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Decontamination As A Precursor to Decommissioning

Status Report
Task 2 - Process Evaluation

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Pacific Northwest Laboratory
Operated by
Battelle Memorial Institute

Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

Current work on a U.S. Nuclear Regulatory Commission supported program on decontamination as a precursor to decommissioning is described. The work includes a description of ongoing laboratory efforts in compiling a unified comparison of decontamination ability and corrosiveness of twelve decontamination solvents. Some of the solvents, too reactive for use in normal operating plant decontamination, were found to be suitable for decommissioning purposes.

ABSTRACT

Current work on a U.S. Nuclear Regulatory Commission supported program on decontamination as a precursor to decommissioning is described. The work includes a description of ongoing laboratory efforts in compiling a unified comparison of decontamination ability and corrosiveness of twelve decontamination solvents. Some of the solvents, too reactive for use in normal operating plant decontamination, were found to be suitable for decommissioning purposes.

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RECOMMENDED OPERATING CONDITIONS

Solution	Time	Temp °C	pH
AS	1-2 hrs	105	N.A.
AC	1-2 hrs	80-85	N.A.
Citrox	1-2 hrs	80	3-5
MS-1 (No Static Corrosion Testing)	100-200 hrs	120	N.A.
EDTA-CITRIC-ox	N.A.	100	4.8-5.2
ox-HF-H ₂ O	1-4 hrs	85	5-6
OP	1-4 hrs	80	4-5
Automatic - Formaldehyde	1-4 hrs	45-50	N.A.
EDTA + Citric + H ₂ O	N.A.	90-100	5-6
OPG	1-4 hrs	80	4-5
HNO ₃ + HF + Al(NO ₃) ₃	N.A.	N.A.	0-1
RDS	N.A.	80	N.A.
H ₂ O	1-4 hrs	70-85	0-1

EXECUTIVE SUMMARY

As part of the U.S. Nuclear Regulatory Commission's program to reduce occupational exposure and waste volumes, the Pacific Northwest Laboratory is studying decontamination as a precursor to decommissioning. Although the total program is comprehensive, this report is concerned only with the current status of Task 2 - Process Evaluation.

Eleven processes or solvents were examined for their behavior in decontaminating BWR carbon steel samples. The solvents included NS-1, a proprietary solvent of Dow Chemical Corporation, designed for BWR use, and AP-Citrox, a well-known, two-step process designed for PWR stainless steel; it was used to provide a reference for later comparison to other systems and processes. The decontamination factors observed in the tests performed in a small laboratory scale recirculating loop ranged from about 1 (no effect) to 222 (about 99.6% of the initial activity removed).

Coordinated corrosion measurements were made using twelve chemical solvents and eight metal alloys found in a range of reactor types. As a result of these tests, a number of solvents, normally considered too strong for operations related to decontamination, could be used during decommissioning programs if their decontamination capability is also high--an example is the use of 10% HNO_3 + 0.3% HF inhibited with $\text{Al}(\text{NO}_3)_3$. Modern PWRs, particularly if some fuel debris is present, could use this solvent for decommissioning.

Discussion is also provided on chemical safety requirements for specific chemicals found in the twelve solvents used in this work.

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Coordinated corrosion measurements were made using twelve chemical solvents and eight metal alloys found in a range of reactor types. As a result of these tests, a number of solvents, normally considered too strong for operations related to decontamination, could be used during decommissioning operations if their decontamination capability is also high - an example is the use of 10% HNO₃ + 0.5% H₂O₂ combined with H₂SO₄. Modern pipe, particularly if some fuel debris is present, could use this solvent for decontaminating.

Discussion is also provided on chemical safety requirements for specific chemicals found in the twelve solvents used in this work.

INTRODUCTION

The Pacific Northwest Laboratory (PNL) operated by Battelle Memorial Institute, initiated a program for the U.S. Nuclear Regulatory Commission (NRC) to examine decontamination as a precursor to decommissioning. Specific objectives of the program are to examine the effect of the decontamination step on reduction of occupational and population exposure and on the reduction of waste volumes during the decommissioning of LWR plants.

The overall program consists of a six task effort concerned with: 1) a review of the literature and acquisition of additional background information, 2) the experimental evaluation of decontamination processes, 3) the evaluation of waste solidification and disposal decontamination, 4) an examination of safety considerations and radiation exposure anticipated in such operations, 5) the cost factors involved, and 6) evaluation and reporting.

The findings of this study are being published as topical reports which will be drawn together as a whole in a final comprehensive program report. The literature review has been published (Nelson 1981). The present report reviews the current status of Task 2, Process Evaluation, which is a laboratory scale examination of the major decontamination processes. It is being performed to provide decontamination factors (DF) and corrosion data on a common basis as well as to be able to provide estimates of difficulty of application of each process. It is anticipated that future reports will include an expansion of the literature review into other areas including design and planning and a final program report. All other information including waste management, safety, health physics, and costs will be incorporated in the final program report.

BACKGROUND

The current study is directed toward LWR systems and facilities now in operation. Decontamination, decommissioning and dismantling of separations plants, mixed oxide fuel facilities and UO_2 production, preparation and fabrication are not included nor are designs of advanced light water reactors examined.

The overall project encompasses work to evaluate existing or develop new information about decontamination before decommissioning and dismantling, and to evaluate procedures for removing contamination from LWR facilities, equipment and structural components. Background and amplifying information needed to do this are the recently completed (Perrigo 1979) and concurrent NRC and DOE sponsored projects on decontamination and decommissioning. Specifically, the NRC studies on the decommissioning of reference PWR and BWR power stations are expected to provide generalized cost data and background information for this study. A related program at PNL entitled "Characterization of Radionuclide Contamination Throughout Light Water Reactor Power Stations" supplies the samples used in the tests. Additional data comes from samples solicited from various operating reactors.

The subject of this report is the status of Task 2, Process Evaluation, of the overall program. Task 2 is directed at a preliminary evaluation of processes that appear applicable for decontamination prior to dismantling and/or decommissioning. These processes are being evaluated in the laboratory to define their:

- Effectiveness of removing radioactivity
- Corrosion rate of materials of construction.

Information on specific compound and process safety is also being collected and is presented here. It does not include an overall review of waste management, safety needs, estimates of time and manpower requirements or the efficiency of use of labor and materials which will be made and presented in the final report.

The chemical decontamination solvents being evaluated are given in Table I. These solutions were selected because they had been demonstrated to be effective, had been shown effective in related applications (such as fuel reprocessing), or had characteristics that suggested they would have potential. It is important to keep in mind that these solutions are being reviewed for decommissioning purposes where aggressive chemicals may be used that are not appropriate for restorative decontamination. For example, it has been suggested that in restorative decontamination the allowable corrosion should not exceed about 10% of the material's corrosion allowance. In decommissioning there are no set limits as long as the system is not perforated during the decontamination, there are no mechanical failures or severely weakened components, and the process is effective.

In reviewing the data available on the processes (Nelson 1981), it is apparent that they are not well described in terms of OF's, corrosion, safety or operating needs. There are exceptions such as Dow Chemical's NS-1 and the old standby AP-Citrox. The CAN-DECON process also appears to be well defined, but so much of the information is proprietary it is difficult to be certain.

As a consequence of the shortfall of data, the Task 2 assignment includes expansion of the data base. The goal is not to provide a detailed picture of corrosion rates and decontamination factors, but to make comparative judgments for different solutions and different materials, and to suggest problems or advantages of the process. For example, a factor important to decommissioning which does not receive a great deal of publicity is the acceptable variation in temperature of the decontamination operation. Decontamination performed as a precursor to decommissioning might be performed in systems which have been shut down for long periods of time with attendant deterioration of equipment, where equipment which has been partially dismantled, or where the equipment has failed because of an accident. As a consequence, additional heating may not be available. For this reason corrosion and decontamination experiments are being conducted in the laboratory at and below the recommended operating temperatures of the decontamination solutions.

TABLE I

Condensed List of Decontamination Solutions

Solution	Primary Application	
	BWR	PWR
Sulfamic Acid	X	
Peroxide-Oxalic	X	X
H ₃ PO ₄ *	X	
EDTA, Citric Acid	X	X
NS-1	X	
CAN-DECON	X	
AP-CITROX		X
APAC		X
EDTA/Citric/Hydrazine	X	
Oxalic/Citric/HF/H ₂ O ₂		X
HNO ₃ /HF		X
Oxalic/Peroxide/Gluconic (for fuel debris)	X	X
RDS (Reducing Decontamination Solution)		X

* H₃PO₄ has also been used repetitively in the Hanford-N Reactor (Nelson 1981). Initially it was selected because of the large amounts of carbon steel in the system that had to be cleaned; but, the process is also ideally suited for Hanford-N Reactor and is relatively straightforward to use.

Surface Types

The type of surface to be decontaminated influences the decontamination process selected, the method of application, and the time needed for the decontamination. A number of surface types have been identified through our collective familiarity with reactor sites, from personal visits to different reactors, from information supplied by vendors, and from samples obtained at reactors.

In this study we are examining surfaces contaminated by the accumulation of radioactive deposits during normal operation of a power plant. Excluded are components internally activated by neutron exposure in or near the reactor core. Examples of components not considered are: fuel, core components including control rods, the pressure vessel, and activated shield materials. Candidates for decontamination in this study include system piping, pressurizer, and pumps in PWRs. In BWRs, the steam line, turbine, and condenser system are also included. In each of these, internal surfaces are the primary interest. However, because of spills and leaks, other surfaces also become contaminated. Most of these surfaces will be concrete, either bare or painted. Examples include floors, walls, rad-waste systems and soil in the environs immediately around the plant.

Samples from reactor sites are being obtained through a companion program at PNL, "Characterization of Radionuclide Contamination Throughout Light Water Reactor Power Stations" (FIN/189a No. B2299), under the direction of D. E. Robertson.

Our initial decontamination studies have concentrated on a series of pipe samples in the form of cores obtained with a 5 cm diameter hole-saw drill. These were obtained at the partially decommissioned Pathfinder Generating Plant during the summer of 1980. Pathfinder is a 66 MWe boiling water type nuclear power station located 5.5 miles northeast of Sioux Falls, South Dakota. The plant was completed in 1964 and operated intermittently over a 42 month period until shutting down in September 1967 due to failure of the steam separators. For economic reasons, nuclear operations were terminated and the plant was converted to a gas/oil fired unit.

More detailed descriptions of Pathfinder are included in descriptions of the sampling effort in 1980 (Woodruff 1980). The distribution of residual radionuclides found at Pathfinder are detailed in a report undergoing final stages of review (Robertson, et al. 1982). Pathfinder samples used in this study are described in Table II.

Similar deposits listed for feedwater and steam by-pass pipe samples represent those laid down under relatively high temperature conditions while the shield pool clean-up line sample (Sample SPC-B in Table II) represents a low temperature deposit.

Concrete samples were also obtained from Pathfinder, Humboldt Bay, Monticello, and Turkey Point reactors. Samples were collected using a Korit® concrete coring device to remove 10-cm-dia by 12-cm-deep cores.

TABLE II
Core Samples From Pathfinder Piping

SAMPLE*	PIPE SOURCE	TYPE OF PIPE	INNER SURFACE DEPOSIT CHARACTERIZATION (X-RAY DIFFRACTION)
WP74 (301B)	Reactor feedwater line, loose pipe cut during deactivation, original orientation uncertain.	8" dia. carbon steel	Red layer of hematite (Fe_2O_3) over a thin layer of magnetite (Fe_3O_4). Scattered deposits of lepidocrocite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) also present as light brown spots.
RFW-B	Reactor feedwater line, vertical run.	6" dia. carbon steel	Same detail as above.
MSB-C	Main steam by-pass line, vertical run.	6" dia. carbon steel	Same detail as above.
SPC-B	Shield pool clean-up line, side of horizontal run.	4" dia. carbon steel	Mixed upper layer, white and light orange brown over an underlying black magnetite layer. The white is non-crystalline and the brown is lepidocrocite. Several greenish calcite crystals were also found.

* Specific sample numbers are included for the reader who may wish to relate information in this report (Tables V and VI and Figures 2 and 4) to photos of the source piping taken during sampling (Woodruff 1980) or to the detailed analyses of radioactivity (Robertson 1982).

Areas were selected for coring by surveying with a G-M detector to locate "hot spots" of contamination. These often coincided with cracks or surface chips that penetrated the protective paint seal. The sources and descriptions of concrete samples are given in Table III. The coring operation is described in Reference 1.

After shipping the cores to our Richland laboratory, they were repackaged, counted directly on Ge(Li) gamma-ray spectrometers and then cut into 1-cm slabs and recounted to determine contamination as a function of depth. The top surface slab was then sliced in half to provide an archive sample and a sample for further characterization and decontamination studies.

The small size of the core samples, both metal and concrete, means that a compromise must be made between a realistic (large scale) and a practicable decontamination study. Basically this means conducting laboratory scale decontamination studies on the samples, which includes characterizing the type and distribution of radioactivity, and then evaluating and interpreting the results based on our experience to infer the behavior of a decontamination in an actual reactor system. In this report only the data to date are presented--interpretation as related to full scale systems will be provided in the final report.

Corrosion

Corrosion occurring during decontamination performed as a precursor to decommissioning is of concern only if it could lead to catastrophic system failure during the decontamination process or afterwards during other decommissioning operations. Because no further high pressure operations will be performed, the strength requirements of components become minimal--only sufficient to provide structural stability under decontamination and later ambient conditions. Consequently, larger corrosion rates are acceptable than for operational decontamination.

Features which would disqualify a process would be stress corrosion cracking or excessive uniform corrosion rates. The latter would only be of concern if the process chemicals had to remain overly long in the system or if the gases produced, such as hydrogen, were present in sufficient quantity to cause an explosion hazard; other gases, such as oxygen, would be less of a problem if adequate degassing capability is available in the radwaste system. There has been no limit defined on the allowable corrosion for decommissioning. Because of the generally good nonaggressive behavior of decontamination solutions, it is recommended the corrosion limit be set by the amount of iron and other corrosion products, including gases, that the radwaste system can handle rather than by the total corrosion. A secondary limit could be defined by the amount of hydrogen that can be processed, a concentration well below 4.1 vol % (lower explosion limit) in the vapor phase should not be exceeded. Of the other types of corrosion, the one most likely to cause problems is galvanic corrosion, particularly in those systems in which piping modifications have been made. Because of the imminent decommissioning, the tendency will be to use carbon steel components. If these are placed in non-carbon steel systems, the tendency will be for the

TABLE III

Source and Description of Concrete Cores

SAMPLE NUMBER	SOURCE REACTOR	LOCATION	SURFACE CONDITION
PCC-9A	PATHFINDER	Steam Chase	Clear sealer
HBCC-8	HUMBOLDT BAY	Reactor Bldg., 66' level outside step-off pad at bottom of manlift	Gray paint
HBCC-9	HUMBOLDT BAY	Reactor Bldg., 66' level inside step-off pad and inside exclusion fence	Gray paint
HBCC-16	HUMBOLDT BAY	Condensate demineralizer regeneration room	White over black over red paint, cracked, chipped and scratched
HBCC-17	HUMBOLDT BAY	Near HBCC-16	White paint over black over red, uncracked but scratched
MCC-1	MONTICELLO	Reactor Bldg., tool decon area	Bare
MCC-3	MONTICELLO	Reactor Bldg., reactor clean-up pump room	Gray paint, chipped, scratched
MCC-7	MONTICELLO	Radwaste shipping area	Gray paint, scratched
MCC-8	MONTICELLO	Radwaste compactor area	Gray paint over gritty surface
TPCC-2A	TURKEY POINT	Radwaste Bldg., South filling room floor	Gray over red paint
TPCC-2B	TURKEY POINT	Gutter near TPCC-2A	Rough cement like deposit over gray over red paint
TPCC-10A	TURKEY POINT	Auxiliary Bldg., hall next to drain sump	Green paint
TPCC-10B	TURKEY POINT	Pipe tunnel near 10A	Gray paint over gritty seal

carbon steel to rapidly corrode unless the solution has only a low corrosiveness to carbon steel. While such failures are not expected to be catastrophic, significant leaks and contamination problems can arise.

Decontamination Effectiveness

Generally speaking, the best average surface decontamination factors (DF) occur with mechanical processes. Electropolishing has also proven in some instances to be highly effective. Most concentrated chemical methods yield DF's of 5-50 with extremes in both directions. The actual results are highly dependent on materials of construction, temperature, flow rate, and the amount of material removed. Weed, for example, found in high flow conditions that alkaline permanganate/ammonium citrate could give DF values as low as 46 and as high as 27,000 (Weed 1962) on 304 stainless steel depending on velocity. The effect of temperature is complex. Looking at temperature effect very simply, we would expect the decontamination effectiveness to increase with temperature (chemicals are more reactive). However, this must be shaded by the more rapid self-destruction of the chemicals as well as by the increased amount of dissolved corrosion products that can precipitate an insoluble component (e.g., excessive ferrous iron in the presence of oxalate can lead to precipitation of ferrous oxalate).

It is not expected that chemical methods will reduce the amounts of radioactivity to levels that will permit unrestricted release. Instead, the levels, particularly in piping systems where other methods are not readily applied, can be reduced chemically to a point where disassembly can be done with little accrued radiation exposure. Once disassembled, the components could be further decontaminated by more effective methods if unrestricted release is desired.

EXPERIMENTAL

Laboratory decontamination and corrosion measurements were made on selected carbon steel specimens in a small recirculating test loop; static corrosion measurements were made on a larger number of materials. These measurements will be used, together with solution behavior during the tests and PNL decontamination experience, to extrapolate to actual decontamination effectiveness:

SAMPLE CHARACTERIZATION

Pipe samples collected for decontamination are characterized in several ways depending on the stage of recovery and examination. This begins with selection of the sample source in a plant and ends with examining the final specimen condition after decontamination tests. During sample collection, field surveys were made with G-M detectors to locate "hot spots," establish background radiation levels, and determine the extracted sample's activity for packaging and shipping procedures. When possible, field survey radioactivity measurements are included with the more detailed laboratory measurements as a means of relating subsequent decontamination results back to plant conditions. Upon return to the laboratory, samples were re-packaged in clean plastic bags and counted directly on Ge(Li) gamma-ray spectrometers. Results for Pathfinder pipe samples described earlier in Table II are given in Table IV.

Autoradiography

To supplement information on the level and species contributing to the activity, the physical form or distribution of activity as determined by autoradiography (Rogers 1967) was considered desirable at an early stage. Conventional methods (Perrigo and Taylor 1962 and 1964) involving special film, darkroom capabilities, and the associated processing equipment for developing film are not conveniently available at our particular hot laboratory. A method devised utilizing Polaroid® film has proven to be a useful capability which is compatible and convenient in our laboratory study.

As illustrated in Figure 1, the equipment used for producing autoradiographs includes:

- Polaroid® #545 Land Film Holder modified with two additions:
 - a. An aluminized mylar film (25 gauge) is taped over the exposure opening to prevent contamination of the negative during exposure. Before taping, a piece of cardboard cut to fit into the opening is used to assure the mylar conforms with the bottom of the recess. This eliminates the possibility that the mylar might span the opening and prevent close sample contact with the photo negative.
 - b. A wooden frame or shallow box is taped to the holder on the side opposite the film opening to serve as a stand. This keeps the film level during exposure and avoids the tendency for samples to slide on the inclined film in an unmodified holder.

TABLE IV

Pathfinder Pipe Sample Activity Surveys

Sample (See Table II)	Reactor Surveys		Laboratory Survey Gamma Spectroscopy OPM/cm ²				
	Background	Sample	⁶⁰ Co	¹³⁴ Cs	¹³⁷ Cs	¹⁵² Eu	¹⁵⁴ Eu
WP74(301B)	0.3 mr/hr	25,000 c/m through pipe* (5 mr/hr @ contact) 50,000 c/m sample direct*	83,200 ±2,000	<8	22 ±12	7.2 ±2.9	<10
RFW-B	4 mr/hr	45,000 c/m through pipe 55,000 sample direct	125,000 ±300	<9	<20	<3	<7
MSB-C	1 mr/hr	15,000 through pipe 17,000 sample direct	17,390	<1	<2	0.91 ±.41	<0.8
SPC-B	10 mr/hr	55,000 through pipe 25,000 sample direct	328,700 ±300	<5	<7	<2	<3

*Through pipe measurements were made on the outer surface of the pipe before sample removal. Direct counts were made on the inner surface after the sample had been cut out.

(a) Modified Polaroid® Film Holder

(b) Cut-Away of Accessories for Exposures

FIGURE 1. Autoradiography Technique.

- Film Changing Bag:

A light-tight enclosure allows for retracting the film envelope for exposure and placement of a sample on the mylar covered negative. The reverse of this procedure terminates the exposure.

- Sample Weight:

A small weight is placed on the sample during exposure to ensure close contact and prevent movement if the sample and film holder is to be moved.

- Light-Tight Box:

By placing the film holder in a light-tight box (cardboard photographic print paper box ~ 8 1/2 x 11 x 4" is convenient), the box lid can be lowered over the sample and the folded over film envelope in darkness. The bag can then be opened, the box moved to a storage shelf during exposure, and, in the meantime, other autoradiographs may be initiated or terminated in the bag.

We found that sixteen hour or overnight exposures with Polaroid Type 57 film gave satisfactory exposures for the as-received Pathfinder pipe samples. Typical pre-decontamination autoradiographs are shown in Figure 2. These exposures were made with the samples cast in resin holders for insertion in the decontamination loop to be described later.

DECONTAMINATION LOOP

While aware of the difficulties of extrapolating loop data to actual reactor system decontamination, PNL recognized the need for a small dynamic system in which various decontamination solutions could be tested under similar physical constraints. Therefore, a small loop was constructed to compare decontamination solutions on samples collected from reactor piping or other components. In designing the loop, a number of factors were given consideration--some of which imposed restrictions on the final components and configuration. The loop is required to handle:

- Samples from a variety of compositions and configurations including 2" diameter cores from piping,
- A broad range of decontamination solutions (see Table 1),
- Temperatures from ambient to 120°C without flashing, and
- Dynamic flow.

There is an additional limitation that the available working space was confined to a laboratory hood.

WP-74-B 16 HR

RFW-B-D 17 HR

MSB-C-D 16 HR

SPC-B-D 16 HR

MAGNIFICATION - 1X

EXPOSURES AS INDICATED

FILM - POLAROID® TYPE 57/HIGH SPEED RATED 3000 ASA; 36DIN

**SAMPLES - CORED FROM CARBON STEEL PIPE WITH 2" HOLE SAW AND SECTIONED
WITH PORTABLE BANDSAW**

**FIGURE 2. Pre-Decontamination Autoradiographs of Pathfinder Pipe Samples.
See Table II for Sample Descriptions.**

The loop that evolved is shown in Figure 3a. It is based on 1/4" diameter PTFE tubing and uses PTFE for all internal surfaces (except a Kel F tube in the flowmeter) and has a total volume of 250 ml. All components and fittings except the heater and sample holder were off-the-shelf purchases. The positive displacement pump has PTFE internals and delivers 400-600 cc/min. The heater was assembled in the laboratory by inserting a PTFE tube inside a 10" long copper tube that was in turn wound on a 2" diameter aluminum core in which a stainless clad immersion type heater was mounted.

The sample holder (Figure 3b) provides the desired flexibility in accommodating various sample sources. Exposure of the sample to decontamination solutions is through a "window" slot cut in the bottom of the flow passage in a Teflon block. To expose only the contaminated surface of the sample it is imbedded in a resin mount with provision on the outer perimeter of the mount for an O-ring seal. Quickmount resin used in metallographic mounts was found to be resistant to most solutions while providing the dimensional stability required for maintaining seals.

Contaminated surfaces on samples are protected during the casting operation with double wraps of Teflon pipe tape. The protected surface of interest is centered against the bottom of the mold. After removal from the mold, a miniature handheld grinding tool, a scalpel, and tweezers are used under a low power microscope to trim away the tape and excess resin.

The loop also includes a small PTFE reservoir which serves two functions. The reserve fluid capacity is used in start-up procedures in which solution bypasses the sample holder during filling, warm-up and flow adjustment. Fluid in the reservoir is then diverted to fill the sample leg for normal operation. A corrosion coupon, 4.5 cm², is also suspended in the reservoir to provide dynamic corrosion data. Coupons are also counted after weighing for information on redeposition of contamination. Because the coupons are clean surfaces, as needed for good corrosion information, they are more reactive and therefore more likely to become contaminated during the decontamination test; the activity of these coupons should be construed as an indication of what could happen in practice.

Loop Operating Parameters

Test conditions are as follows:

Temperature range - ambient to 120°C

Pressure - atmospheric to 30 psig

Flow rate - 400-600 cc/min

Flow velocity at sample surface - 6.9 to 10.3 cm/sec
(.23 to .34 ft/sec)

FIGURE 3. (a) Test Loop; (b) Sample Holder.

For a typical run the following data are collected:

Pre-Run	• ^{60}Co activity on the sample, and background for the corrosion coupon and solution• Autoradiograph of sample• Weight of corrosion coupon
During Run	• Pressure• Temperature• Flow• Observations on gas evolution evidenced by entrained bubbles showing in the flow gauge tube
Post-Run	• ^{60}Co activity for sample, coupon, solution and rinses• Autoradiograph of sample• Coupon weight

DF's calculated for the sample are based on the net area for the ^{60}Co peak at 1332.4 keV obtained in 1000 second counts.

STATIC CORROSION TESTS

The two types of static corrosion tests performed to date in the solutions listed in Table I have been unstressed immersion tests (with weight loss determination, visual examination to note pitting, crevice or other types of attack) and stress corrosion cracking tests.

The weight loss tests were performed on the metals listed in Table V. The list is limited but representative of the various metals found in reactor systems, including some early test reactors not representative of commercial reactors. The tests were run for 1, 3, and 24 hour intervals. Temperatures of ambient (about 25°C), 50°, and the recommended process operating temperatures were selected for testing. Solution volume to surface ratios were selected at approximately 8 ml/cm².

The tests were performed in PTFE containers to eliminate silica or other test method contamination; all solutions tested to date were air saturated. The specimens were suspended off the bottom of the container with PTFE tape, which produced a crevice.

Stress corrosion cracking tests to date have used C-ring specimens made of 304 and 304L SS. Future tests will use modified U-bend specimens made by bending weight loss coupons. This type of U-bend specimen provides an inexpensive screening test but is not used for basic research into stress corrosion cracking (Ailor 1971).

TABLE V

Metals Used During Corrosion Testing

Cu-Ni Alloy (70% - 30%)

Aluminum 6061

Zircaloy 2

304 Stainless Steel

304L Stainless Steel

316 Stainless Steel

Hastelloy X

Haynes Stellite

Carbon Steel

Inconel 600

DYNAMIC CORROSION TESTS

The dynamic tests were conducted in the test loop, Figure 3, at the same time as the decontamination tests. To date, only BWR carbon steel specimens have been tested. Stainless steel samples from PWR systems will be examined in the near future.

RESULTS

AUTORADIOGRAPHY

A group of samples illustrating the use of autoradiography for characterizing the effectiveness of decontamination is collected in Figure 4. In general, the activity registered on film appears to be composed of two components--one, a uniform overall background; the other, scattered points or particles of higher activity. These two patterns of activity evident in autoradiographs can be related to conditions of deposition. The spot patterns on a more uniform background (SPC-B) are from the low temperature shield pool clean-up line. More uniform radiographic density is associated with deposits laid down at higher temperatures in the reactor feedwater and steam by-pass lines. A tendency for these latter deposits to display a brittle lamellar fracture in response to sample cutting operations is also evident in the autoradiographs (see also Figure 2).

As decontamination with low DF's takes place, the uniform background diminishes in intensity while the hot particles persist and sometimes appear to become more intense (RFW-B-B). In this case it is difficult to establish whether deposit materials that had shielded the particle were removed or contrast of the particle against a darker background makes it appear brighter. The particulates in SPC-B-E diminish in number although the two most intense sources before decontamination were still there after decontamination.

At higher DF's, both particles and background disappear with only an occasional particle or ghostlike film remaining at an edge or near the end of a sample as in WP-74-D, Run 20, or RFWB-B-E, Run 16. These locations suggest stagnant flow areas produced by the sample being recessed slightly below the resin mount. Samples with DF's higher than the 41.2 shown for RFW-B-E, Run 16, produced entirely black autoradiographs.

In summary, this relatively simple and convenient method considerably enhances our perception of the character of contamination and the manner in which it responds to decontamination solutions. Results to date suggest potential for applications beyond the scope of this work in which particulates could be individually identified in combination with microprobe analysis or activity distributions mapped by quantitative image analysis.

DECONTAMINATION

Data from test runs in the decontamination loop are summarized in Table VI. Our standards for reference have been established as AP-Citrox and NS-1. NS-1 is a proprietary formulation designed as a decontamination solution for BWRs and AP-Citrox is a standard process for PWRs. Both solvents are being tested on both PWR and BWR specimens to provide points of comparison. Furthermore, the Pathfinder (BWR) reactor (source of the samples) has been shut down for nine years which undoubtedly modifies film properties and therefore may affect the results. Another

PRE- AND POST-DECONTAMINATION AUTORADIOGRAPHY PATHFINDER CARBON STEEL PIPE SAMPLES

SAMPLE NUMBER	PRE-DECONTAMINATION	POST DECONTAMINATION	RUN NUMBER	DF
WP-74-D			19	1.03
		20	11.6
RFW-B-B			14	1.5
MSB-C-B			13	1.9
SPEC-B-E			6,7	2.3
RFW-B-E			16	41.2

EXPOSURE TIMES - 16 HRS
FILM - POLAROID® TYPE 57

Figure 4. Pre- and Post-Decontamination Autoradiographs of Pathfinder Carbon Steel Pipe Samples. See Table II for Sample Descriptions.

TABLE VI

Decontamination Results From Test Loop

NUMBER	SAMPLE SOURCE	RUN NUMBER	DECON SOLUTION (SEE APPENDIX I)	RUN TIME (HRS)	TEMPERATURE (°C)	DECONTAMINATION FACTOR, DF	CORROSION* mils/yr	POST RUN ACTIVITY IN SYSTEM **		
								CORROSION COUPON	RINSE I	RINSE II
SPC-B-B	SHIELD POOL CLEAN-UP LINE	1	CITROX	2	85	3.4	-	-	-	-
		2	CITROX	2	85	4.2	-	-	-	-
		3	AP (LOW CHLORIDE)	4	50	4.1	-	-	-	5
		4	CITROX	4	50	6.5	26	-	-	20
		5	OXALIC	2	50	14.7	5560	-	-	-
SPC-B-E	SHIELD POOL CLEAN-UP LINE	6	AP	12	105	0.9	32	-	-	16
		7	CITROX	12	85	2.3	-	78	-	-
SPC-B-A	SHIELD POOL CLEAN-UP LINE	8	EDTA, CITRIC, OXALIC	6	100	5.9	2986	30	-	-
SPC-B-D	SHIELD POOL CLEAN-UP LINE	9	OXALIC, HYDROGEN PEROXIDE	2	80	1.5	NO CHANGE	-	22	-
MSB-C-E	STEAM BY-PASSLINE	10	EDTA, CITRIC, HYDRAZINE	4	95	21.1	4730	148	61	26
MSB-C-D	STEAM BY-PASSLINE STEAM BY-PASSLINE	11	EDTA, CITRIC, HYDRAZINE	4	50	4.4	1965	28	-	-
		12	EDTA, CITRIC, HYDRAZINE	2	75	56.7	-	18	-	-
MSB-C-B	STEAM BY-PASSLINE	13	EDTA, CITRIC, OXALIC	5	100	1.9	112	-	-	-
RFW-B-B	FEEDWATER LINE	14	OPG	4	80	1.5	80	3116	22	-
RFW-B-A	FEEDWATER LINE	15	RDS	3	80	5.2	2512	38	17	-
RFW-B-E	FEEDWATER LINE	16	PHOSPHORIC	3	70	41.2	164	-	75	19
RFW-B-D	FEEDWATER LINE FEEDWATER LINE	17	AP	3	105	1.0	1.1 GAIN	-	-	-
		18	AC	3	85	48.7	1810	667	36	-
WP-74-D	FEEDWATER LINE FEEDWATER LINE	19	AP	3	105	1.0	5	-	19	-
		20	SULFAMIC	1.6	70	11.6	8971	104	39	-
WP-74-B	FEEDWATER LINE FEEDWATER LINE	21	NS-1	96	120	58.6	434	2239	33	-
		22	NS-1	100	120	222.0	512	227	19	16

*FROM CARBON STEEL COUPON EXPOSED TO SOLUTION CIRCULATING THROUGH RESERVOIR. 1 mil/yr = 25.4 μ m/yr**NET AREA OF ^{60}Co PEAK AT 1332.5 keV FOR 1000 SECOND COUNTS

***BRACKETS INDICATE SEQUENTIAL RUNS ON THE SAME SAMPLE

(-) DENOTES ACTIVITY AT BACKGROUND LEVEL.

factor to consider is the length of time taken to produce the film. Ayres (1970) points out, for stainless steel, that short term films are more easily removed than long term films; this could also be a factor for the Pathfinder carbon steel films.

Runs 1 through 5 using one sample in a series of loop "shake down" runs include the AP-Citrox combination (Runs 3 and 4). The two prior Citrox runs (1 and 2) make the sample condition atypical for evaluating AP-Citrox performance. In Runs 6 and 7, a new sample was used for the AP-Citrox sequence.

When the results are arranged according to DF values obtained as in Figure 5, the reference solutions become the high, NS-1, and low, AP-Citrox, brackets for all remaining solutions or combinations. It should be noted, however, in making comparisons that a longer exposure time (~ 25 times the average for the other runs) was used for the NS-1 runs. All exposure times were values recommended for use in the literature except as noted. Additional observations made during the runs follow.

Temperature Effect for EDTA, Citric, Hydrazine

Although the available supply of samples and overall program objectives did not permit extensive experimentation with test parameters, Runs 10, 11 and 12 explore the effect of solution temperature. Run 10 at 95°C gave the highest DF (21.1) that had been observed in loop runs at that time. Run 11 was an attempt to see if lowering the temperature to 50°C would have a major effect and the resulting DF of 4.4 was a significant reduction. Run 12 tested a compromise temperature of 75°C using the Run 11 sample for an additional two hour run. The resulting DF of 56.7 was much better than the original result at 95°C. Offgassing was noted during Runs 10 and 12 but not during 11. These results suggest further tests are needed to establish the cause of the offgassing and whether a two-step, low temperature/high temperature process is equivalent to a single process in which the temperature is raised after an initial low temperature phase.

Change in H₂O₂ Molarity Monitored

During Run 9, solution samples were recovered and analyzed to monitor the shift in H₂O₂ molarity. The starting solution was formulated using 0.025 M oxalic acid, 0.5 M H₂O₂ and distilled water. The following analyses for H₂O₂ were made on Run 9 loop samples:

Beginning of run	0.4895 M
After one hour	0.2207 M (-55%)
After two hours	0.0750 M (-85%)

Offgassing Noted

In addition to the offgassing noted for Runs 10 and 12 using EDTA, citric acid, hydrazine solutions, minor offgassing was also noted in Run 15 with RDS. In Run 20 using sulfamic acid, the offgassing became severe enough to

FIGURE 5. Graphic Presentation of Decontamination Results.

inhibit flow in the loop and the run was terminated after 1.6 hrs, about halfway through the run scheduled for 3 hrs.

Deterioration of Sample Mounting Resin

The AP solution in Runs 17 and 19 caused the Quickmount resin in which samples were cast to swell, loosening the imbedded sample, and distorting seal surfaces on the mount. In both cases, the sample was removed and cast in a new mount.

Successive runs were completed without further difficulty.

Redeposition Monitored

After the runs were completed, corrosion coupons and samples of two distilled water loop rinses were included in gamma counts. The data are included in Table VI. Redeposition on the corrosion coupon was highest for the OPG solution in Run 14 which also gave one of the lowest DF's (1.5). In contrast, the next highest coupon count was for NS-1 in Run 21 with a DF of 58.6. Some persistence of radioactivity in final rinse solutions for Run 16, phosphoric acid, and Run 10, EDTA, citric acid, hydrazine is noted. Particulates were also noticed in the reservoir after Run 10, and their entrainment in rinses probably accounts for high counts in this instance.

CORROSION TESTING

Corrosion testing was performed under both static (all alloys) and flow conditions (carbon steel only) as described earlier. The static tests to date have been performed, for the most part, only at 50°C. Higher temperatures have been used in several tests with carbon steel. For those solutions and metals where past experience is available, the data are in fair agreement (Ayres 1970; Nelson 1981). There are, in some cases, significant effects of flow, pH, or concentration of key components which greatly change corrosion rates and are not always reported in the literature.

The average corrosion rates are simply calculated from the weight loss during the test period and are expressed in mils/year (mpy). They should not be confused with the instantaneous corrosion rate (equal to the slope of the weight loss/time curves) at a given time. As seen in Appendix 2, these average corrosion rates generally decrease with time.

Both static and, where available, flow data will be described in the following paragraphs by process. Not all processes listed in Table I have been used.

AP-Citrox

Alkaline Permanganate (AP) and Citrox (Appendix I for formulations and abbreviations) have been tested both at the recommended operating temperatures, 105°C and 85°C respectively, and under static and flow conditions. The AP was also tested at 50°C as a reagent grade chemical (low chloride ~ 0). The average corrosion rate for the different conditions is presented in Table VII. Curves are also presented for Tests 2 and 7 in Appendix 2.

TABLE VII
Average Corrosion Rates After 24 hrs (mpy)

TEST MATERIAL	TEST 1A AP 105°C	TEST 1B CITROX 85°C	TEST 2 AP 50°C	TEST 3 CITROX 50°C	TEST 4 OPP 50°C	TEST 5 HNO ₃ + HF (20% + 30%) 50°C	TEST 6 HNO ₃ + HF (10% - 0.3%) 50°C	TEST 7 AP 50°C	TEST 8 AC 50°C	TEST 9 OP 50°C	TEST 10 OPG 50°C	TEST 11 CITRIC + EDTA + N ₂ H ₄ 50°C	TEST 12 INHIB. SULFAMIC ACID 50°C
Cu-Ni ALLOY	-0.75	52	-0.2	27	TESTING DISCONTINUED, OPP UNSTABLE AT 50°C.	TESTING DISCONTINUED, SOLUTION TOO AGGRESSIVE, MODIFIED.	435	0	7.1	4.3	13.7	6.6	18
6061 ALUMINUM	N/T	N/T	N/T	N/T			1410	N/T	3.4	54	166	2.3	164
ZIRCALOY 2	-0.75	0	0	0			330	0	0	0	0	0	0
304 STAINLESS STEEL	-0.75	0.34	0	0.2			0.8	0	0	0.13	0	0	0
304L STAINLESS STEEL	-0.53	0.24	0	0.2			0.1	0	0	0	0.11	0.55	0.12
316 STAINLESS STEEL	N/T	N/T	N/T	N/T			N/T	N/T	0	0.13	0.11	0	0
HAYNES STELLITE	1.8	1.9	0.1	0.1			0.	0	0	0	0	0	0
HASTELLOY X	N/T	N/T	N/T	N/T				N/T	0	0	0.19	0	0
CARBON STEEL	-1.4	18	0.2	1.3			5100	0	175	30.6	66	277	1440
INCONEL 600	-0.53	9.3	0	1.0			15.3	0	0	0.20	5.2	0	10

Negative values are indicative of the formation of deposits.

Basically these data show little effect of AP on most metals and no significant effect of the chloride. Aluminum is, of course, rapidly consumed and Stellite undergoes attack as is reported elsewhere (Ayres 1970). In most cases the corrosion rates decreased with time or did not vary significantly from the initial value. In some cases an initial deposit is produced which appears as a negative corrosion rate, but this begins to disappear after a few hours with the effective corrosion rate approaching zero. The major concern with the negative corrosion rates is the implication for redeposition of radioactivity; this will be less of a concern with AP than with other solutions because it is primarily a film conditioner and not a decontamination agent.

No stress corrosion cracking of 304 S/S has been observed in six months at room temperature or during the 24 hour tests at 50°C with or without chloride; no high temperature tests have been run.

In the Citrox solutions the corrosion rates decrease with time. Tests at 85°C showed no deposition whereas there was deposition in short time periods (three hours or less) at 50°C. The Zircaloy-2 has essentially zero corrosion but there may be a slight tendency to accumulate a deposit. Carbon steel at 50° had by far the largest deposit (FeC_2O_4), but by 24 hours it had disappeared.

During flow tests run at the recommended temperatures, a carbon steel specimen placed in the loop corroded at a rate of 25-32 mpy in four and twelve hour periods. The corrosion rates are averages for the combined AP, Citrox, and rinse steps.

HNO_3 + HF

This solution was selected because it is used in fuel reprocessing operations to dissolve fuel and cladding yet can be controlled to be only moderately aggressive towards stainless steel. In an initial test, 30% HNO_3 plus 3% HF was used. This proved to be completely unacceptable for all alloys. Therefore, 10% HNO_3 plus 0.3% HF plus .08 M $\text{Al}(\text{NO}_3)_3$ was used. As seen in Table VII and Test 5 in Appendix 2, the corrosion rates at 50°C were spectacularly low. As expected, the Cu/Ni, Zry-2 and Al corrosion rates were by far the highest. Carbon steel was not tested because it is not compatible with the dilute nitric acid.

Stress corrosion cracking specimens (304 S/S) at room temperature showed a slight dulling of the surface finish after six months, but no sign of cracking.

Flow tests have not been run, but, as a preliminary result, the solution looks promising for decommissioning operations.

AP-AC

The alkaline permanganate (AP) step is the same as in AP-Citrox. The ammonium citrate (AC) step was selected for this study because of its effectiveness in cleaning carbon steel (Ayres 1970; Blair 1980) and because it is

the basis for an improved AP-AC process developed by KWU in Germany (Riess 1980).

Corrosion rates are given in Table VII and Test 8, Appendix 2. The corrosion rates are all very low except for the carbon steel which is high but constant with time.

No stress corrosion cracking of 304 S/S was observed in six months at ambient conditions or during 24 hour tests at 50°C.

Flow tests at 85°C produced a corrosion rate of 1800 mpy on carbon steel. This is consistent with Table VIII which indicates a large increase in DF with flow rate increases. It has been reported, in personal communications, that AP-AC was designed for use as a stagnant system. However at PNL, AP-AC has always been used in dynamic systems. Indeed, Weed (1962) reports data, Table VIII, that demonstrates the strong influence of flow on AP-AC produced decontamination factors.

OP

A solution consisting of only oxalic acid and hydrogen peroxide was used rather than the original OPP which included peracetic acid.* At 50°C, Table VII and Test 9 in Appendix 2, the OP has a tendency to form deposits as seen when looking at the metals with low corrosion rates. The corrosion rate of carbon steel at 85°C is about the same as at 50°C.

Carbon steel apparently corrodes rapidly enough to prevent deposit formation. The presence of oxalic acid and peroxide suggests that redeposition will occur with time, however, as oxalic acid is destroyed by peroxide.

No stress corrosion cracking of 304 S/S was observed in six months at room temperature or during 24 hr tests at 50°C.

OPG

OPG is noted primarily for its ability to dissolve fuel debris. Thus, while it is not likely to be used except in post-accident conditions, it is felt that it is a worthwhile process to review. Data are given in Table VII and Test 10 in Appendix 2 at 50°C.* In most cases, the corrosion rate appears approximately constant. However, in several cases deposits, as indicated by weight gains/negative corrosion rates, appear after one hour. These weight gains diminish with continued exposure, but it was not determined whether the deposit is redissolving or whether base metal corrosion is the contributing factor. In the cases of 6061 aluminum and carbon steel, the corrosion rates show an increase with time. It is known (Ayres 1970) that the peroxide level decreases with time and this can increase the corrosion rate. For this solution, and others containing hydrogen peroxide, additional tests will be performed

*In both tests the peroxide stabilizer, 8-hydroxyquinoline, was not used; further tests are planned with it present.

TABLE VIII

Effect of Velocity on the Decontamination Factor Achieved
With the Alkaline Permanganate - Ammonium Citrate Procedure

Test	Linear Velocity of Decontaminants (fps)	Average Decontamination Factor*
1	0.15	46
2	0.25	92
3	0.40	93
4	1.0	1,150
5	5.0	657**
6	5.0	158**
7	5.0	8,820**
8	10.0	27,000

* AISI Type 304 Stainless Steel.

** The range of these results show the variability possible in decontamination testing and practice.

Data from R. D. Weed (1962).

to better define the lifetime of the solutions, the effectiveness of adding additional hydrogen peroxide, and their effectiveness at a given temperature.

No stress corrosion cracking of 304 S/S was noted in 6 months at ambient temperature or during 24 hour tests at 50°C. The corrosion rate in flow tests at 80°C was about 80 mpy using carbon steel.

Citric Acid/EDTA/Hydrazine

This process provides acidic complexing agents in a reducing medium and is aimed at removing iron base deposits. The corrosion data, Table VII and Test 11 in Appendix 2, show low corrosion rates on all components except carbon steel. For short term use it is satisfactory even with carbon steel. For all of the metals examined except carbon steel, the corrosion rates fell rapidly with time. In the case of carbon steel, the corrosion rate remained approximately constant at about 200-300 mpy.

No stress corrosion cracking was observed in five month tests at ambient or in 24 hour tests at 50°C.

In a flow test, a corrosion rate of 4700 mpy was obtained on carbon steel at 95°C.

Sulfamic Acid

Sulfamic acid is a strong acid that is used in the chemical cleaning business to remove calcium containing compounds (NACE 1982). To remove iron deposits the sulfamic acid has to be decomposed to ammonium bisulfate. Normally this is done by heating. The decomposition of sulfamic acid also consumes the formaldehyde used as an inhibitor.

The corrosion data are presented in Table VII and Test 12 in Appendix 2. Except for aluminum and carbon steel, the corrosion rates are very small. The aluminum rate increases with time. The carbon steel data are rather scattered but quite high. In the flow test, carbon steel at 70°C corroded at an extremely high rate of 9000 mpy (9 inches/year).

No stress corrosion cracking was observed at ambient temperature in six months or at 50°C in a 24 hr test.

Miscellaneous Processes

Phosphoric Acid

A short series of static tests were performed in inhibited 10% phosphoric acid on carbon steel. The corrosion rates measured after 24 hours were 12 mpy (ambient), 27 mpy (50°C), and 100 mpy (85°C). The rate at 85°C was increasing with time. These numbers are about an order of magnitude lower than those observed in N-Reactor (Perrigo 1979) during actual decontamination operations which were conducted at high flow rates.

No stress corrosion cracking was observed in a six month test at ambient temperatures.

Reducing Decontamination Solution (RDS)

This solution was examined only for carbon steel in the range of 80-85°C. Lower temperatures were not looked at because the chemicals will not remain in solution. At 85°C, the corrosion rate was 490 mpy in stagnant conditions. Under flow conditions, the corrosion rate rose to 2500 mpy.

HEALTH AND SAFETY CONSIDERATIONS

Health and Safety Appraisal

As noted earlier in this report, the health and safety considerations reported here are process/chemical specific. The general overview of safety and health as related to the decontamination process and operation will be discussed in the final report.

A detailed discussion of first-aid and follow-on medical treatment for chemical injuries is outside the scope of this section. Throughout the decommissioning planning, it is incumbent on the project manager to maintain a liaison with the responsible medical authorities who will assure the best possible treatment for conceivable injuries associated with decontamination chemicals.

Although most of the chemicals have a strong impact on health and safety concerns (as might be expected based on the task they have been selected to do), it is important to keep in mind that the chemical process industry safely handles the same chemicals daily (Gosselin 1976). Therefore, proper procedures and training will permit safe operations.

A comprehensive tabulation of the various chemical solutions used for a wide range of decontamination procedures is given in Table A.1 of Nelson and Divine (Nelson 1981). A review of the solutions shows that there are a number of chemicals common to various decontamination techniques. An attempt is made to give some characterization of the health and safety hazards presented by a number of the chemicals in this category. The chemicals are grouped by function in Table IX, a classification which is obvious in most cases, but somewhat arbitrary for multi-functional chemicals.

Any assessment of the health and safety hazards attributable to decontamination chemicals is complicated by a number of factors, namely:

- the wide range of the concentration of a given chemical between the supply and use stages;
- the numerous possible combinations of the various chemicals within the decontaminating solutions and during the supply, solution makeup, solution application, waste treatment, and waste disposal phases of the decontamination operation;
- the range of possibilities for human exposure to chemicals and their derivatives within these phases of the decontamination operation;

- the very limited information available for many chemicals on their health hazards as a function of concentration and exposure persistence.

Accordingly, health and safety statements for many chemicals are brief and qualitative and are intended only to identify precautions in the use of the chemicals. References consulted for this appraisal are given at the end of the reference section. Some of the sources for information on health and safety hazards for various chemicals and for handling and disposal on a routine or emergency basis are given below:

- Division of Chemical Health and Safety, American Chemical Society.
- CHEMTREC - A 24-hr response service of the Chemical Manufacturers Association.
- CHRIS - A 24-hr information service available through the U.S. Coast Guard.
- EPA-OHM-TADS - Technical assistance information available from regional EPA offices.
- Information on toxicity is available from the following:
 - Chemical Industry Institute of Toxicology, Research Triangle Park, N.C.
 - U.S. Government Toxicology Program (contact through National Institute of Health, Bethesda, MD).
 - National Institute of Environmental Health Services.
 - OSHA (Office of Safety and Health Administration, Washington, D.C.).
- Information on carcinogens, mutagens and teratogens is available from the National Cancer Institute.

TABLE IX

Health/Safety Appraisal for Prominent Decontamination Chemicals

Chemical Category: Acid/Acidic Reagent

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Ammonium Bi-Fluoride (NH_4HF_2) and Ammonium Fluoride (NH_4F)	Emits highly toxic fumes when heated to decomposition; exothermic reaction with strong bases; reactive, oxidizing chemicals.	High hazard potential all routes.		
Boric (H_3BO_3) Acid	Non-combustible.	Apparently innocuous in dilute solutions; in concentrated form it is reported to be highly toxic via ingestion and moderately toxic via intravenous route, affecting the central nervous system.		
Chromic (CrO_3) Acid	Non-combustible; powerful oxidizing agent, hence high fire/explosion hazard with fuel materials.	High with dry powder or mists and fumes of solutions	High over wide range of concentration	High
Hydrochloric Acid (HCl)	Non-combustible; will generate H_2 upon reaction with most metals; with strong oxidizing agents chlorine gas can be evolved.	High	High	High

TABLE IX (Continued)

Chemical Category: Acid/Acidic Reagent (Continued)

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Hydrofluoric (HF) Acid	Non-combustible; anhydrous HF reacts explosively with H ₂ O; can yield explosive mixtures with a number of chemicals.	High (extremely hazardous in all health categories over wide range of concentration)	High	High
Nitric (HNO ₃) Acid	Non-combustible; powerful oxidizing agent producing fires/explosions with many fuel materials.	High	High	High
Phosphoric (H ₃ PO ₄) Acid	Non-combustible; will liberate H ₂ with active metals.	Moderate	Moderate to high, increasing with concentration	Moderate to high, increasing with concentration
Sulfamic (H ₃ NO ₃ S) Acid	Not readily flammable.	Moderate irritant	Moderate irritant	Low to moderate
Sulfuric (H ₂ SO ₄) Acid	Non-combustible; products of reaction with many materials are flammable/explosive; exothermic reaction with H ₂ O and organic materials.	High	High	High

TABLE IX (Continued)

Chemical Category: Base

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Ammonium Carbonate ($(\text{NH}_4)_2 \text{CO}_3$)	Non-combustible; decomposes in hot H_2O and air.	Moderate irritant of nasal passages	Moderate skin and eye irritant	Toxic effects in large doses
Sodium Carbonate (Na_2CO_3)	NO HAZARD CITATIONS			
Sodium Hydroxide (NaOH)	Non-combustible; strong exothermic reaction with H_2O ; may ignite combustibles; reaction with many materials generates H_2 .	High	High	High

TABLE IX (Continued)

Chemical Category: Chelating/Complexing Agent

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Acetic Acid (CH_3COOH)	Vapors form explosive mixtures with air; dangerous in contact with strong oxidizing agents, bases; toxic gases released on burning; concentrated liquid can ignite spontaneously.	Moderate to high depending on concentration	Moderate to high	Moderate to high
Ammonium Citrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_7$)	Non-combustible.	Irritant of mucous membrane and upper respiratory tract	Skin and eye irritant	Mouth, throat and stomach irritant
Ammonium Oxalate ($\text{C}_2\text{H}_8\text{N}_2\text{O}_4$)	When heated to decomposition emits toxic fumes; reacts violently with strong OX agents.	Avoid inhalation	Skin and eye irritant	High, even with very small amounts
Ascorbic Acid ($\text{C}_6\text{H}_8\text{O}_6$)	Non-combustible	NOT GENERALLY CONSIDERED TO BE HAZARDOUS		
Citric Acid ($\text{C}_6\text{H}_8\text{O}_7$)	Slight fire hazard when heated.	Avoid inhalation	Skin and eye irritant	Mouth, throat and stomach irritant

TABLE IX (Continued)

Chemical Category: Chelating/Complexing Agent (Continued)

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
EDTA (ethylenediamine- tetraacetic acid)	Non-combustible	Irritant of upper respiratory tract	Skin and eye irritant	Possible stomach irritant; EDTA is an <u>experimental</u> <u>teratogen</u>
EDTA Na ₄ (tetra sodium salt of EDTA)	Non-combustible	Avoid inhalation	Skin and eye irritant	May cause kidney injury and severe negative calcium imbalance
Glycolic Acid (C ₂ H ₄ O ₃)	Slight fire hazard; emits acrid fumes on heating.	Avoid inhalation	Skin and eye irritant	Moderate to high
Gluconic Acid (C ₆ H ₁₂ O ₇)	50% solution not readily flammable but will burn in fire.	Avoid inhalation	Skin and eye irritant	Moderate
HEDTA (hydroxyethylethylene- diaminetriacetic acid)		Avoid inhalation	Skin irritant; avoid eye contact	High, possible kidney injury and severe negative calcium imbalance
NTA (nitrilotriacetic acid)	Combustible	Avoid inhalation	Skin and eye irritant	Chronic toxicity; suspected <u>carcinogen</u> , <u>mutagen</u> , <u>teratogen</u>

TABLE IX (Continued)

Chemical Category: Chelating/Complexing Agent (Continued)CHEMICALSEVERITY OF HEALTH/SAFETY HAZARDS

	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Oxalic Acid ($C_2H_2O_4$)	Non-combustible; exothermic reaction with strong OX agents, may ignite combustibles.	Moderate to high; chronic inflammation	High	High; 5 g dose has been fatal
Oxine (C_9H_7NO)	Slight fire hazard; emits highly toxic NO _x fumes on heating to decomposition.	Avoid inhalation	Avoid skin and eye contact	Moderate to high; <u>suspected</u> carcinogen
Tartaric Acid ($C_4H_6O_6$)	Moderate fire hazard.	NO PHYSIOLOGICAL HAZARDS IDENTIFIED		

TABLE IX (Continued)

Chemical Category: Corrosion Inhibitor

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Diethylthiourea ($C_5H_{12}N_2S$)	Emits highly toxic SO_x fumes when heated to decomposition.	Avoid inhalation	Avoid contact	<u>Suspected carcinogen</u>
Formaldehyde (CH_2O)	May react explosively with oxidizing agents; solutions with H_2O and Alcohol are flammable.	Moderate to High; <u>lethal in large doses</u>	Moderate to High eye hazard; skin irritant	<u>Suspected carcinogen</u>
Hydroxylamine (NH_2OH) and Hydroxylamine Sulfate	Solid very unstable; deteriorates when heated; rapidly decomposed by H_2O ; solutions should be prepared in explosion proof hood.	Avoid inhalation	High	<u>Hydroxylamine and its derivs. are suspected carcinogens</u>
Propynol (Propargyl Alcohol)	High fire hazard; reacts with oxidizing agents.	Moderate	Toxic to skin; avoid eye contact	High toxicity

TABLE IX (Continued)

Chemical Category: Oxidizer

CHEMICAL	SEVERITY OF HEALTH/SAFETY HAZARDS			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Hydrogen Peroxide (H_2O_2)	Powerful oxidizing agent; may decompose violently if exposed to a number of catalysts (e.g., $KMnO_4$, Pb salts); reacts explosively with many reducing (fuel) materials. When spilled on combustibles, may lead to immediate or delayed ignition.	Moderate to high	High danger potential to eyes; moderate skin irritant	Moderate to high
Potassium Permanganate ($KMnO_4$)	Non-combustible; a powerful oxidizing agent capable of reacting explosively with many reducing materials (fuels); releases Cl_2 in reaction with HCl .	Moderate to high	Skin and eye irritant	High
Sodium Peroxide (Na_2O_2)	Powerful oxidizing agent; reacts violently with water/steam, generating heat and toxic fumes.	High	High	High

TABLE IX (Continued)

Chemical Category: Reducing Agent

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Hydrazine N_2H_4	A powerful reducing agent, concentrated solutions may decompose explosively on heating or upon reaction with an oxidizing agent (e.g., HNO_3 , H_2O_2); explosive decomposition can be catalyzed by a number of substances; forms explosive compounds with a number of materials.	Moderate	Moderate to high	Moderate to high; <u>suspected carcinogen</u>
Hydrogen (H_2)	High explosion/fire hazard; has widest explosive range with O_2 of all gases; its low density can lead to dangerous stratification of explosive H_2 - O_2 mixtures.	ASPHYXIATION IS PRIMARY HAZARD		

TABLE IX (Continued)

Chemical Category: Solvent

<u>CHEMICAL</u>	<u>SEVERITY OF HEALTH/SAFETY HAZARDS</u>			
	<u>Fire/Explosion</u>	<u>Inhalation</u>	<u>Skin/Eye</u>	<u>Ingestion</u>
Acetone (CH_3COCH_3)	High in presence of oxidizing agent; explosions may be triggered by static electricity discharge.	Mild irritant of respiratory tract	Mild skin and eye irritant	--
Ethyl Alcohol ($\text{CH}_3\text{CH}_2\text{OH}$)	Moderate to high depending on strength of oxidizing agent and reaction conditions.	Irritant of respiratory tract and mucous membrane	Skin and eye irritant	Denatured form is toxic depending on type/amount of denaturant
Methyl Alcohol (CH_3OH)	High fire hazard; moderate explosion hazard depending on strength of oxidizing agent.	Slight irritant of mucous membrane	Avoid eye contact; affects optic nerve	High, forms formaldehyde and formic acid in body; a cumulative poison
Polyvinyl Alcohol	Slight fire hazard; reacts with oxidizing agents.	Rated as non-toxic		<u>Suspected carcinogen</u>

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APPENDIX 1

DECONTAMINATION SOLUTIONS

- Compositions
- Abbreviations
- Recommended Operating Conditions

APPENDIX 1

Decontamination Solutions Compositions and Abbreviations

	<u>Compositions</u>
Inhibited Sulfamic Acid	9.0% $\text{NH}_2\text{SO}_3\text{H}$ (sulfamic acid) 5.0% formaldehyde DI water
EDTA + Citric Acid + N_2H_4	0.5% EDTA 0.25M citric acid 0.15M N_2H_4 (hydrazine) DI water
OPG	1.0M $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) 0.02M H_2O_2 (hydrogen peroxide) 0.013M gluconic acid DI water
AP	2.5M NaOH (sodium hydroxide) 0.2M KMnO_4 (potassium permanganate) DI water
AC	0.4M $(\text{NH}_4)_2 \text{HC}_6\text{H}_5\text{O}_7$ (ammonium citrate) DI water
Citrox	0.3M $\text{H}_2\text{C}_2\text{O}_4$ 0.2M $(\text{NH}_4)_2 \text{HC}_6\text{H}_5\text{O}_7$ 0.01M $\text{Fe}(\text{NO}_3)_3$ (ferric nitrate) 0.01M $(\text{C}_2\text{H}_5\text{NH})_2 \text{CS}$ (diethylthiourea) DI water
HNO_3 + HF	10% HNO_3 (nitric acid) 0.3% HF (hydrofluoric acid) 0.08M $\text{Al}(\text{NO}_3)_3$ (aluminum nitrate) DI water

Decontamination Solutions Compositions and Abbreviations (Continued)

	<u>Compositions</u>
RDS	0.25M $\text{NH}_2\text{SO}_3\text{H}$ 0.012M EDTA 0.007M $\text{C}_6\text{H}_{12}\text{N}_4$ (hexamethylenetetramine) 0.15M N_2H_4 DI water
EDTA + Citric Acid + $\text{H}_2\text{C}_2\text{O}_4$	0.0017M EDTA 0.00119M citric acid 0.00198M $\text{H}_2\text{C}_2\text{O}_4$ DI water
$\text{H}_2\text{C}_2\text{O}_4$ + HF + H_2O_2	0.4M $\text{H}_2\text{C}_2\text{O}_4$ 0.1M HF 1.0M H_2O_2 DI water
OP	0.025M $\text{H}_2\text{C}_2\text{O}_4$ 0.5M H_2O_2 DI water
H_3PO_4	1.3M H_3PO_4 0.01M diethylthiourea DI water

RECOMMENDED OPERATING CONDITIONS

<u>Solution</u>	<u>Time</u>	<u>Temp °C</u>	<u>pH</u>
AP	1-2 hrs	105	N.A.
AC	1-2 hrs	80-85	N.A.
Citrox	1-2 hrs	80	3.3
NS-1 (No Static Corrosion Testing)	100-200 hrs	120	N.A.
EDTA+CITRIC+OX	N.A.	100	4.8, 2.2
OX+HF+H ₂ O ₂	1-4 hrs	95	2-4
OP	1-4 hrs	80	4.5
Sulfamic + Formaldehyde	1-4 hrs	45-80	N.A.
EDTA + Citric + N ₂ H ₄	N.A.	90-100	6-8
OPG	1-4 hrs	80	4.5
HNO ₃ + HF + Al(NO ₃) ₃	N.A.	N.A.	N.A.
RDS	N.A.	80	N.A.
H ₃ PO ₄	1-4 hrs	70, 85	N.A.

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