion can be removed by scrubbing or by transferral to a tape or other adhesive surface, but even the most diligent scrubbing will not remove all the film.

The films formed on primary system surfaces are crystalline in nature. Electron scan micrographs for carbon steel (Figures 1 and 2) and stainless steel (Figure 3) show the oxides to be generally similar in physical appearance. In the areas shown, the crystals on stainless steel vary up to 3.3μ and on carbon steel up to 6μ . If one attempted to remove the so-called loose portion of any of these films with an adhesive surface, the amount removed would depend on the area of contact between the adhesive surface and the crystals, degree of attachment to the other oxide particles, size of crystals, position in the film, and other variables, but it is doubtful whether the portion removed would differ materially in size, size distribution, physical appearance, or chemical composition from that remaining on the surface.

Figure 1 represents a film that had a relatively low activity level ($\sim 10^6$ dis/min-cm²), while Figure 2 shows a film with a level two times that shown in Figure 1. There appears to be no readily discernible differences in size, shape, density, or size distribution of particles in the film.

The film on the carbon steel surfaces is about 3 mg/cm² and on stainless steel surfaces about 0.66 mg/cm². If the apparent density is assumed to be 2, the average thickness of the films on carbon steel will be 15μ and of those on stainless steel, 3μ . The largest crystals on stainless steel (Figure 3) have a diameter greater than the average film thickness.

With these figures and those for surface area of the primary system, one can calculate the amount of crud on carbon steel surfaces to be about 570 lb Fe₃O₄ and on stainless steel surfaces 645 lb Fe₃O₄. In addition, the loose crud accumulated in various portions of the system will be approximately equivalent to the amount on the carbon steel surfaces. Therefore, the total crud in the N Reactor primary system will be approximately 1800 lbs of Fe₃O₄.

METHODS FOR DECONTAMINATION

The film itself is of little consequence to the reactor operation. The films are thin ($<3\mu$), crud* levels in the water can be kept to low values (<0.01 ppm of insoluble corrosion products, and in pressurized water reactors at least) localized deposition has never increased to such an extent that it interferes with flow or heat transfer. The film actually protects the surfaces, especially those of carbon steel, from corrosion. The corrosion rate after film is formed is less than 0.1 that when a bare surface is exposed. The only undesirable constituents in the films are the radionuclides. If the fuel elements are designed properly so that failures do not occur too often, fission products contribute only a small percentage of total activity to the film. The radionuclides of most importance are activated corrosion products, especially the long-lived gamma emitters. In most reactors, the activity levels could be decreased materially if only the ^{60}Co were removed. Other isotopes, also important but to a lesser extent, are ^{58}Co , ^{54}Mn , ^{59}Fe . Therefore, the most desirable approach would be to leach out the offending radionuclides, especially the cobalt isotopes, and leave the film intact. Quite a great deal of effort was spent along these lines but to no avail. It is not possible to remove the ^{60}Co or any other radionuclide without removing the entire film. The reason for this is obvious from an examination of the electron photomicrograph of the film (Figures 1-3). The film is composed of well-defined crystals of varying sizes. It would be necessary for the chelating agent to diffuse through the crystal lattice to even contact the cobalt isotope.

The only method available for removing the radionuclides is to remove the entire film. In fact, the degree of decontamination can be correlated to a certain extent with the degree of film removal.

The optimum decontaminating agent then is one that will remove the film without attacking the underlying metal. Other characteristics that would enhance the value of the decontaminant are:

- Removes film effectively
- Does not cause problems of redeposition

* Crud is a term used to designate insoluble materials, principally corrosion products, transported or suspended in the coolant or as a loose deposit on the interior surfaces.

- Is inexpensive and readily available
- Is effective in dilute concentration
- Is very soluble in water or is a liquid
- Is nontoxic
- Does not cause problems in waste disposal
- Does not cause problems in reactor

These criteria are qualitative, principally because one advantage in one reagent must be traded off against a disadvantage or a different advantage in another reagent. For example, the corrosion (attack of underlying metal) that one can afford will depend on the number of times the reactor must be decontaminated, which in turn depends on efficacy of the reagent. The cost of the reagent is only a portion of the total cost and even a major economy in cost of reagent may be offset by a minor increase in cost of waste disposal.² It is preferable to have a reagent that can be handled safely without special clothing or equipment, but this again may be a minor consideration. Probably the most important criteria are: overall cost, including reagents, handling, downtime, and waste disposal; reactor safety; and overall corrosion.

The most effective reagents for removing the film without attacking the underlying metal are inhibited acids. Dilute HCl (4-6 N) suitably inhibited defilms and decontaminates carbon steel at room temperature very effectively (DF>100) in less than 5 minutes with very little attack on the underlying metal (0.01 to 0.02 mg/cm²). The acid could stay in the system for hours without excessive attack of the metal. Hydrochloric acid is cheap, readily available, is a liquid, and could be evaporated to small volume, thus simplifying waste disposal. Hydrochloric acid has been used extensively for cleaning boilers and other systems in fossil fuel plants, but is not considered for the nuclear industry for several obvious reasons, the most important being the tendency of small amounts of chloride to cause localized attack of stainless steel at higher temperatures even at low oxygen concentrations. Sulfuric acid (35%) inhibited with phenylthiourea decontaminates and defilms carbon steel at room temperature in about six hours with low corrosion. Inhibited sodium bisulfate has been used to decontaminate carbon steel reactors, but it is not as satisfactory as some other reagents, because of potential corrosion at higher temperatures. Uninhibited bisulfate is very corrosive; if the inhibitor is not present in sufficient amounts, very severe localized corrosion can occur.

Oxalic acid is a good derusting agent and if suitably inhibited is a good reagent for removing film and scale from carbon steel. A very dilute solution of oxalic acid (0.02 M) and hydrogen peroxide (0.05 M) has been suggested for removing film and scale from carbon steel at room temperature. Although this solution purportedly removes some films and rust from carbon steel, it will not remove the films formed on carbon steel in N Reactor. Even after six hours, the films were essentially untouched (DF <2). At higher temperatures or higher concentrations mixtures of oxalic acid and peroxide are very effective decontaminants, but they are also exceedingly corrosive.

Inhibited oxalic acid solutions are generally unsatisfactory for cleaning carbon steel systems because on long contact (2-4 hr) a greenish basic oxalate precipitates on the surfaces and carries down some of the activity. Decontamination factors are low. Mixtures of citric and oxalic acid, suitably inhibited, may be used to decontaminate carbon steel systems with good efficiency and low corrosion, but they are not the most effective nor the least corrosive. The low solubility of oxalic acid (~100 g/liter at room temperature) also limits the application of oxalic or citric-oxalic (Citrox) reagents.

Reagents containing inhibited sulfamic acid are among the most satisfactory decontaminating reagents of this type. With suitably inhibited reagents and careful observance of specified conditions, corrosion rates are low and corrosion is uniform. There is no observed pitting, knifeline corrosion at weld junctions, stress corrosion, or galvanic attack. In solutions at high temperature, sulfamates are hydrolyzed to bisulfates

and bisulfates are more corrosive.

Inhibited phosphoric acid (8-10% H_3PO_4) is very effective reagent for defilming, descaling, or decontaminating carbon steel if the contact time is limited and if the inhibitor is effective. On longer exposure, a phosphate precipitate forms on the surfaces and absorbs some activities to give low decontamination factors. When an inhibited phosphoric acid solution was recirculated through a contaminated loop, the solution removed the activities

but then partially redeposited them. The decontamination factor after a short contact time was high but then gradually and continuously decreased with time.³ With a satisfactory inhibitor, average corrosion rates are low but the solution does show a tendency to selectively attack carbon steel at weld junctions with stainless steel. Samples of carbon steel contaminated in N Reactor were decontaminated effectively ($DF > 100$) by inhibited H_3PO_4 at $70^\circ C$; average corrosion rates for carbon steel were 0.1 to $0.2 \text{ mg/cm}^2\text{-hr}$; carbon steel galvanically coupled to stainless steel corroded at rates of 0.5 to $0.6 \text{ mg/cm}^2\text{-hr}$; after four hours exposure, attack at weld junctions were as deep as 8 mil (Figures 4 and 5). Since H_3PO_4 is liquid at concentrations 7 to 10 times that normally used, this material can be used in feed and bleed procedures, and has been used successfully at N Reactor in this fashion.

In summary, dilute acids are very effective reagents and if inhibited suitably and used correctly are not too corrosive. If feed and bleed is the only feasible method of operation and if the total contact time is short, inhibited H_3PO_4 is the best acid reagent. When recirculation is feasible, inhibited sulfamic acid is preferred, but again it must be used with careful control.

Against the advantages of dilute inhibited acid solutions, one may pose the disadvantages or shortcomings.

In acid solutions, localized attack is very likely to occur. At galvanic junctions, the attack of the more anodic material is accelerated; in crevices, attack may increase; and at weld junctions, attack may be concentrated. In weld junctions of carbon steel with stainless steel, this attack may cause rapid failure of the component.

Acids are so corrosive to some materials (e.g., copper or carbon steel) that they must be inhibited. The inhibitor added is an organic compound usually one containing sulfur (e.g., thioethers, mercaptans, thioureas). In a complex assembly, such as a reactor primary system, it may be necessary to add several different types of inhibitors.⁴ This poses several real or unevaluated dangers:

- The acid may not be sufficiently inhibited. The inhibitor concentration may drop below an effective value because:

the inhibitor may be partially destroyed by heating; the solution may not be properly mixed; the inhibitor may separate during storage, solution preparation, transferral or, addition; or the solutions may be diluted.

- Residual amounts of the inhibitor may cause localized corrosion.⁵ Inhibitors are effective principally because they adsorb on the metal surface. The most effective inhibitors adsorb strongly and are removed only with difficulty. Even extensive rinsing does not remove them completely. If a portion of the inhibitors are removed and the remainder protects certain areas, local cathodes and anodes may be set up and cause localized attack such as pitting and ridges. This has been noted in systems where inhibitors are present in insufficient quantity. In addition, because inhibitors contain sulfur, during high-temperature operation they might decompose to form sulfur compounds that are especially corrosive to Inconel. These suggestions are hypothetical as there have been no data to substantiate such conclusions, but if inhibited acids are used, residual effects of inhibitors should be evaluated.
- Inhibitors usually do not eliminate localized attack but only reduce extent of attack from catastrophic to accelerated. For example, Figure 5 - 7 show attack of a weld junction (carbon steel to stainless steel) by an inhibited phosphoric acid after four hours and after eight hours of contact at 70 °C, the recommended use temperature. Normally, inhibited H_3PO_4 is used only for short contact times (20 to 30 min.) in systems containing carbon steel for reasons given above, and attack is usually mild after such short contact times. However, since the system may be decontaminated several times, the cumulative time, including feed time and rinses, may be several hours and the long-exposure effects are important and must be evaluated.

EVALUATION OF NEW TYPES OF DECONTAMINANTS

In the fossil fuel industry, chemical cleaning of boilers, heat exchangers, and similar equipment is an important operation. Over the years, much effort has been expended to improve these procedures. Probably the most exciting development has been the use of very dilute complexing solutions on a periodic or continuous basis to remove film and scale and to keep film and scale from forming. Several reports written over the past ten years describe procedures that have been used successfully in large installations to keep boiler surfaces free of any but a very thin protective film.⁶⁻⁸

Friedle⁶ describes use of EDTA solutions for continuous internal cleaning of 1325 psi boilers. Initially, a higher concentration (5 to 6 ppm EDTA) was added to remove deposits already present, and then this rate was dropped to maintain 2.5 ppm EDTA. If oxygen was kept from the system, corrosion rates were very low.

Roosen⁷ discussed use of EDTA solutions to treat water for a 900 psi boiler. The initial dosage was 30 ppm EDTA to remove deposits already formed. After the boiler was clean, EDTA was fed continuously to maintain a 2 to 5 ppm free residual at the economizer inlet. The OH^- concentration was maintained at 25 ppm as measured at room temperature. The corrosion of carbon steel, as measured from coupons, was $\sim 6 \mu/\text{year}$ (2.5×10^{-4} in/year). No deposits accumulated during treatment, and a very dense protective coating of iron oxide (0.025μ) formed on the waterside surfaces. Without EDTA feed, the boiler needed cleaning every eight months, but with EDTA feed, it remained clean.

Margulova⁸ suggested chelating acid blends for routine cleaning of thermal power equipment. Initially, he suggests 500 to 1000 ppm EDTA to remove accumulated deposits, with subsequent reduction to much lower values. If iron oxides are present, he suggests mixtures of citric acid, EDTA, and hydroxylamine sulfate. The Mosonagro TP-70 boilers were cleaned with monosodium EDTA (2.8 ppm) and with a mixture of EDTA (3 to 4 ppm), citric acid (1 to 2 ppm) and $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ (0.3 ppm). The blend was much more effective, removing about three times as much iron oxides as the solution of monosodium EDTA.

This general procedure appears very attractive for cleaning nuclear reactor primary systems. A program to evaluate the possibility of using chelating agents was started at Battelle Northwest in 1965. Two possibilities were envisaged:

continuous feed of very dilute solutions during reactor operation to keep films from forming; and intermittent cleaning of the system during reactor downtime.

The first unknown to be evaluated in this program was the stability of EDTA and other chelants to irradiation.

DECOMPOSITION OF EDTA BY GAMMA RAYS

Solutions of the disodium salt of EDTA were placed in glass tubes and exposed to gamma rays to give the results shown in Table I.

TABLE I
Decomposition of EDTA by Gamma Rays

<u>Sample No.</u>	<u>Concentration g/l</u>	<u>M</u>	<u>Irradiation 10^6 R</u>	<u>m mol/liter Destroyed</u>	<u>m mol Destroyed $/10^6$ R</u>
1	8.54	0.0230	0		
	6.59	0.0177	3	5.3	1.8
	4.80	0.0129	6	10.1	1.7
2	17.9	0.0481	0		
	13.7	0.0368	6	11.3	1.9
	6.4	0.0172	18	30.9	1.7
3	38.46	0.1035	0		
	33.28	0.0895	6	14.0	2.3
	21.99	0.0591	18	44.4	2.6
4	43.57	0.1171	0		
	37.45	0.1008	6	16.3	2.7
	29.18	0.0784	18	38.7	2.2
	21.11	0.0568	30	60.3	2.0
5	22.39	0.0602	0		
	16.20	0.0435	6	16.7	2.8
	8.40	0.0226	18	37.6	2.1
Average					2.2

These results are in the same order of magnitude as those obtained by other workers. Matsuura⁹ obtained a G value of 3.6 and Zittel¹⁰ had a value of 1.4 M Moles EDTA destroyed/ 10^6 R. A solution of approximately 0.05 M EDTA with 10 g/liter N_2H_4 was exposed to gamma rays (Table II).

TABLE II

Decomposition of EDTA in Hydrazine Solution

Concentration g/l	M	Irradiation 10^6 R	m mol/l Destroyed	m mol Destroyed / 10^6 R
17.5	0.0470	0		
15.2	0.0409	6	6.1	1.0
11.4	0.0306	18	16.4	0.9

The presence of N_2H_4 apparently reduced the decomposition rate of EDTA by a factor of 2.

A solution of TTHA was tested (Table III).

TABLE III

Decomposition of TTHA by Gamma Rays

Concentration g/l	M	Irradiation 10^6 R	m mol Destroyed	m mol Destroyed / 10^6 R
33.5	0.0670			
27.2	0.0544	6	12.6	2.1
20.1	0.0402	18	26.8	1.5

The rate appears to be lower than that for EDTA. However at the time the tests were made, there was no available procedure for analyzing for TTHA in the presence of EDTA, and the results do not differentiate between TTHA and EDTA. Therefore, the lower rate may merely reflect the decomposition of TTHA to DPTA or EDTA. These tests should be repeated to determine decomposition rates for TTHA and DPTA with the aid of new analytical techniques that can be used to analyze these chelants in mixtures.¹¹

The primary loop in N Reactor has a volume of 150,000 gal. The feed and bleed rate is 500 gal/min and can be increased, but increased bleed flow for decontamination increases expense (loss of chemicals, larger waste volumes). At 500 gpm bleed rate, any given molecule dissolved in the coolant will be in the reactor 12 min. For each 10^6 R/hr flux, this will cause a decomposition of 0.44 M Mole or 0.13 g/liter. In a reactor core, 1 or 2% solutions would be completely destroyed. In N Reactor, the estimated gamma flux three days after

shutdown is estimated to be 2.5×10^6 R/hr.¹ Approximately only 3.6 g/liter would be destroyed and solutions at concentrations greater than 0.1% could be used.

It was clear from these results, chelating agents could not be used continuously during reactor operation, but could be used during reactor shutdown. Within a short time after shutdown, the reagent could be recirculated throughout the primary system using a feed-and-bleed procedure.

The best formula appeared to be a mixture of EDTA or similar chelant, citric acid, and hydrazine. These reagents are all readily decomposed by heat and radiation to form volatile compounds, and residual amounts of reagents from incomplete rinsings would probably not be a hazard. Hydrazine, used to adjust the pH, also destroys any oxygen which might be present. Corrosion rates of carbon steel in EDTA solution are low if oxygen is not present, but even slight amounts of oxygen can cause accelerated and nonuniform attack of carbon steel.

Citric acid and EDTA (as well as its homologues) are general spectrum chelating agents, forming complexes with Fe, Co, Ni, Mn, Th, U, and many of the fission products.

Although EDTA is a satisfactory chelating agent, some of its homologues form much more stable complexes with these ions over wider pH ranges. Of especial interest are the homologues of higher molecular weight. EDTA is a member of the series:

which includes nitrilotriacetic acid (NTA, $n=0$), EDTA ($n=1$), diethylenetetraminepentaacetic acid (DTPA, $n=2$), triethylenetetraminehexaacetic acid (TTHA, $n=3$), and tetraethylenepentamineheptaacetic acid (TPHA, $n=4$). It has been found that the complexing strength increases as n increases up to $n=3$ and then remains essentially constant.¹² The complexes with iron, cobalt, and manganese are also much more stable in the higher pH region.

The advantages of TTHA seemed evident but it was necessary to evaluate the power of TTHA and other complexing agents to remove the contaminated film and scale formed during reactor operation.

Although it had been reported¹³ that TTHA was available in the United States, it was impossible to find a vendor. Geigy held the patent, based on work done in Switzerland. Geigy in England manufactured batches of TTHA on an ad hoc basis, but Geigy in the United States had no facilities and were not interested in supplying TTHA. Some TTHA was obtained from England as the impure sodium salt solution. The liquid had a specific gravity of 1.206, 50% total solids, and purportedly contained 30% complexing power as TTHA. The material cost \$1.33/lb in 100 lb lots from England, which is equivalent to \$4.40/lb of TTHA. The free TTHA was obtained by crystallization from an acidic solution (pH = 1.7-2.0) at temperatures between 5 and 15 °C.

DTPA was obtained as the free acid from Geigy. (Trade name CHEL-DTPA) at \$1.46/lb in 100 lb lots. The other materials used were reagent grade chemicals obtained usually in 5 lb lots.

The samples used to evaluate decontamination efficiency and corrosion were portions of spacers (Figure 8) that had been exposed in N Reactor. Spacers are essentially perforated thick (1/8 in.) carbon steel tubes, 24 in. long. Samples varied in size from 1/2 x 2 in. to 2 x 2 in. Exposure history

Figure 8. Spacer from N Reactor

varied from spacer to spacer. Some had been in for two months, and some had been in considerably longer. All spacers had been stored sufficiently long that the only activities measureable were ⁶⁰Co and ⁵⁴Mn. These are the principal radionuclides of interest, and it had been observed in all reactor decontaminations it is not possible to remove any radionuclide selectively by any decontamination procedure.

Some spacers had been decontaminated and consequently the activity level was lower than on those that had not been decontaminated. In preliminary tests, samples with the highest radioactivity level (and presumably the thickest films)

were the hardest to decontaminate. Reagents that removed films with lower activity levels in one hour did not completely remove films from the most active samples even after five hours.

Decontamination factors obtained by any procedure depended to a large extent on the type of sample used. In the exploratory tests, no particular care was given to choice of samples and direct quantitative comparison of DF is not possible. In the final tests, samples were taken from the same spacers.

Additional samples were exposed to obtain corrosion data: carbon steel samples, $1/8 \times 1 \times 1$ in. and $1/8 \times 1 \times 1/2$ in.; stainless steel samples, $1/8 \times 1 \times 1$ in.; and samples of carbon steel welded to stainless steel, $1/8 \times 1/2 \times 1-1/2$ in. and $1/8 \times 1/2 \times 2-1/2$ in. In the weld samples, carbon steel area was approximately equal to stainless steel area. The stainless steel and the weld samples were sanded to remove scale and film, scrubbed in detergent, dried, and weighed. The carbon steel samples were prepared by different methods: descaling in inhibited HCl (1-1 H Cl with propynol), degreased in trichloroethane, scrubbing in detergent, drying, and weighing; sanding, drying, and weighing; descaling, drying, and weighing; and polishing in oxalic acid, peroxide mixture (0.3 M HCl, 0.3 M H₂O, room temperature, 15-20 min.). Some carbon steel samples were re-used, either without any treatment or after defilming in inhibited HCl. Defilming of used samples seemed to have no effect on corrosion rates. Residual films on carbon steel samples after decontamination in a chelant mixture were extremely thin (0.04 ± 0.02 mg/cm²) and were not protective.

Exploratory tests were carried out in 400 ml beakers with samples hung from stainless steel wires. Stirring was done using either magnetic stirring bars or motor stirrer. Lower temperatures (70 - 95 °C) were maintained by thermocouples attached to a controller. Boiling temperatures 98 ± 2 °C were maintained by adjusting thermostat on a hot plate.

Several conclusions were drawn from these tests:

- Mixtures of chelants, hydrazine, and citric acid at pH values between 6 and 8 successfully removed film, scale, and accompanying radionuclides from N spacer samples.
- Addition of detergent increased the efficiency but caused some problems: some detergents tend to form a second phase either at room temperature or at some intermediate or operating temperature; some detergents caused excessive foaming.

- All chelants tried (EDTA, DTPA, and TTHA) were effective.
- In all tests, TTHA removed the film most rapidly and efficiently.
- Variations in concentration from 0.008 M (4 g/liter of TTHA) to 0.1 M (50 g TTHA, the highest concentration tested) did not appear to affect the decontamination efficiency, providing the chelant was present in sufficient amount to complex the iron ions.
- Presence of $\text{SO}_4^{=}$ or Na^+ did not appear to affect efficiency or corrosion.
- Substitution of NH_4OH for N_2H_4 did not appreciably affect corrosion or efficiency. However, since the beaker tests were done at atmospheric pressure, ammonia concentration and pH changed during the test and it was not possible to evaluate operation with NH_4OH at any pH above 6.
- Addition of hydroxylamine increased efficiency, but also increased corrosion of carbon steel.
- Substitution of glycollic acid for citric acid appeared satisfactory.
- Substitution of oxalic for citric acid appeared to increase corrosion rates. In general oxalates are not satisfactory for decontaminating carbon steel.

More quantitative tests were completed using resin jars equipped with a stirrer, thermometer, and condenser (Figure 9). The jar was enclosed in a heating jacket. A thermocouple in the lining of the jacket was attached to a recorder. With this type of control, it was possible to control the temperature to $\pm 2^\circ\text{C}$; after equilibrium was attained, the control was to less than $\pm 1^\circ\text{C}$.

At this time it became apparent that it was useless to evaluate TTHA because of the higher cost and comparative unavailability. We could locate no source in the United States willing to supply this material or even willing to give any hope for supply in the future. Both EDTA and DTPA are available at a much lower cost. DTPA forms stronger complexes with the ions of interest than does EDTA and is available in large quantities at a reasonable price (\$1 to \$1.50/lb). Consequently DTPA was used in most of the later tests.

The results of these tests are summarized in Table IV. The samples to be decontaminated were placed on wire hooks which were hung from the lid of the pot. Agitation was by stirring and was not very effective. The velocity past the sample surface was a factor of the sample shape and size and the relative placement in the pot. Consequently some areas received sufficient agitation and others did not. The larger samples (those exposed for five hours), especially, had shaded areas. On those samples in high-velocity areas, the films were removed much more effectively; samples in near-stagnant areas often had patches of residual film and relatively low decontamination factors.

The inhibited phosphoric acid was the most effective decontaminant, providing high DFs in less than one hour. No differentiation could be made among the chelating agents (NTA, EDTA, DPTA, and TTHA) at pH 7.0; DTPA seemed slightly less corrosive than the rest, but more data are required. One would not expect too much difference under the conditions employed in these tests. Higher temperature (96 °C) increased both rate of decontamination and decontamination factors, but also increased corrosion. Higher temperatures should not be used with these concentrated solutions unless it is necessary to have a short contact time. Surfactants improved contact of surface with liquid and consequently improved decontamination. Addition of hydroxylamine to these solutions at either pH 7 or 8 definitely increased corrosion rate (by factors of 5 - 10). In two experiments (5, 14) $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ was added. To determine the effect of SO_4^{2-} , ammonium sulfate was added to one solution (15). Sulfate did not affect either corrosion or decontamination efficiency of the solutions. The lowest corrosion was observed with the solutions at higher pH (~8.0). This was consistent with the beaker exploratory tests. At pH 8, corrosion was entirely uniform with no evidence of pitting or accelerated weld attack. Both corrosion and decontamination rates are decreased considerably by lowering the temperature to 70 °C. In Experiment 23, satisfactory decontamination was obtained only after six hours.

DISCUSSION

The results corroborated previous findings that inhibited phosphoric acid is very effective decontaminant, but can cause accelerated attack at galvanic junctions on longer exposures. Figure 10 is a plot of corrosion of the carbon steel welded to stainless steel. Corrosion rate up to four hours is very low

but increases rapidly with longer exposures. The galvanic samples show protected areas and areas of advanced attack. The attack, because it is nonuniform, is much deeper than would be calculated from the average rate. The attack is concentrated at weld areas; and at some points, deep crevices are formed. The greatest danger, however, from use of any inhibited acid is the concentration of residual solutions not rinsed from the system. At higher concentrations and temperatures with destruction of the inhibitor, extremely deep attack would be possible. Presumably other inhibited mineral acids would present the same danger. The average rate for galvanically coupled carbon steel samples is about four times that for samples not coupled.

Mixtures of chelant, citric acid, and hydrazine are effective decontaminants and are not too corrosive to carbon steel; rates are $0.2 - 0.6 \text{ mg/cm}^2$ hour. In the limited experiments completed to date, the best formula appears to be DTPA, citric acid, and hydrazine at a pH of 8.0. In a feed-and-bleed operation to clean the primary system of a large reactor such as N Reactor, the minimum contact time will probably be about 12 hours. The temperature for such a long contact time should be about 70°C . Corrosion rates under these conditions are $\sim 0.2 \text{ mg/cm}^2\text{-hr}$. The total corrosion for a decontamination would be about 1×10^{-4} to 2×10^{-4} inches. Corrosion would be uniform even at weld junctions of carbon steel to stainless steel. If the contact time is longer, the temperature should be lowered after suitable decontamination is obtained. Corrosion rates decrease rapidly with temperature. If it is desired to decontaminate in a shorter time, the temperature should be raised to 86°C .

FUTURE WORK

The results to date have shown only that decontamination with chelant mixtures is possible. Not all basic information has been obtained. Some limits were selected arbitrarily to limit the amount of experimentation. A more careful definition should be made of some variables of solution composition, especially pH and ratio of components.

Most of the experimentation was done in the narrow pH range of 6 to 8. The lower limit was chosen because in exploratory tests, corrosion of carbon steel at pH below 6 was too high and tended to be nonuniform. Perhaps, high efficiency with very low corrosion could be obtained at a higher pH, between 8 and 9. Above pH 9, the iron hydroxides have such a low solubility that they precipitate even in the presence of DTPA and citric acid.

In most of the tests described in this report, equimolar mixtures of citric acid and DTPA were used. Effects of varying this ratio were not examined. Some other ratio may present advantages of increased DF, decreased corrosion, simplification of waste disposal or economy.

Test conditions in the laboratory tests were not at all similar to reactor operation and data were only qualitative. Future tests should be done under prototypical conditions in loop systems, preferably in the reactor. The ideal experimental assembly would be a recirculating loop using one or more N Reactor tubes.

The most readily available facility is TF-9, an out of reactor loop at 100-K. One test was completed in TF-9 using an EDTA-citric-hydrazine solution at pH 7.35, but the operational procedures was not exactly like that expected or recommended for reactor operation.¹⁴ After the samples had been decontaminated, the EDTA solution was drained, and the loop was opened. The carbon steel samples had a surface that was defilmed and very reactive. Consequently, some rusting occurred. The loop is being modified to permit displacement of the chelant solution with deionized water with pH adjusted to 10 with N_2H_4 . This will tend to passivate the surfaces and prevent rusting.

The ideal procedure would be to use the minimum amount of chelant and citric acid. If considerable crud is present, the initial concentration should be relatively high. For example, a system having a capacity of 150,000 gal and a film and crud load of 2000 lbs Fe_3O_4 , would require 13,000 lb DTPA to complex the iron ions. In a batch process, the concentration would need to be at least 14 oz/gal (~10%). In a feed-and-bleed process, the initial concentration should be relatively high (1 to 2%) and then adjusted downward so that at the end of the feed-and-bleed operation, the residual uncombined DTPA would be near zero. If the system is relatively clean, the initial feed concentration should be between 0.1 and 0.2%.

The total amount of DTPA required for a crud load of 2000 lb Fe_3O_4 would be 13,000 lb plus that destroyed by radiation. If the average dosage in the reactor during shutdown is 2.5×10^6 R/hr and the in-core volume is x gal, the rate of decomposition of DTPA will be $0.02x$ lb/hr. If hydrazine does protect DTPA, the rate will be much lower.

Several loop experiments must be completed to evaluate use of chelant solutions as decontaminants. In TF-9, the 2% chelant formulation (DTPA, 0.05 M;

N_2H_4 to pH 8) should be tried at 70 and 86 °C under prototypical conditions with pH 10 water to displace the chelant. These experiments are needed to check DF, corrosion rates, and type of attack, especially at weld junctions and galvanic couples. The test at 70 °C should be run for at least 12 hours. Tests in TF-9 should be made to check efficiency of concentrated chelant solutions on samples with thick films, and of dilute chelant solutions on samples with thin films.

In-reactor tests should be done to determine decomposition rate of DTPA (with and without N_2H_4) in the N Reactor flux during shutdown. One test could be designed to obtain rates for several levels of activity. Another in-reactor test should check DF when other isotopes (^{144}Ce , ^{59}Fe , ^{58}Co , ^{106}Ru , etc.) are present. Finally an in-reactor test should be made to check DF, corrosion, and chelant decomposition under conditions expected for a full reactor decontamination.

For a full reactor decontamination, the feed-and-bleed operation must be designed carefully to ensure sufficient contact time with solution of adequate concentration with a minimum of chemicals. Longer contact times will result in a greater loss of DTPA, unless bleed rates are very low. In an actual reactor decontamination, one should note that the bleed, especially the initial fractions, will be very radioactive. Any uncontrolled loss of bleed cannot be tolerated.

Decontamination with chelant mixtures will be most attractive when crud and film loads are low and radiation levels are high. Periodic dosage with chelants should clean and passivate the systems so that large amounts of crud do not form.

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Figure 1 Film formed on carbon steel spacers
in N Reactor - low level. ESM, 3000X

Figure 2 Film formed on carbon steel spacers
in N Reactor - high level. ESM, 3000X

Figure 3 Film formed on stainless steel coupons placed in spacers in N Reactor. ESM, 3000X

Figure 4 Stainless steel-carbon steel Weld Interface
After Treating in Proprietary Phosphoric Acid
Decontaminant at 70 °C for 4 hours. 250X

Figure 5 Stainless steel-carbon steel Weld Interface
After Treating in Proprietary Phosphoric
Acid Decontaminant at 70 °C for 4 hours. 250X

Figure 6 Stainless steel-carbon steel Weld Interface
After Treating in Proprietary Phosphoric
Acid Decontaminant at 70 °C for 8 hours 250X

Figure 7 Stainless steel-carbon steel Weld Interface
After Treating in Proprietary Phosphoric
Acid Decontaminant at 70 °C for 8 hours 250X

Figure 9 - Assembly for Laboratory Evaluation of Decontaminants.

Figure 10 Corrosion of Carbon Steel welded to Stainless Steel. Inhibited H_2PO_4 solution, 8%, at $70^\circ C$.

TABLE IV
RESULTS OF LABORATORY EVALUATIONS OF DECONTAMINANTS

Experiment Number	Composition	Corrosion of Carbon Steel mg/cm ² -hr					Corrosion of CS welded to SS mg/cm ² -hr					Decontamination Factors				
		1 hr	2 hr	3 hr	4 hr	5 hr	2 hr	3 hr	4 hr	5 hr	6 hr	1 hr	2 hr	3 hr	4 hr	5 hr
1	a	1.13	0.78	0.68	0.88	0.62	0.44	0.63	0.53	0.71		13	88	220	-	150
2	b	1.18	1.02	0.78	0.88	0.46	1.02	0.67	0.67	1.02		130	90	160	170	160
3	c	0.3	0.5	0.4	0.35	0.35	0.75	0.43	0.48	0.46		30	80	220	190	370
4	d	0.56	0.45	0.52	0.55	0.36	0.75	0.60	0.60	0.74		135	30	140	220	85
5	e	0.05	0.7	0.65	2.9	13.2	0.7	5.5	0.65	3.5		60	140	60	86	120
6	f	1.12	0.73	0.60	0.57	0.47	0.60	0.63	0.66	0.62		160	150	60	150	135
7	g	1.1	0.83	0.67	0.71	0.40	0.9	0.54	0.6	0.6		43	210	60	83	100
8	h	1.01	0.77	0.72	0.57	0.41	0.84	0.61	0.52	0.57		60	130	250	200	140
9	i	1.07	0.68	0.73	0.66	0.35	0.57	0.43	0.47	0.59		80	150	260	80	280
10	j	1.14	0.90	0.78	0.70	0.57	0.96	0.78	0.62	0.54		50	80	175	245	150
11	k	1.37	0.93	0.77	0.71	0.62	0.77	0.76	0.74	0.72		150	150	365	485	210
12	l	0.80	0.64	0.71	0.68	0.56	0.75	0.61	0.57	0.80		155	250	250	240	90
13	i	1.21	0.86	0.86	0.62	0.61	0.90	0.73	0.86	0.68		145	115	425	325	450
14	m	18.4	9.5	5.7	4.6	4.7	8.1	6.4	4.0	3.7		185	230	180	280	250
15	n	0.59	0.42	0.38	0.59	0.58	-	-	0.68	0.75		-	-	-	-	-
16	o	1.00	0.64	0.57	0.65	0.77	-	-	0.70	0.66		90	265	250	200	250
17	o	1.40	0.81	1.05	0.94	0.90	0.70	-	0.95	0.96		255	80	260	340	65
18	p	2.1	1.5	1.3	0.9	0.86	-	-	1.02	1.00		90	600	85	450	170
19	q	1.32	0.75	0.68	0.66	0.53	-	-	0.71	0.71		-	-	-	-	-
20	r	1.65	0.84	0.42	0.68	0.48	-	-	-	0.66	0.75	15	40	210	65	270
21	s						0.49	-	-	-	0.25	-	12	-	-	95
22	t	0.36	0.22	0.15	0.16	0.17	-	-	0.20	0.46		1000	2800	970	410	1600
23	t	-	-	-	-	0.17					0.47 0.67 (7 hr)	-	-	-	-	-

Corrosion of Carbon Steel Galvanically
Coupled to SS, mg/cm²-hr
6 hr in Exp. No. 20 - 0.58
7 hr in Exp. No. 23 - 0.54

TABLE V
EXPERIMENTAL SOLUTIONS COMPOSITIONS

Experiment Number	Solution	Chelating Agent	g/liter	Citric Acid g/liter	Hydrazine g/liter	pH	Temperature	Other Reagents Special Conditions
1	a	DTPA	20	10	8.8	6.0	85 ± 2	
2	b	"	20	10	9.8	6.75	85 ± 2	
3	c	"	20	10	11.2	7.42	85 ± 2	
4	d	"	20	10	12.8	7.75	85 ± 2	
5	e	"	20	10	17.5	7.8	85 ± 2	(NH ₂ OH) ₂ ·H ₂ SO ₄ , 10 g/liter
6	f	"	40	20	22.4	7.4	86 ± 2	
7	g	"	40	20	18.8	6.5	86 ± 2	
8	h	"	40	20	-	7.0	86 ± 1	NH ₄ OH to pH 7.0
9, 13	i	"	40	20	20.1	7.0	86 ± 1	
10	j	TTHA	50	20	22.7	7.1	86 ± 1	
11	k	EDTA	30	20	20.0	7.0	86 ± 1	
12	l	NTA	20	20	16.7	7.0	86 ± 1	
14	m	DTPA	40	20	20	7.0	86 ± 1	(NH ₂ OH) ₂ ·H ₂ SO ₄ , 20 g/liter
15	n	"	40	20	20	7.0	86 ± 1	(NH ₄) ₂ SO ₄ , 20 g/liter
16, 17	o	"	20	10	10.3	7.0	*	
18	p	"	20	10	8.8	6.0	86 ± 1	4 ml surfactant, vigorous stirring
19	q	"	20	10			86 ± 1	
20	r	"	20	10	9.5	7.05	86 ± 1	2 ml surfactant, vigorous stirring
21	s	"	20	10	20	8.0	86 ± 1	0.2 ml surfactant, vigorous stirring
22, 23	t	**	~80	-	-		70 ± 1	vigorous stirring

* Temperature, 70 ± 1 °C for Exp. 16 and 96 ± 1 °C for Exp. 17

** Proprietary inhibited H₃PO₄ solution used for comparison