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DOW NUCLEAR SERVICES

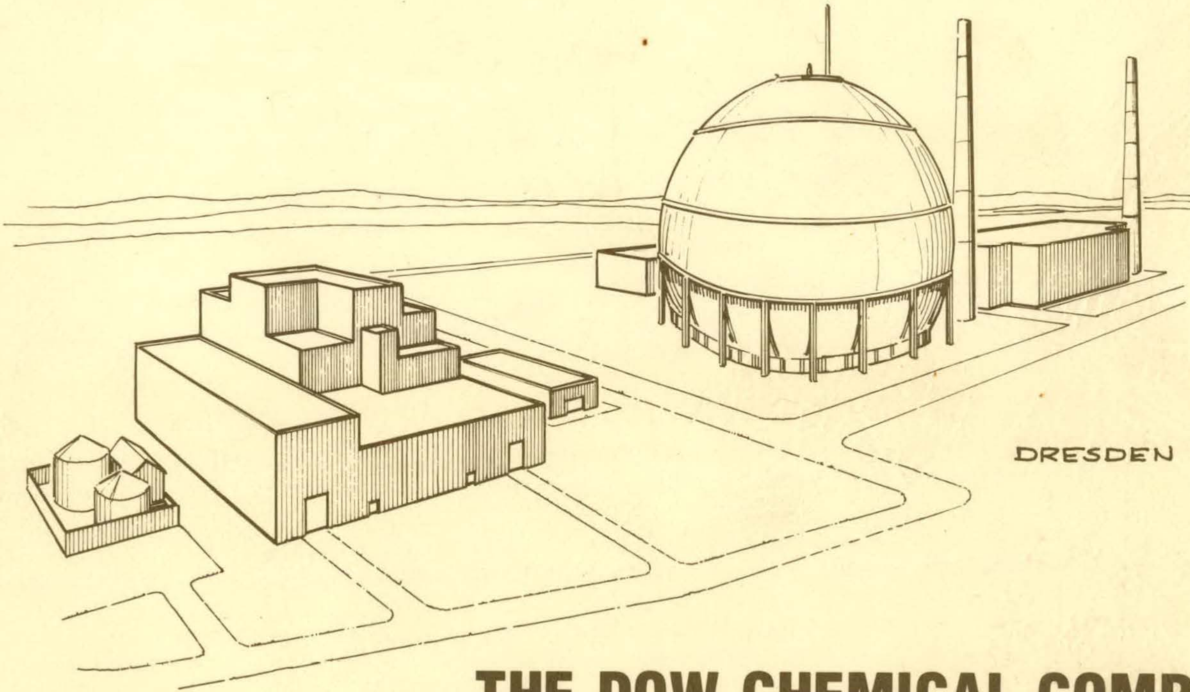
MASTER

TECHNICAL STUDY FOR
THE CHEMICAL CLEANING OF DRESDEN-1

DNS-D1-016

VOLUME I

Sections 1 and 2



THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN 48640

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Section 1 and 2

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ABSTRACT

A feasibility study has been completed to decontaminate the primary system of the Dresden-1 Nuclear Power Unit operated by Commonwealth Edison Compnay of Illinois. Available data initially were searched to determine the state of the art. Solvents based on organic acids and chelates gave unsatisfactory decontamination factors or unacceptable corrosion rates when evaluated for cleaning of specimens from the Dresden-1 primary system, under static and dynamic conditions. A new proprietary cleaning solution, Dow Solvent NS-1, was successfully applied in these laboratory studies.

Scales on specimens cut from the Dresden-1 primary system were analyzed by high resolution gamma ray spectrometry to determine total radioactivity, relative concentrations of isotopes, superficial density, and activity per unit surface of the scales. Isotopes of cobalt were the major constituents of these scales. The scales also were subjected to quantitative wet chemical analyses. Radiochemical and wet chemical analyses were carried out on sludge from the Dresden-1 primary system prior to the final choice of a cleaning solution.

Solvents which had been developed to decontaminate pressurized water reactors did not effectively remove the oxide-laden deposits from scaled Dresden-1 specimens. However the Dow-developed solvent, NS-1, gave decontamination factors of 500-2000, along with acceptable reactor material corrosion rates and an absence of sloughing of undissolved deposits or sludging of solvent components.

Extensive corrosion trials of alloys representative of those used to fabricate the boiling water reactor of Dresden-1 led to the conclusion that serious corrosion should not occur as a result of using Dow Solvent NS-1 for 100 hours at 250°F under nitrogen padding to decontaminate the reactor. Tests of 304 stainless steel specimens of different configurations and stress levels indicated that Dow Solvent NS-1 will not produce intergranular stress corrosion cracking (IGSCC) at Dresden-1, and that the solvent is no more agressive then deionized water under the same conditions. Some 304 stainless steel specimens did exhibit IGSCC, however, when sensitized and exposed in the unscaled condition to either Dow Solvent NS-1 or to deionized water, or when sensitized, descaled, and exposed to either Dow Solvent NS-1 or deionized water which contained >0.12 wt% Fe^{+3} or Cr^{+6}. The above con-

ditions caused IGSCC only in U-bend specimens which were formed after the metal was sensitized.

No excessive general corrosion rates, crevice corrosion, galvanic corrosion coupling effects, or other localized attack occurred when the alloys characteristic of those found at Dresden-1 were exposed to Dow Solvent NS-1. The tests indicated general corrosion rates of <5 mpy can be expected on 300 series stainless steels. These rates would yield a maximum metal loss of 0.06 mils at the end of the decontamination. The corrosion tests also indicated maximum metal losses of 1-5 mpy for 1020 carbon steel, some low alloy steels, 2-1/4 Cr - 1 Mo alloy, and 400 series stainless steels, and losses of <0.1 mils for copper, nickel, chromium, and specialty alloys.

Thermal decomposition of Dow Solvent NS-1 did not appear to produce breakdown products potentially harmful to Dresden-1 construction materials.

Experiments were carried out to optimize the concentration of inhibitor and other components in Dow Solvent NS-1 in order to provide maximum removal of radioactive deposits. The decontamination performance of the solvent was demonstrated in dynamic loop tests with contaminated metal specimens from the Dresden-1 primary system.

A pilot-plant based on a natural circulation, long tube evaporator with a one gallon/minute capacity was developed to concentrate spent solutions of Dow Solvent NS-1. This radwaste system was designed to give maintenance-free operation with a minimum risk of personnel exposure. Heat and mass balances, and concentration efficiency, were determined for the pilot plant. The adsorption capabilities of activated carbon and an acidic ion exchange resin were evaluated for purification of the NS-1 concentrate. The specific gravity, heat capacity, viscosity, and thermal conductivity of Dow NS-1 solvent, and of the distillate and concentrate from the evaporator were determined.

Safety evaluations indicated that personnel could handle nonradioactive NS-1 solutions with ordinary protective equipment, and that shock sensitivity or explosivity were not likely to be hazards associated with the solvent. Thermal burns during use of the solvent and during evaporative operation are expected to constitute the chief hazard.

An on-site study of Dresden-1 was performed to identify all plant-related aspects for the proposed decontamination and radwaste treatment facility. Health physics monitoring was carried out simultaneously. New piping, storage, and associated facilities, and a radwaste facility, subsequently were designed for the proposed decontamination. A subcontractor-prepared safety and design basis was used to develop specifications for the proposed decontamination system.

Photographs, figures, tables, and extensive metallurgical data are included in the document.

1.0 INTRODUCTION

1.1 PROJECT DEFINITION

In May 1972, Dow Industrial Service - Nuclear Services (DIS-NS), a division of the Dow Chemical Company U.S.A., was chosen by Commonwealth Edison to perform services necessary to remove radioactive deposits from the primary side of the steam supply system of Dresden-1 Nuclear Power Station operated by Commonwealth Edison Company of Illinois.

Included in this service are the design of a radwaste treatment facility to process waste generated during cleaning, installation, and removal of piping, and recommissioning of Dresden-1. Finally, DIS-NS will, concurrent with and after the cleaning, instruct and train Commonwealth Edison personnel in the operation of the radwaste facility prior to transfering the facility to Commonwealth Edison.

DIS-NS, with the approval of Commonwealth Edison, contracted Suntac Power Division, a division of Catalytic Inc. to perform the Architectural-Engineering tasks for this project.

DIS was developed 35 years ago within The Dowell Division which provides a broad range of services to oil field operations. Since December of 1976, Nuclear Services has been a part of the Functional Products and Systems Department (FP&S). DIS-NS established an organization comprised of personnel experienced in the handling and processing of nuclear products. The analytical, chemical, and research facilities of the Dow Chemical Company are available for DIS-NS assistance.

Catalytic, Inc.'s scope of operations encompasses engineering, construction and contract maintenance, including process design and development, technical and economic analyses, site studies, and engineering construction management.

The initial concept of the project included dividing it into Phase I, the initial feasibility study, Phase II, construction and chemical cleaning; and Phase III, recommissioning. Phase I consists of laboratory studies, solvent development, corrosion studies, and the analysis of the feasibility of cleaning Dresden Unit-1. The information contained within this report documents the data obtained in Phase I and supports the consensus that Dresden-1 can be safely decontaminated.

1.2 PROBLEM STATEMENT

Most commercial nuclear power plants use water as the heat transfer agent between the nuclear fuel and the electric generator plant. The continuous exposure of metals in the system to high temperature water results in corrosion of the surfaces. The metals in the primary systems of nuclear plants are selected for their corrosion resistance, and corrode at a much lower rate than fossil fuel plant boilers which are made of thick-walled carbon steel pipes. While conventional plants have to be cleaned every few years to restore their heat-transfer properties, nuclear plants do not have to be descaled for this purpose for much longer intervals. The deposits in fossil fuel plants are at times up to 1/4" thick while in nuclear plants they are measured in fractions of a millimeter. Restoration of the heat transfer properties is not a problem in nuclear plants. Engineers maintain that nuclear plants need not be descaled during their design life of about 40 years. There is, however, an added dimension to the corrosion-deposit problem in nuclear plants: the buildup of radioactivity in the corrosion scale.

The corrosion products undergo nuclear reactions with neutrons and give rise to radioactively activated products which deposit on the inner walls of the primary system with the corrosion deposit and contaminate the walls with radioactivity. The type of radioactivity found on a specific surface depends on the history of corrosion of the system as well as on the local environment of that surface, i.e., on the temperature, pressure, and flow rate in that section of the primary piping system as well as on the roughness of the surface. The radioactivity in the deposit also depends on the length of system service. Only long-lived radioactive species remain in the older parts of the deposit, while fresh scale contains short-lived radioactive species.

In addition to the neutron activation products of metal ions brought into solution by corrosion and activated in the neutron flux, there are radioactive species stemming from the fission reaction occurring in the nuclear fuel. These species reach the primary heat transfer agent through cracks in leaking fuel elements. While leaks are kept to a minimum and most fission products are retained in the fuel, some gaseous fission products escape into the water and transform into nonvolatile elements by beta-transitions. These decay products of the gaseous ion products find their way into the corrosion scale and contribute to its radioactivity.

The typical species found in radioactive scale are given in Table 1.2. Copper and its activation products are conspicuously absent from this list. Copper does not give rise to long-lived neutron activation products and thus does not contribute to the radioactivity of the scale.

Nuclear plants require periodic maintenance and occasional thorough inspection. During the initial plant operation such activities are straightforward, and ordinary precautions against contamination of personnel and the environment are sufficient. As the plant ages and radioactive deposits accumulate, radiation fields in the plant become sizeable even after a plant outage of several weeks. Repairs become a major undertaking, since they have to be done in the radiation environment which on occasion is so high that a person accumulates the permissible quarterly dose of radiation within a few minutes of exposure.

Table 1.2

Nuclides Found in Corrosion Deposits of Water Cooled Nuclear Reactors

Isotope	Nuclear Reaction	Half-Life	Significant γ Rays (Mev)	Encountered in Dresden-1 Specimen
^{46}Sc	^{45}Sc(nγ)	85d	1.1	
	^{46}Ti(np)			
^{51}Cr	^{50}Cr(nγ)	27.8d	0.31	Yes
^{54}Mn	Fe^{54}(np)	303d	0.83	Yes
^{55}Fe	^{58}Ni(n,α	5y	x-ray	
^{57}Co	^{58}Fe(pγ)	270d	0.12	Yes
	^{58}Ni(n,pn)			
^{58}Co	^{58}Ni(np)	72d	0.81 (β^+)	Yes
^{59}Fe	^{58}Fe(nγ)	45d	1.29	Yes
^{60}Co	^{59}Co(nγ)	5.2y	1.17	Yes
	^{60}Ni(np)		1.33	
^{63}Ni	^{62}Ni(nγ)	92y	β Only	Yes
^{65}Zn	^{64}Zn(nγ)	245d	1.11	Yes
^{89}Sr	FP	50.5d	β^-Only	Yes
^{90}Sr	FP	28.1y	β^-Only	Yes
^{95}Zn	^{94}Zn(nγ)	65d	0.724	Yes
			0.757	
^{95}Nb	Zn ^{95}(B$^-$)	35d	0.766	Yes
^{103}Ru-Rh	FP	39.6d	0.49	Yes
^{106}Ru-Rh	FP	367d	0.62	Yes
^{124}Sb	^{123}Sb(nγ)	60d	2.11	Yes
^{125}Sb	FP*	2.7y	0.43	Yes
^{137}Cs	FP*	30.y	0.66	
^{140}Ba	FP*	12.8d	0.54	
^{141}Ce	FP*	32.5d	0.14	Yes
^{144}Ce-Pr	FP*	284d	2.18	Yes
^{181}Hf	FP*	42.5d	0.54	
^{239}Np	^{238}(n,γ—Jb)	2.3d	0.33	

*from fuel element leaks

Repair work which in a conventional plant could be completed by five persons in a week might require up to 1500 welders working over half a year to complete in a nuclear plant.[1] This "burning up of bodies," as referred to in Science[2] has been standard practice. This procedure, now unacceptable, was allowed since there were a few nuclear plants in existence until recently.

With an increased number of nuclear plants on line or coming on line in the immediate future, there will not be available a large enough labor pool of skilled and semi-skilled people to perform the needed work. In addition there is increased emphasis on the reduction of total man-rem radiation exposure.

The project was initiated in 1971 with these considerations in mind in order to have an alternative approach available when needed by the nuclear utility industry. The Commonwealth Edison Company (CECo) also realized the need for, and sought, alternate approaches.

1.3 THE DRESDEN-1 PROBLEM

Dresden-1 which was commissioned in 1962, is the oldest privately owned nuclear plant in the United States. Its primary loop consists almost entirely of 304 series stainless steel. While 304 stainless steel has excellent general corrosion resistance it is prone to stress crack corrosion in certain environments.

In the course of its operation, the plant experienced piping failures caused by stress cracking. Most failures seemed to occur in pipes where flow rates were low or in pipes which were isolated from the system for extensive times. Cracks seemed to occur most frequently in the stressed areas about 1-2" from field welds. They tended to run in a circumferential direction and did not enter the weldment itself.

Nuclear Regulatory Commission (NRC) regulations require periodic examination of the primary system components and piping to reveal possible trouble before failure occurs. The necessity of these examinations with "as low as practicable" personnel radiation doses indicated the desirability for decontamination at Dresden-1.

Studies of occupational radiation exposures at U.S. light water reactors show a three-fold increase in yearly average exposure per plant between 1969 and 1973 (188 man-rem in 1969 compared to 544 man-rem in 1973).

Roughly 80% of this exposure occurs during plant maintenance. Certain plants show higher year-to-year increases because repairs are performed in high-radiation areas. At one plant, operational exposure increased from 834 man-rem in 1972 to 5160 man-rem in 1973, largely because workers were involved in repair of defective welds.

Radiation levels also have increased significantly at Dresden-1. Since access to primary components is necessary, a method of reducing occupational radiation exposures at operating plants had to be developed. Total plant decontamination is one possible method. Dow Industrial Service was engaged to evaluate existing technology and to develop new technology for the total decontamination of Dresden-1.

The following goals were identified as of primary importance in establishing this program:

1. Reduce radiation levels to improve plant accessibility.
2. Ensure future safe and efficient operation of Dresden-1.
3. Develop and prove techniques usable on other reactors.
4. Encourage broad vendor, manufacturer, and consultant participation.

In addition to DIS-NS and Suntac Power Division of Catalytic Inc., Commonwealth Edison contracted with the following to serve as consultants:

1. The Nuclear Energy Division of General Electric Company.
2. Craig F. Cheng of Argonne National Laboratory.
3. T. A. Hendrickson of Burns & Roe, Inc.
4. Roger W. Staehle of the Ohio State University.

2.0 STATE OF THE ART

2.1 LITERATURE SEARCH

The initial task prior to the decontamination the Dresden-1 nuclear reactor involved searching all available data to determine the state of the art. Available publications were analyzed to determine (1) feasibility of decontamination, (2) solvent selection, (3) expense, and (4) anticipated decontamination factor. Materials researched included various publications, results reported at the June 1974 American Nuclear Society (ANS) meeting, decontamination manuals, and a text on decontamination edited by J. A. Ayres.[3] Advice also was obtained from consultants familiar with the problems of nuclear decontamination and from DIS service personnel.

Evaluation of available methods led to the conclusion that the approaches attempted previously were inadequate from either the standpoint of the decontamination factor (DF), redeposition factor, or corrosion factor. Following is a summary of data that led DIS-NS to develop a specific decontamination solvent for Dresden-1.

2.2 "NUCLEAR DECONTAMINATION AND LOW LEVEL WASTES"

Summary of the Special Session ANS Annual Meeting in Philadelphia June 25, 1974.

A special session attended by about 90 people was sponsored by the Isotopes and Radiation Division of the ANS in an attempt to present the state of the art in the areas of nuclear decontamination and low level wastes handling. Experts from the Atlantic Richfield Hanford Company and industrial firms associated with nuclear equipment manufacturers and nuclear utilities gave presentations followed by a one hour panel discussion with audience participation. In general, attendees concluded that the state of the art in nuclear decontamination had not progressed technically since 1967 and was still well represented by the book, Decontamination of Nuclear Reactors and Equipment, edited by J. A. Ayres.[3]

The first speaker, Eugene A. Saltarelli of NUS corporation and formerly associated with Westinghouse Electric Company, was one of the persons primarily responsible for decontamination of the Shippingport Nuclear Plant in 1964. In discussing "The Considerations for Total Nuclear Plant Decontamination," Saltarelli pointed out that in an operating nuclear plant the inspection, maintenance, and repair effort becomes increasingly more difficult and expensive as the radiation fields increase around the primary system of the reactor and the total exposure rate of the crews increase. Maintenance can be done initially, if closely controlled schedules for individuals are adhered to, but ultimately a reduction of the radiation fields becomes mandatory to retain the effort within reasonable proportions. Saltarelli then related his experiences at Shippingport, which verified Ayres' reports, and brought out criteria as follows to apply to selection of decontamination solutions:

1. The aggressiveness of the solution must be such as to remove oxide films without damaging the parent metal.
2. The consequences of incomplete removal of the solution on plant chemistry requirements for normal operation must be addressed.
3. The solution must be able to remove oxide films in low-flow areas as well as in complicated geometrical configurations such as heat exchangers.
4. The compatibility of the solution with various plant materials it contacts and any deleterious consequences must be addressed.
5. The consequences of allowing the solution to remain in the plant primary system for periods longer than desired as a result of system malfunction while the decontamination operation is conducted must be addressed.

Saltarelli further pointed out the need for good estimates of the amount of radioactivity and other material to be removed in order to be able to plan effective and safe handling of the wastes. Consideration must be given to dead-leg areas, where loosened scale can settle and become inaccessible due to high radiation fields. He pointed out that there is no substitute for having actual samples from the plant to be decontaminated so that corrosion deposits can be identified and the effectiveness of the planned decontamination procedures can be tested in the laboratory. This, he found, is mandated by the fact that, due to differences in operating conditions, the nature of the corrosion film can differ from plant to plant and even within the same plant. Saltarelli warned that undertaking a total plant decontamination is a large task which requires significant planning as well as basic development work, if damage to the plant, on the one hand, or total ineffectiveness of the decontamination effort, on the other hand, is to be avoided.

Available at the special session were reprints of the paper "Maintenance and In-Service Inspection"[4] by Bridenbaugh, Lloyd, and Turner of General Electric Company, presented at the October 1973 International Atomic Energy Association (IAEA) symposium. While these authors avoided concluding the ultimate necessity of decontamination of boiling water reactor (BWR) plants, their data corroborated some points made by Saltarelli. Graphs showed radiation levels near the primary system of a typical BWR increased from 50 mrem/hr to 700 mrem/hr in less than four years of operation, with no leveling indicated. These data correlated with data for mechanical crews whose exposure to radiation increased from 50 mrem/week to 550 mrem/week per person in the same time interval.

The second speaker, Charles B. Foster of the Research and Engineering Division of Atlantic Richfield Hanford Company, addressed "Decontamination of Obsolete Processing Facilities at Hanford." He presented an overview of the decontamination work associated with the remodeling of the large fuels processing plant (B-Plant), preparation of a reprocessing plant for stand-by (Redox), and the dismantling of the plutonium scrap processing facility (Recuplex).

The methods used for B-Plant decontamination consisted of initial water rinses and lancing of the cells, and rinsing the process equipment with 60% nitric acid. Tanks were decontaminated by alternately filling them to overflow with alkaline permanganate and nitric acid. This treatment was followed by steam cleaning the tanks with alkaline permanganate, water, and oxalic acid and again by water.

Decontamination of the Redox plant was accomplished by an initial acid flushing of the reaction vessels with 57% nitric acid-1% boric acid, followed by dissolution of the sludge with 20% nitric acid-6% ammonium fluoride-1% boric acid and liberal water rinses. Again some vessels were treated with solutions of 25% NaOH and 1% $KMnO_4$ followed by water and a subsequent 10% nitric acid treatment.

The canyon deck of the Redox plant was decontaminated by spraying it with a solution of 25% NaOH and 1% $KMnO_4$ followed by water and a subsequent 2.5% oxalic acid spray. Sprays were applied with pressures of 150 lb/in^2 at rates of 30 gal/min. Radiation fields were reduced from 1000 rad/hr to 100 rad/hr by these treatments.

Processing equipment in the Recuplex facility was decontaminated by flushing it with nitric acid and hydrofluoric-nitric acid mixtures to remove plutonium. The external surfaces were then painted with latex paint to fix any residual contamination.

From his experience, Mr. Foster recommended that facilities which might have to be decontaminated should be designed without "cul-de-sacs" (dead legs), or cracks and crevices, and that provisions should be made for accomplishing proper containment prior to decontamination operations. Unplanned events should be anticipated. He emphasized that each job is unique, and that planning, which involves factors of design, operations, personnel and community relations, is the most important ingredient.

The third paper was given by J. F. Nemec, United Power Association, on the subject: "Demolition of Radioactive and Contaminated Concrete Structures by Use of Explosives." He reported on demolition of the Elk River Reactor, a 58 MW(th) BWR, which had been in operation for four years and was shut down in 1968 for economic reasons. This project encompassed the first complete removal of a nuclear power plant from a site followed by return of the site to normal usage. Dismantling of the reactor proceeded "inside out" to effect contamination control. Pieces of the reactor cavity were removed via an opening near the top of the containment by means of a long-boom crane. They were crated outside and prepared for off-site burial. The biological shield was then collapsed in layers by means of explosives and the debris was removed. These methods efficiently prevented the spread or release of radioactive contamination.

The fourth paper was presented by M. J. Szulinski, Research Department, Research and Engineering Division, Atlantic Richfield Hanford Company, and was titled "The Hanford Decontamination Facility." In addition to describing the facility itself, Mr. Szulinski discussed some of the decontamination procedures used at Hanford. He stated that the high-pressure spray technique (lancing) has become the favored decontamination method in recent years. For stainless steel surfaces the decontamination center used a sodium hydroxide and potassium permanganate wash, followed by a water flush, a nitric acid-ferrous ammonium sulfate bath and water flushing. Recently this procedure was replaced by use of commercial cleaners, e.g. TURCO[a] 4502D (caustic permanganate) and TURCO 4518

[a] Trademark of the Colgate Palmolive Co.

(oxalic acid base) with water flushes between treatments. TURCO 4512 (phosphate-base) in a 1:10 dilution was used to decontaminate carbon steels.

Commercial laundry detergents such as TIDE were employed where needed.

Sodium bisulfate was usually used to remove alpha contamination at the decontamination center while chloride based solutions were used at the plutonium facility. The latter were used sparingly and with caution because of their corrosiveness.

Ultrasonics were used occasionally to decontaminate small parts.

The speaker also reported on some basic decontamination studies carried out recently at Hanford. The use of molten salts was shown to have no advantage over the conventional methods. It appeared that successful decontamination required significant dissolution of metal and left large amounts of contaminated salt for disposal.

Electron microscopy studies showed that decontamination was proportional to the amount of debris removed from the metal grains and the grain boundaries. Debris, and thus contamination, was easier to remove when the grain boundaries were five microns in width, than when they were one or two microns wide. The speaker then discussed some of the pros and cons of large-scale decontaminations and the resulting complex economic considerations.

The final paper of the session was presented by Mr. Peter Tuite of Hittman Nuclear and Development Corporation, who reviewed the present technology of "Shipment and Disposal of Low Level Wastes." He classified the wastes into: (1) solids, i.e. rubbish and contaminated hardware and filters; (2) process solids which consist of contaminated ion exchange resins and filter sludges; and (3) liquids. The latter are evaporator concentrates, bottoms and miscellaneous waste solutions.

Low level wastes are packaged in 55 gallon drums or containers of up to 222 cubic feet capacity. Liquids must be solidified or immobilized by absorption since free water is not acceptable for transportation or burial. Process solids must be dewatered or solidified for transportation or burial. The containers may be transported without shielding if they meet Department of Transportation (DOT) specifications. How they are shipped depends on the dose rate at the surface of the disposal container, the specific activity of the material and its form, as well as the total amount of radioactivity contained.

For shipping purposes, wastes can be classified into three categories:

1. Low Level - Where the surface dose, form and curie content of the disposal container are compatible with shipment in an exclusive-use closed van.
2. Intermediate Level - Where the surface dose of the disposal container is such that additional shielding is required and the material satisfies the DOT requirements for low specific activity (LSA) material.
3. High Level - Where the surface dose of the disposal container is such that additional shielding is required, but the form of the material and/or the curie content of the shipment is such that the material must be shipped as Type B or Large Quantity Material.

Mr. Tuite then compared the waste outputs from typical BWR and pressurized water reactor (PWR) nuclear power plants as follows:

Waste Volumes by Shipment Type
Typical 1000 mwe BWR's and PWR's

	High Level ($Ft.^3$)	Intermediate Level ($Ft.^3$)	Low Level ($Ft.^3$)
BWR	300	2200	5000
PWR	200	700	2100

Waste is transported by truck or rail. Each state regulates the maximum allowable gross weights for trucks. Typically this is 73,000 lbs per vehicle. Special permits can be obtained when up to 115,000 lbs are moved. Rails can transport casks with weights as high as 200,000 lbs.

The final step is underground burial. There are presently six burial sites in the U.S. located in Idaho, Illinois, Kentucky, Nevada, New York and Washington. At the burial sites, individual packages are removed from the transport casks and placed into slit trenches or individual holes depending on surface dose rate or curie content of each package.

Mr. Tuite concluded with the fact that the burial grounds are government owned and leased to the burial site operator who is monitored closely by state and federal authorities.

During the subsequent panel discussion the following items were discussed:

There have been other efforts to decontaminate the primary systems of nuclear reactors in addition to Shippingport, e.g., the Hanford N-Reactor, the Rheinsberg PWR reactor in East Germany, and the SENA PWR in Belgium. Decontamination involved use of alternating alkaline permanganate-water-acid-water cycles where the acid phases contained ammonium citrate or oxalic acid with various additives. In general, decontamination reduced contamination levels by up to one order of magnitude, but produced large amounts of contaminated liquids, corrosion (although claimed acceptable), and at times redeposition of radioactive material in other parts of the reactor.

In working on "on-line" decontamination procedures for their heavy water nuclear reactors, Canadian workers decontaminated a loop of the Gentilly Reactor by removing about 40 curies of material at a decontamination factor (DF) of 3. No further details were available to the audience.

Questions for information about the Navy's experience with reactor decontaminations at Newport News met with warnings that the topic is "classified" but assurance was given that the techniques used are not out of line with those utilized by other nuclear installations. No information was available about Russian experience.

Other questions of interest which did not probe general philosophies of nuclear power, waste disposal, or dismantling of reactors brought out that there were no uniform criteria for liquid waste solidification methods nor any official methods to test solidified wastes for leach rates and/or stability in the radiation field. Mr. Tuite pointed out that use of vermiculite or other imbibing agents soon may not be permissible for disposal of liquid wastes.

The special session left the impression that the entire subject was somewhat in a state of suspension. Apparently people were not carrying out significant research and development work which they were willing to report publicly, and which would signal technological advances both in the decontamination or the waste handling and disposal area over the state of the art available in the middle 1960's.

Attendees felt that with the nuclear utilities' need for satisfactory methods to handle oncoming issues at their plants and with intervenors focusing attention onto the issues, both areas might see significant development in the near future.

2.3 J. A. AYRES TEXT

Decontamination of Nuclear Reactors and Equipment edited in 1970 by J. A. Ayres extensively discusses development of decontamination processes for nuclear reactors. Ayres' history of work accomplished up to 1970 is considered by the nuclear industry as the latest significant report on decontamination processes.

Methods for ordinary cleaning of conventional power plants can be applied partially to nuclear reactors from the standpoint of removing nonradioactive scale. However, in nuclear reactors radioactivity is removed along with nonradioactive elements. In nonnuclear power plants, removing 99% of the scale would be sufficient for return of the plants to service, but in nuclear reactors removal of 99% of the scale does not always result in 99% removal of radioactivity. The effectiveness of cleaning includes not only removal of scale but also involves effective radioactive decontamination. Complicating the decontamination is the fact that nuclear reactors often are constructed with numerous types of metals in complex geometries. Any solvent used for cleaning must be compatible with these metals and be capable of cleaning areas where flow velocities may reach zero.

The text by Ayres begins with a discussion of conventional cleaning, its associated problems, and application of these restrictions to decontamination. The history of the art is summarized based on applicable research in the area of decontamination.

2.4 A REVIEW OF THE STATE OF THE ART

The state of the art of nuclear plant decontamination is relatively unsophisticated and of limited experience. The recent recognition of the serious impact of the buildup of radioactive corrosion products on the operation of the light water cooled nuclear plants requires rapid development of decontamination technology. The state of the art as reported in the literature is presented in the following pages as a starting point for a report on the contributions of the Dow Chemical Company to the field. This report first compares nuclear plant decontamination with conventional chemical cleaning practices and then discusses the issues involved in the former. The decontamination operations reported for individual cases in the literature are reviewed. They are subdivided into decontamination operations involving low temperature water cooled reactors (LTWCR), pressurized water reactors, and boiling water reactors. For the present purpose, the state of the art for decontamination of boiling water reactors is of prime interest. However, review of procedures used to decontaminate LTWCR's and PWR's is valuable because of the similarity in techniques used for all three types of reactors and because of the lack of available information.

2.4.1 Conventional Chemical Cleaning

Conventional fossil fuel heated utility boilers accumulate deposits on the inside surfaces during operation. Periodic removal of these deposits is required in order to restore both the heat transfer capabilities of the surfaces and the efficiency of the units. Chemical cleaning has been used to remove deposits since the 1940's.

The schedule followed for the periodic chemical cleaning of conventional boilers depends on the operating pressure and the type of firing. For pressures of 1600-2000 psi, chemical cleaning is performed every 4-5 years. For boilers operating in the pressure range of 2000-2500 psi, chemical cleaning is scheduled every 3-4 years. For operating pressures of 2400 psi, once-through type boilers are cleaned every 2-3 years. Coal fired boilers with pressures up to 3500 psi are chemically cleaned every 2-4 years. Oil fired boilers with 3500 psi operating pressures require cleaning every 1-2 years. Units in peaking service require frequent cleaning regardless of the pressure. The choice of solvents depends on tye type of materials present in the feedwater system and shether internal corrosion problems have developed. If heater or feedwater systems contain copper alloys, treatment with a bromate stage or a copper complexing agent may be necessary as part of the chemical cleaning operation. Hydrogen damage may dictate against the use of hydrochloric acid in favor of ethylenediaminetetraacetic acid (EDTA).

In general, most drum boilers are cleaned with HCL, and most of the once-through units are cleaned with a mixture of 2% hydroxyacetic acid, 1% formic acid, and 0.3% ammonium bifluoride.

2.4.2 Nuclear Plant Decontamination

Although in nuclear plants care is taken to control the water chemistry in the boilers and to select corrosion resistant materials for construction, corrosion does occur on the surfaces of the heat transport systems. Indeed, formation of oxide scale on stainless steel is desirable since it provides surface passivation.

Radioactive core material and activated corrosion products are transported from the reactor core, via the reactor coolant, as cooloids, ions, or particulates to the external portions of the primary system where they deposit in areas of low flow (crevices, valves, vents, tees), onto cooler or hotter portions of the system, or by sorption onto piping surfaces. Since these materials are radioactive, the buildup of deposits is associated with increased radiation fields near the primary system piping.

The most troublesome and recurring contamination problems are the gradual buildup of radioactivity in the portions of the primary system, outside of the core, especially in pipes, valves, pumps and heat exchangers, which require periodic inspection and maintenance.

The film which forms on carbon steel surfaces is primarily magnetite. In stainless steel systems the deposit appears to be a mixture of magnetite, other oxides of iron, along with oxides of chromium, and nickel.

Radioactive fission products enter the coolant after a failure of a fuel element in a nuclear reactor. Experiments carried out at Battelle Memorial Laboratories showed that these fission products are rapidly and irreversibly sorbed into the magnetite film and cannot be removed selectively.[5] A considerable amount of radioactive debris may be removed by flushing the system with water. "Dead legs" in the system are likely to collect particulate residue, and should be flushed with water, if possible, to remove radioactive residue which will be difficult to remove later by chemical cleaning. Flushing the system with water to remove much of the highly radioactive residues also decreases personnel

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No single decontamination procedure is applicable to all jobs. Physical techniques such as water flushing, operational cleaning, etc., have limited application in system decontamination because they can be used only on relatively accessible surfaces. Also, they tend to remove underlying metal along with the corrosion deposit, roughen the surfaces, and cause some work hardening. Treatments capable of removing radioactive oxide films from a wide variety of materials in a system, without causing harmful attack onto some, are difficult to identify. Chemical procedures involve use of solutions, foams or vapors, but only solutions have been used thus far to decontaminate reactors.[3]

2.4.3 Removal of Uranium and Uranium Oxides

Uranium or uranium oxide may enter the coolant during failure of a fuel element. These materials can be dissolved readily in acids with mild oxidizing agents to convert uranium to uranyl ion. In stainless steel reactors, nitric acid may be used both as the acid and the oxidizing agent. The most satsifactory solvent is a mixture of oxalic acid and hydrogen peroxide. The pH is critical for maintaining high efficiency and low corrosion, and buffering is required. In addition, other components such as complexing agents, inhibitors and surfactants usually are added.

2.4.4 Removal of Adsorbed Activities

Experience shows that removal of activated corrosion products from deposits by leaching or partial dissolution of the surface films does not give a satisfactorily low decontamination factor unless the entire film is removed. Presumably, radionuclides diffuse into the film, or corrosion product layers are formed and deposited over the radionuclides in such a manner that radioactive material is dispersed throughout the film. Similiarly, fission products released from a failed fuel element tend to become fixed on or in the surface film and may remain to cause radiation problems even after losse debris has been removed.

One theory as to how the radioactivity is deposited in the surface films assumes that a corrosion film forms in situ on the metal surface, that radioactive ions diffuse into the pores of this deposit, and that they form inclusions in the resulting film after the associated water has evaporated from the portes.

The films formed on stainless steel in high temperature water are refractory. Preliminary conditioning with a strongly alkaline permanganate solution at elevated temperature is required to remove these films. The decontaminating agents are usually complex solutions. In addition to the acid or alkali, the solutions may contain inhibitors to reduce nonuniform attack or pitting, surfactants to increase wetting of the surfaces, chelants to prevent reprecipitation, and other additives.

2.4.5 Morphology of Films on Stainless Steel Surfaces

Films on stainless steel surfaces tend to change with time and become more difficult to remove as they are exposed for longer times to the high temperature coolant.

Warzee, et al,[5] subjected a film on stainless steel, produced by exposing the steel to 500°C steam, to to electron probe analysis and found that the composition of the film changed with the depth of the film. At the metal surface the film consisted of approximately 75% iron, 18% chromium, and 8% nickel whereas at 1.4 µm from the metal surface the iron content decreased to about 57% and the chromium and nickel contents increased to about 27% and 17% respectively.

The amounts of iron, chromium and nickel found in the high temperature coolant water are not proportional to the amounts of these elements present in the alloys of the primary system but depend on some of the reactor operating variables, especially the oxygen concentration of the coolant, the pH, and the temperature. Thus, some elements may gradually leach from the film and the film composition may slowly change with time.[7]

This change in film characteristics has been encountered by several workers in decontamination studies.

Reagents that effectively removed films from test coupons exposed for two to three months in a reactor were ineffective in defilming specimens exposed one year or longer. Therefore, it is necessary in any experimental program to use as test specimens, those coupons that have been exposed under reactor operating conditions for long periods of time (Ayres, P. 447).[3]

2.4.6 Theoretical Approach to the Removal of Surface Deposits Encountered in nuclear Plants

A reasonable approach for understanding the dissolution of products on surfaces of the type of interest to decontamination is to consider the potential vs pH, or Pourbaix, diagrams of these materials. These diagrams show regimes of stability of soluble metal ions, insoluble deposits, and metal in its nonreacted form.

The Pourbaix diagram for iron shows that in acidic regions, ferrous ions are stable and in caustic regions, the dihypoferrite ion ($HFeO_2^-$) is stable. At midrange pH values, iron oxides are stable. At low oxidizing conditions, magnetite (Fe_3O_4) is stable; at higher oxdizing conditions, hematite (Fe_2O_3) is stable.

The removal of these deposits from metal surfaces involves one of three approaches. First, the solution can be acidified to stabilize ferrous ions. Here the oxide dissolves according to the equation:

$$Fe_3O_4 + 8\,H^+ + 2\,e^- = 3\,Fe^{2+} + 4\,H_2O.$$

Secondly, caustic solution may be used to dissolve iron oxide to produce the dihypoferrite ion according to the equation:

$$Fe_3O_4 + 2\ H_2O + 2\ e^- + 3\ HFeO_2^- + H^+$$

A third alternative for removing the oxide involves maintaining the pH and the use of reducing agents such as hydrazine.

Deposits more complex than the above may contain oxides of chromium and/or nickel.

The formation of surface deposits also may be understood from Pourbaix diagrams. Deposits can form in the presence of increased oxidizing conditions. For iron, initially at deoxygenated conditions and at pH 6, increased oxidizing conditions, e.g., the presence of oxygen as in a BWR, will shift the potential into the regime where the oxide is stable. This accounts for the fact that deposits are more easily stabilized under BWR conditions that PWR conditions. Furthermore, deposits will form as the pH shifts from acid conditions toward higher values. Conversely, as solutions with high hydroxide concentrations shift toward lower pH, ferric hydroxide may precipitate.

In decontamination processes, oxidizing agents, such as hydrogen peroxide, potassium permanganate, or dissolved chlorine gas, are employed to break up or loosen oxide deposits. The relatively high potentials involved in these media assure a substantial increase in oxidizing capacity. The media probably operate in the so-called "trans-passive" regime, and reduce the intergrity of the oxide film. The oxideized material so affected is treatable by either acidification, basification, or reduction to effect defilming or dissolution.[8]

2.4.7 Chemical Decontamination Systems

Several options are available for decontamination of components removed from a nuclear reactor:

1. chemical defilming with various solutions
2. electrochemical defilming in 1-10% sulfuric acid
3. abrasive blasting
4. ultrasonic agitation
5. use of strippable films

Stainless steel fuel rods have been cleaned by electropolishing techniques in which a rod is made anodic, and a current of 1 amp/in^2 is applied. This technique may result in severe local attack on the alloy being treated. When reactor components are cleaned outside the reactor, stubborn deposits may be loosened mechanically by brushing, scrubbing or steaming them. Whether solubilized or simply dislodged, deposits are removed and decontamination is achieved. In piping systems, on the other hand, dislodged deposits will accumulate dowstream in "dead legs," and effective decontamination cannot be achieved by these mechanical methods.

Early in the development of decontaminating agents for reactor systems. persons recognized that highly noble corrosion films generally required multi-step treatments for removal of radioactive material. Alkaline permanganate treatment followed by treatment with an acidic solution were developed as essential steps for removal of these films.

The use of alkaline permanganate (AP) solution as a preconditioner for the film was generally accepted as early as 1957[8] and 1958.[9] A typical formulation contained 180 g/l NaOH, 30 g/l $KMnO_4$, and 790 g/l water, and was applied at 80-105°C. The solution appears to be an essential step in PWR scale removal, although only ^{51}Cr is solubilized.

The development of solutions for the acid step produced a greater variety of potentially useful mixtures. The following are several of the most common products evaluated in this step to effect removal ofthe radioactive corrosion products:

1. Ammonium citrate (di-basic) (AC)
2. Acid sulfate (SUL)
3. Oxalic acid (OX)
4. Ammoniated citric - Oxalic acids (Citrox)

The AP-OX system consists of an AP treatment followed by 100 g/l oxalic acid, 2 g/l ferric sulfate, 1.8 g/l nitrilotriethanol, and 1 g/l of proprietary inhibitor. For the reasons mentioned previously, the AP-OX procedure is primarily useful for once-through decontamination and for decontamination of reactor components dismantled from the primary systems.

Of the processes mentioned, AC and Citrox solutions have been the most useful for stainless steel surfaces exposed in pressurized water reactors. Experience in both loop facilities and operating plants has confirmed the utility of these solutions.[10,11,12] Extensive corrosion tests of materials used to construct reactor coolant systems gave acceptable results with the AP-Citrox process.[14]

In his review of the procedures discussed for PWR decontaminations, Ayres[3] (P. 570) mentions: "...In the ideal procedure, the temperature would be reduced slightly, say from 250°C to 15°C, the chemicals would be injected, and after sufficient recirculation time, the decontaminant-coolant would be circulated through a bypass deionizer to remove the chemicals... Before such a procedure becomes a reality, some reagent must be developed that will be effective at very low concentration (in the range of 0.01 to 0.1%) and will not be corrosive to any of the materials in the system at the temperatures and times considered."

2.4.8 Low Temperature Water Cooled Reactors

The first water cooled reactors were not power plants, but were swimming pool type research reactors as well as the large plutonium producing reactors at Hanford, which were built during and after World War II. Swimming pool type reactors contain mainly aluminum and stainless steel as structural materials. The films and deposits consist primarily of alumina. Because of the short-lived nature of the activation products of aluminum, no radiation problems arise from such deposits. However, if there were leaking fuel elements in the reactor during operation or if the construction materials contained uranium as impurities, the deposits can be quite radioactive.

Cleaning this type of reactor was first tried at the Chalk River Laboratory in Canada.[14] Experiments were carried out with various types of reagents: H_3PO_4, CO_2, HNO_3, H_2O_2-HNO_3, H_2O_2-NH_4OH, CrO_3-H_3PO_4, CrO_3-HNO_3 and $Fe_2(SO_4)_3$-H_2SO_4. The most suitable reagent was found to be 0.1M CrO_3.

Work at the Savannah River Plant has shown that freshly discharged aluminum-clad fuel elements can be effectively decontaminated with CrO_3-H_3PO_4.[15] Also at this plant, early efforts to remove corrosion films from stainless steel piping systems led to the development of a procedure that used oxalic acid inhibited with $Fe_2(SO_4)_3$. Subsequently, use of a proprietary mixture containing phosphoric acid became the accepted method. Most of this work was done on components outside of the reactor.[16]

2.4.9 Heat Exchangers at Savannah River Plant

The process heat exchangers of the Savannah River plant were decontaminated in stainless steel tanks. The pieces were scrubbed by hand. Where low flow regions had served as traps for suspended alumina in the coolant, the decontamination procedure used was as follows:

1. The heat exchanger was connected to the decontamination system and filled nearly full with water.
2. A solution of ferric sulfate corrosion inhibitor was added to give a final concentration of 2.6 g/l Fe^{3+} during high temperature flushing of the system.
3. Steam was added to heat the solution to 70°C.
4. A solution of oxalic acid was added to give a final concentration of 2%.
5. Temperature and recirculation were maintained until analyses of the recirculating liquid indicated no further radioactivity increase.
6. The flow of steam was stopped and the oxalic acid solution was drained to the waste system.
7. The decontamination system was filled with water which was circulated for 1/2 hour.
8. 50% KOH was added to give a pH of 6.0-6.5.
9. The solution was drained to the waste system.
10. The decontaminated system was filled with water which was recirculated for 4 hours and then drained to the waste system.
11. The above treatments were repeated as needed to improve decontamination or to remove the oxalic acid.

The oxalic acid procedure gave decontamination factors of 1 to 3 at the inlet end of the tube sheet. Decontamination factors of up to 60 have been measured exrernally to the shell of the heat exchangers. By this procedure 71% of the ^{95}Zr-Nb, 17% of the ^{103}Ru-^{106}Ru and 5% of the ^{60}Co were removed.

Increasing the temperature of the oxalic acid to 90° in an attempt to improve decontamination of one heat exchanger led to formation of a yellow precipitate within the heat exchanger. Apparently the $Fe_2(SO_4)_3$ inhibitor failed to protect the stainless steel at the higher temperature, and corrosion produced Fe^{++} ions which reacted with the oxalic acid to form insoluble ferrous oxalate. Or, at the higher temeprature, oxalic acid reduced the ferric ions to ferrous ions which reacted with the oxalic acid to form insoluble ferrous oxalate.

2.4.10 Plutonium Production Reactors at Hanford

The large reactors at Hanford ahve a single-pass coolant system in which water passes through the reactor core and then is discharged. Water supplied to the reactor core contained 0.03 ppm iron as a result of having passed through carbon steel (Ayres[3], P. 439ff; Carlson[16]).

The in-reactor tubes and many of the individual tube connections are aluminum or ZIRCALOY[a]-2. Effluent piping near the reactor consists of 304 stainless steel, while the remainder consists of carbon steel. Small amounts of copper and brass in the instruments and sampling lines also contact the water.

Treated river water supplied as the coolant to the reactors contained up to 90 ppm of dissolved solids. From this coolant the following materials remained in the reactor:

1. Particulate materials which settled in low flow regions.
2. Colloidal materials which coagulated and sorbed onto the in-reactor surfaces.
3. Dissolved constituents that chemically reacted with in-reactor surfaces or with other materials added to the water to form solids which sorbed onto the surfaces.

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[a] Trademark of the Westinghouse Electric Co.

The results of these processes was formation of an in-reactor film situated in the boundary between the coolant and a structural surface. At any one time, this nonstatic film may under go a net growth or a net reduction. At all times the film is receiving new material and is releasing old material to the cooling stream. The films are heterogeneous, consisting principally of iron, aluminum and chromic oxide corrosion products from the reactor piping and calcium salt deposits from the coolant.

Fine particulate material suspended in the rapidly flowing coolant settles in the quiet regions of the cooling system. Settled material may include bits of film produced by coagulation or adsorption of colloidal or dissolved materials which were subsequently released from the film surface.

At Hanford, treatments with mixtures of oxalic and sulfuric acids and a proprietary sulfamic acid mixture were effective at temperatures as low as 45°C for decontaminating aluminum and stainless steel surfaces. A proprietary sodium bisulfate mixture was effective at 66-70°C. The procedure used to decontaminate the low temperature water cooled reactors at Hanford is as follows (Carlson[16], P. 460):

1. The chemical solution is prepared and heated by steam injection to 90°C in a makeup tank which is connected to a large secondary drain pipe at the discharge face of the reactor.

2. Initial flow adjustment is made on the charging face of the reactor to provide adequate shutdown cooling without excessive water flow into the working area at the discharge face.

3. An initial, predecontamination radiation survey is made of the reactor discharge face.

4. The effluent piping is prepared by loosening or replacing the caps on the fuel discharge nozzles.

5. Final valving adjustments are made to provide a 1.5 to 2.0 gallons per minute shutdown cooling flow through each of the channels.

6. The chemical solution is pumped through the prepared piping for 10 minutes at a flow of 3-4 gallons per minute per nozzle. This amount assures good distribution of the chemical solution with effective temperature and flow conditions.

7. Piping is returned to normal, after completion of the decontamination flush, by replacing or retiqhtening the nozzle caps, and standard shutdown cooling water flow is reestablished.

Up to 34 effluent piping decontaminations were performed during a two year period. Results indicated a 40-86% reduction of the discharge area radiation levels.

The first material used to decontaminate the Hanford reactors was a proprietary mixture of sulfamic acid, sodium chloride, ammonium fluoride, a corrosion inhibitor, and a wetting agent. Concenrn that this corrosive mixture might cause stress corrosion cracking in the stainless steel portions of the effluent piping led to subsequent use of a solvent system based on TURCO 4306-C, a mixture that contained NH_2SO_3H, $NaHSO_4$, and oxalic acid. Although successfully used for decontamination, TURCO 4306-C produced obnoxious fumes. WYANDOTTE-5061, a mixture that contained sodium bisulfite, was a less effective treatment but did not produce objectionable fumes.

The time required to completely decontaminate effluent piping varied from 4-20 hours with an average of 10-11 hours.

Waste at Hanford was disposed of by passing the solution into a large storage basin in the rear of the reactors, or alternately into the normal reactor effluent coolant lines. Waste solutions then were diluted with clean process water prior to their discharge into the river.

Decontamination methods used at Hanford for the one-through cooling systems of LTWCR's and the techniques developed at Chalk River and the Savannah River Plant are not applicable to the Dresden-1 decontamination project since the films encountered differ chemically. The mehtods employed at Hanford tolerate "necessary" corrosion and were ineffective for dissolving deposits encountered at Dresden-1.

Since these decontamination efforts constituted the first on record, and demonstrate the philosophy followed, it was thought worthwhile to review them here.

2.4.11 Decontamination of Pressurized Water Reactors

The first pressurized water reactors and boiling water reactors for commercial nuclear power generation were built about 1960. While our interest in this project lies with the decontamination of a boiling water reactor, at the time of this writing no complete decontamination of an entire BWR plant had been carried out. Several pressurized water reactors, on the other hand, were decontaminated more or less successfully and the operations re ported in the literature.

In the U.S., modern BWR's and PWR's are constructed to a great extent of stainless steels. Since the sources of corrosion products in the two types of reactors are similar, it could be expected that the deposits also would be similar. Problems encountered and solutions attempted for PWR's may thus appear exemplary for planning the approaches to decontaminate BWR's. Several reactor decontaminations are reported in the literature. However, a large body of experience in decontaminating PWR's, accumulated by the United States Navy on nuclear power plants over the past two decades, is inaccessible at this time.

Pressurized water reactors have steam generators with large heat transfer surfaces in the primary system. The latter is operated with an essentially constant inventory of coolant. The steam generators have, in the past, required substantial maintenance and repairs. The radiation fields in the areas where work had to be carried out were large enough so that chemical decontaminations were indicated.

The highly inert, tenaciously adhering films encountered in PWR's are thin enough to cause no real deterioration of the heat transfer capabilities of heat exchanger surfaces. In fact, the films retard corrosion of the substrate metals. The prime objection to the presence of these films in the reactor stems from the incorporation of radioactive materials and the associated buildup of radiation fields.

Mechanical methods or simple solution techniques had negligible effect on removing films from the inner surfaces of PWR primary systems. The radioisotopes were absorbed on or diffused into the tenaciously adhering oxide films so strongly that contamination could not be removed without removing all of the protective corrosion film.

The films encountered in PWR's consist essentially of oxides of iron, chromium and nickel, and vary in composition from one plant to another and from one point to another in the same plant. The chemical composition and removability of these films change with age.

Table 2.4.11 compares the composition of the corrosion film, the deposit, the circulating suspended solids in the coolant and the base metal oxides fro two typical PWR's.

TABLE 2.4.11

Composition of Corrosion Products in Two PWR's.[22]

YANKEE REACTOR (After 16 mo. of operation)	Fe (%)	Ni (%)	Cr (%)	Mn (%)	Co (%)
Corrosion Film	24	11	36	-	0.17
Deposit	59	8	0.6	0.3	0.2
Circulating Crud	58	8	2	0.4	0.2
Base Metal Oxides 304 Stainless Steel	48	6	12	0.7	0.04
SAXTON REACTOR (After 6.4 mo. of operation)					
Corrosion Film	42	14	14	-	0.17
Deposit	40	8	11	10	0.09
Circulating Crud	40	7	20	1.8	0.3
Base Metal Oxides 304 Stainless Steel	48	6.4	12	0.7	0.04

2.4.12 Decontamination of Carbon Steel Reactor Systems

The corrosion product films on carbon steel in PWR's, principally Fe_3O_4, dissolve readily in acidic solutions of pH 1-3.5.[18]

Inhibited sodium bisulfate, 9% w/w $NaHSO_4$ has been used for decontamination at 80°C but was quite corrosive and not entirely satisfactory. The presence of oxygen accelerates corrosive attack, especially at galvanic junctions, for almost all decontaminants, and especially for HSO_4^-. At high reactor temperatures, above 85°C, an accelarated nonuniform attack occurs.

Oxalic acid, 9% w/w, if satisfactorily inhibited, is a suitable defilming agent for carbon steel. If the solution is in contact with steel for excessive periods, however, iron oxide precipitates. The film sloughs and only partially dissolves with this treatment. Accumulation of radioactive solids in traps also can occur and thus reduce the benefits of decontamination.

Inhibited sulfamic acid, 9% w/w NH_2SO_3H, at 80°C gave satisfactory decontamination factors and low corrosion rates, but film removal was slow.

Inhibited phosphoric acid, 9% w/w H_3PO_4, at 60°C has been used to decontaminate carbon steel systems at contact times of 20 minutes, but unless the phosphoric acid is suitably inhibited, galvanic attack may be serious. Redeposition of a phosphate film can result in low decontamination factors if contact times are excessive.

Phosphoric acid effectively decontaminated carbon steel systems when used in a single-pass procedure. If recirculated, it must remain in the reactor long enough to remove the more adherent compounds containing the radioactive isotopes (Ce, Ru, Zr) but not long enough to allow them to redeposit.

Decontamination of an in-reactor carbon steel loop (KER-1) was carried out during 1960 and 1961 at 60°C with a proprietary inhibited phosphoric acid solution to give DF values of 1.2-8.

The activity levels of the loop were too low to be measured exactly. After about 1 hour, some redeposition of activity occurred.

2.4.13 Decontaminaiton of Stainless Steel Reactor Systems

Although inhibited oxalic acid is effective and relatively noncorrosive for 300 series stainless steels, in attacks 400 series stainless steels and carbon steels to form a precipitate that deposits radionuclides onto the piping surfaces. Oxalic acid also produces copious sloughing of the film, a process which introduces solids into the decontamination solutions. In Citrox formulations, citrate ions are added to complex iron ions and prohibit precipitation of ferrous oxalate. A typical complex AP-Citrox procedure consists of the following steps:

1. Alkaline permanganate (100 g/l NaOH, 30 g/l $KMnO_4$, 870 g/l H_2O) at 105°C is circulated for 2 hrs through the system to be decontaminated. This is followed by a water rinse until MnO_4^- is removed and the pH $\leq$ 10.

2. Dilute Citrox (0.02M oxalic acid, 0.03M citric acid, 0.02M inhibitor such as 0.01M Fe^{3+} and 0.01M diethylthiourea, and ammonia to adjust pH to 3.0-3.1) is circulated for 2 hrs at ambient temperature.

3. Citrox (0.2M oxalic acid, 0.3, citric acid, 0.02M inhibitor such as 0.01M Fe^{3+} and 0.01M diethylthiourea, and ammonia to adjust pH to 3.0-3.1) is circulated at 60° for 2 hrs.

4. A water rinse is performed until the conductivity is <50 μmhos.

The dilute Citrox in the above procedure serves as a rinse to neutralize the last traces of residual NaOH and to dissolve MNO_2.

2.4.14 Evaluation of Procedures for Decontamination of Stainless Steel Systems

The types of testing that have been carried out to evolve decontamination solvents and procedures for stainless steel are illustrated by the following discussion.[19]

Three sections of stainless steel tubing from a reactor primary were treated with AP solution at 105°C for 1 hr.

Each section was placed in a 50 ml graduated cylinder which was then filled with an acidic solution of amonium citrate (ACE), sulfamic acid (SUL), or Citrox. The ratio of the surface area of the metal to the volume of the decontaminant was about 3.0 cm^2/ml, comparable to that expected during an actual reactor decontamination. The specimens were maintained at the prescribed temperature for 1 hr. (2.2 hr. for ACE), then were removed, monitored for radioactivity, and slit for examination.

All solutions removed 95 to 98% of the activity. The film was removed effectively by AP-ACE and AP-Citrox solutions after 1 hr. (2.2 hr. for the ACE process), but not by the AP-SUL solution. The film was dissolved only by the Citrox solution. In the ACE and sulfamic acid reagents, the undissolved films formed a sludge which remained in the bottom of the graduated cylinders.

Laboratory tests which were developed in order to identify decontamination solutions similar in effectiveness to those described above resulted in unsatisfactory reagents. The length of time the primary reactor specimen was exposed to the reactor environment was found to significantly affect the ease with which films could be removed from such stainless steel surfaces. A process which effectively removed films formed during a short exposure sometimes did not remove films formed during lengthy exposures.

This effect of exposure time on the removability of films was not evaluated prior to tests made a Hanford in 1062 (Ayres[3], P. 485 ff). At that time the AP-AC and AP-ACE procedures were accepted for stainless steel decontaminations. Laboratory results for films deposited during short periods of exposure in the reactors, showed decontamination factors were uniformly high, usually greater than 100 and sometimes as high as 2000. Decontamination factors of specimens from reactors which had been in operation for 3 years varied from 1.5 to 2.0. AP-)X was the only solution which removed the film with a decontamination factor in excess of 150.

These results show the danger of extrapolation from data obtained in experiments where operating conditions do not duplicate conditions found in the reactor.

2.4.15 Decontamination of Mixed Reactor Systems

There are two different types of PWR's: the pressure vessel and the pressure tube. In a pressure tube reactor such as the N-Reactor, the in-reactor tubes must withstand the primary system pressure (approximately 1600 psi) have a low neutron cross-section, and resist corrosion. The tubes are made of ZIRCALOY-2, the only material which currently meets these requirements. Other construction materials found in pressure tube reactor primaries include both carbon steel and stainless steel. Primary systems of pressure vessel type PWR's are made entirely of stainless steel, with only the removable fuel clad in ZIRCALOY-2.

A single, optimum procedure has not been found for decontamination of both stainless and carbon steels. Treatment with a single acidic solution which is effective and safe for decontamination of carbon steel, gives a low decontamination factor for stainless steels.

The most effective reagents to decontaminate carbon steels, phosphoric acid and sulfamic acid, are not very effective for treating stainless steel, even when combined with an AP pretreament. Furthermore, unless satisfactorily inhibited, these reagents can cause excessive galvanic corrosion at the junctions between carbon and stainless steels.

The AP-Citrox procedure is the best compromise when both types of steels require treatment. Since oxalic acid combines with iron to form a precipitate after extended contact times, these solutions should be removed as soon as possible after the specified treatment times.

The N-Reactor has six primary loops. Each loop is comprised of two heat exchangers coupled in parallel, the secondary sides of which drive the turbine. Carbon steel piping is used for the ex-reactor portion of the primary system. The in-reactor tubes and fuel cladding are ZIRCALOY-2 and the heat exchanger tubing is stainless steel and INCONEL[a] 600. In total, the system contains 40% INCONEL surfaces, 30% stainless steels (300 series), 15% carbon steel and 15% ZIRCALOY-2, as well as valve trim which has cobalt alloy surfaces, copper alloys, and chromium steels. Stainless steel and carbon steel parts are decontaminated[13] separately to minimize corrosion and redeposition.

The steam generators in the N-Reactor have stainless steel clad carbon steel tube sheets. Each steam generator contains 1916 tubes with approximately 16,000 ft^2 of heat transfer area. The tubing in the original 10

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[a] Trademark of Huntington Alloys, Inc.

of the 12 steam generators was 304 stainless steel. The two units added later contained tubes made from INCONEL 600.

The N-Reactor start-up occurred in 1963. In early 1965, eddy current, and fluorescent dye penetration inspections which were made to determine the condition of the steam generators indicated retubing of the stainless steel was needed. However, high radiation fields (290 mr/hr) on the secondary side adjacent to the tubing restricted workers to conducting inspections and repair for only 3-9 hours each per month. Before the extensive retubing program was defined, an attempt was made to decontaminate the cell #2 steam generators using an AP-SUL type treatment in order to reduce the radiation levels. The overall radiation levels were reduced by one-half, which was not enough to make the process attractive.

Decontamination was carried out with 94 g/l $NaOH$ and 13 g/l $KMnO_4$. At the end of a two hour recirculation period the concentration had decreased to 32 g/l $NaOH$ and 5 g/l $KMnO_4$ because of leakage. Dilution did not occur during the subsequent dilute sulfamic acid treatment after the leaks which caused dilution of the AP were repaired.

Concentrated inhibited sulfamic acid (72.5 g/l) was injected into the steam generators after a water rinse. The first analysis after injection showed a sulfamic acid concentration of 43.7 g/l, again indicating considerable dilution had occurred. After the acid solution was recirculated for 3 hours at 66°C the concentration decreased to about 30 g/l.

The acid was removed from the system by repeated 75°C water rinses that contained hydrazine.

The system was drained in a helium atmosphere, and water which contained ammonia and 30 ppm hydrazine at pH 10.2 was added and heated to 93°C to passivate the system. Decontamination factors ranged from 1.8 to 10.

The AP solution took up 27 μCi/l, the dilute acid rinse 31.6 μCi/l, and the strong acid step 89.1 μCi/l. Based on a volume of 3,700 gallons used per step, decontamination removed a total activity of 2.1 curies.

Corrosion of 12 mg/cm^2 occurred during this operation, possibly because an insufficiently inhibited solution was used during the dilute acid treatment. When full strength and dilute acid solutions are used the latter should not be prepared by simply diluting the former, since the concentration of inhibitor may have to be full strength.

Metal loss measurements of coupons showed that carbon steel and 400 series stainless steels were highly corroded and pitted, while the austenitic stainless steels were in good condition. Iron oxide sludge was found in large quantities in the bottoms of the heat exchanger tubes after the decontamination was completed. Whether the acid lossened but did not dissolve iron oxide from the walls, or whether the constant dilution caused reprecipitation of iron is not certain. This decontamination system had performed well in the laboratory.

A different acid was used to decontaminate cell #3 of the N-Reactor in September, 1967.

A third attempt to decontaminate the steam generator units in cell #4 was made with a second dilute acid rinse inserted into the process to ensure complete removal of the alkaline permanganate. This modified process proved highly satisfactory, and was performed as follows:

1. TURCO 4521 was applied at 8 oz/gal at 170°F for 1 hr.

2. A thorough rinse was performed until the rinse water had a pH of >5.

3. A strong alkaline permanganate solution was applied at 210-220°F for about 4 hr. (The strength of the solution can vary, but 10% NaOH and 4% $KMnO_4$ were effective).

4. A thorough rinse was performed until the rinse water had a pH of >9 and had no more than a slightly pink color.

5. A 1 oz/gal solution of TURCO 4521 at 170°F was used as a final brief rinse.

6. The first acid treatment step (#1) was repeated.

7. Rinsing was performed until the pH was >6.

Results indicated that more dilute solutions actually may have been used and that the contact time of the acid steps should have been reduced to a few minutes. Redeposition seemed to occur almost immediately. Specific activity of the acid peaked after the first few minutes and then declined. Laboratory data indicated that temperatures are perhaps the most critical parameters and should not be reduced appreciably.

The 300 series stainless steels showed about 0.01-2.02 mils corrosion, as calculated from weight losses. No visible or localized attack was noted. Carbon steel had weight losses indicating corrosion of approximately 2-3 mils. Small pits usually were found, and knife-edge undercutting several mils deep was found at junctions with stainless steel, ZIRACLOY-2 or nickel alloys. The 400 series stainless steel was about halfway between carbon steel and the 300 series stainless steel in corrosion effects. Alloys high in nickel content, such as INCONEL 600, reacted similarly to the 300 series stainless steels.

A heavy yellow deposit, probably iron oxalate, formed on all surfaces. The deposit was heaviest on carbon steel surfaces, and contained little radioactivity after decontamination was completed.

In October, 1967, the N-Reactor as a whole was decontaminated by a single-pass application of inhibited phosphoric acid. The treatment involved placing the reactor on single-pass cooling and injecting the concentrated acid into the coolant upstream of the front risers. The dilute acid solution then was passed through the reactor piping and out of the effluent piping to the chemical waste storage tank.

On July 22, 1968, the N-Reactor carbon steel piping was again decontaminated by essentially the same process as used in 1967, except that the application parameters (time, temperature, and concentration) varied from those used previously. The application time was extended to 22 minutes, the outlet solution temperature was increased to 185°F, and the acid concentration was reduced to about 8% w/w. Decontamination factors ranged up to 12 but usually were about 2 to 5.

Pronounced deposition of activity occurred on the clean spacer placed in the rear of the process tubes during the decontamination. More activity was deposited on the clean spacers by the decontamination than was present on the upstream spacers before decontamination was started. Localized pitting was observed on carbon steel welded to stainless steel. Of greatest significance, however, is that this was the first decontamination of a large primary power reactor in the United States, thus illustrating that such decontaminations can be performed safely and effectively.

2.4.16 Decontamination of the Plutonium Recycle Test Reactor (Ayres[3], P. 505ff)

The Plutonium Recycle Test Reactor (PRTR) is a vertical pressure tube type reactor which is moderated and cooled by D_2O and has a thermal power rating of 70MW. The moderator tank is constructed of welded aluminum. Passing vertically through this calandria are 85 fuel channels, 18 shim-rod control channels and 13 flux monitor channels. The primary coolant D_2O is maintained at 1050 psi, 250-280°C and pH 10 in a system with a volume of 3,000 gallons.

The coolant is separated from the low temperature unpressurized moderator by a double-walled fuel channel. Each pressure tube is connected to ring headers by individual jumpers at the top and bottom faces of the reactor. The primary coolant is pressurized with helium. The pressure tubes in the core are of ZIRCALOY-2. The balance of the primary system is largely 300 series stainless steel with small areas of 400 series stainless steel, STELLITE, and INCONEL 600.

On August 21, 1962, an experimental MgO-PuO_2 fuel rod ruptured, releasing 1.8 g of Pu into the reactor coolant.[20,21]

The subsequent decontamination test represents the first application of chemical decontamination to reduce radiation levels in an entire reactor primary circuit.

The PRTR was first rinsed extensively with water. On October 10, 1962, chemical decontamination was initiated lasting until September 11 and consisting of the following steps:

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[a] Trademark of Stellite Division, Cabot Corp.

Step	Solvent System	Temp. °C	Time In Reactor hrs.
1	Operation OPP[a]	80	1
2	Demineralized water rinse	-	-
3	OPG[b]	80	1
4	Demineralized water	-	-
5	AP	105	1
6	Demineralized water	-	-
7	Dilute Oxalic Acid	-	-
8	OX	85	2
9	Demineralized water	-	-
10	AP	105	1
11	Demineralized water	-	-
12	Dilute Oxalic Acid	-	-
13	Demineralized water	-	-
14	OX	85	2
15	Demineralized water	-	-
16	AP	105	1
17	Demineralized water	-	-
18	ACE	85	2
19	Demineralized water	-	-

[a] OPP is a solvent consisting of 32 g/l sodium oxalate, 2.3 g/l oxalic acid, 50 g/l of 30% H_2O_2, 5 g/l peracetic acid, and 1 g/l Oxine pH 4.5.

[b] OPG is a solvent consisting of 32 g/l sodium oxalate, 2.3 g/l oxalic acid, 50 g/l of 30% H_2O_2, 2.5 g/l gluconic acid, and 10 g/l sodium gluconate at pH 4.5.

The oxalic-peroxide reagents were used primarily to dissolve uranium and uranium oxide residues from the ruptured fuel element.

The AP-OX procedure, although very effective in removing films, produced a green oxalate film on the bare metal surfaces. Flushing the surfaces with water, even at high velocities, did not remove this oxalate which was distributed widely on the metal surfaces and incorporated considerable amounts of redeposited radioactivity. Steps 16 and 18 were used to redissolve this iron oxalate.

The overall decontamination factors of the procedure varied from 1.8 to 56.5, depending on when and where the measurement was taken. The higher decontamination factors were obtained when the radioactivity measured prior to decontamination was compared to the values obtained after about one month of subsequent operation of the reactor.

Subsequent operation further removed exposed and spallable radioactive materials which had been loosened by the decontamination.

A corrosion evaluation of metal specimens from the PRTR decontamination showed ZIRCOLOY-2 underwent insignificant weight loss, carbon steels lost about 100 mg/cm^2, INCONEL about 8 mg/cm^2, 304 stainless steel <4 mg/cm^2, and STELLITE #6 approximately 2 mg/cm^2.

The STELLITE samples underwent a general dentritic pitting attack. Pitting was also observed on the PRTR tube-insert snap rings. This attack was attributed primarily to the proprietary oxalic acid solutions OPP and OPG.

Measurement of PRTR radiation levels showed the radioactivity decreased in the freshly decontaminated system and reached equilibrium after about 10 to 20 equivalent fullpower days of operation, and then decreased gradually through about 300 equivalent fullpower days. A five-fold increase occurred in the next 100 fullpower days, followed in the subsequent 10 months by a 10-fold increase in radioactivity.

At certain times during this period, leaking fuel elements in high radiation levels in the vicinity of the primary system were identified. After these elements were removed, the primary system radiation fields rapidly returned to their general trends. A rapid increase in radiation fields toward the end of this time was correlated with increased wear of STELLITE surfaces in the pump seals. Wear products from these seals contained cobalt, and entered the coolant stream to undergo activation in the reactor core.

In early 1965, the reactor again was decontaminated. The procedure for removing activation, corrosion and wear products from the PRTR primary system as specified on October 4, 1965, consisted of:

1. Fuel elements were removed and the primary system heavy water was stored.
2. The system was modified for decontamination.
3. Chemical decontamination was performed with the AP Citrox procedure.
4. Chemicals were drained and rinsed from the system.

5. Film conditioning to reduce radiation buildup after startup was performed.

6. The system was restored to primary operating status by draining all H_2O, rinsing the system with low grade D_2O, and filling it with high grade D_2O.

7. The fuel elements were recharged and returned to operation.

The AP step involved treatment with a solution of 5.8% NaOH and 3.4% $KMnO_4$, with a subsequent water rinse. After use, the AP solution contained 5.8 μCi/l of beta activity, 0.043 μCi/l of ^{54}Mn, 1.8 μCi/l of ^{56}Zn, 18.4 μCi/l of ^{137}Cs and 0.62 μCi/l of ^{124}Sb.

The Citrox procedure involved treatment with a solution of 2.5% oxalic acid, 5% ammonium citrate, 0.2% ferric sulfate and 0.1% diphenylthiourea, and was performed initially at 60°C. The temperature was then maintained for 1 hour at 70°C, and after 2 hours of circulation increased to 77°C.

Decontamination operations, step 3, were begun December 28, 1965. After the decontamination, light water was recirculated through the primary system and the reactor ion exchange clean up system for two days to raise the specific resistance to 10^5 ohm/cm. The recirculated water was heated to 180°C with pump heat in order to form a protective oxide film (step 5).

After use, the Citrox solution contained up to 1.0 mCi/l of ^{60}Co.

About 12.5 Ci of beta activity and 18 Ci of gamma activity were removed by the Citrox solution.

Corrosion data indicated weight losses of 0.03 mg/cm^2 for 304 stainless steel, up to 1.3 mg/cm^2 for 416 stainless steel, up to 33 mg/cm^2 for 440 carbon steel, up to 0.28 mg/cm^2 for 302 stainless steel, 30.4 mg/cm^2 for A245 carbon steel and 6 mg/cm^2 for INCONEL 600. Corrosion occurred primarily during the Citrox treatment, and increased markedly when the pump speeds were increased and when the temperature of the solution increased. INCONEL 600 corroded at a high rate, primarily as a result of a small amount of sulfate ion in the Citrox reagent.

The 1965 PRTR primary system decontamination was more successful than previously reported reactor decontaminations. The average DF was 24, representing an increase in efficiency by a factor of three over the 1962 decontamination of the same system.

2.4.17 Decontamination of the Shippingport PWR

The Shippingport PWR is a pressure vessel type of reactor. The primary system is 304 stainless steel, and the fuel elements are clad in ZIRCALOY-2. The reactor contains a pressurizer and four coolant loops, each of which has a main cooling pump and a steam generator. The primary system, exclusive of the pressurizer, has a volume of 17,100 gallons.

The reactor operated at over 50% efficiency from December 1957 to February 1964, and had accumulated 28,000 equivalent fullpower hours. The radiation during this time increased to an average level of 80 mr/hr. In several areas, radiation fields of up to 626 mr/hr were measured. High fields were encountered near the steam generator inlets and the "hot legs" at interconnections between the boiler and the reactor chambers.

The radioactivity, due almost entirely to activation of corrosion products, consisted primarily of ^{60}Co with minor amounts of ^{58}Co, ^{59}Fe, ^{54}Mn, ^{51}Cr and ^{181}Hf. A decontamination factor of 6-7 was needed to permit modification of the system to proceed.

The Shippingport PWR was decontaminated with a modified AP-AC process[11] in which the reagents were diluted from 9-10% to 1-2% and were used at higher temperatures (120°C vs 80-105°C) and longer treatment times (24 hr cycles) compared to the procedure used to treat components in a decontamination vat. Spent solutions were treated by ion exchange.

The procedure consisted of the following steps:

1. Reactor cooling water was circulated in the primary system to establish a temperature of 120°C and a pressure of 500 psi.

2. A concentrated solution of alkaline permanganate was injected into the primary system until the desired concentration was obtained.

3. The solution was recirculated for 24 hr at 120°C with periodic injections of AP to maintain a $KMnO_4$ concentration of 13 g/l.

4. Spent AP-DIL solution was discharged through the heat exchangers (to reduce the temperature to <50°C) to a waste disposal tank. "Dead leg" sampling systems and bypass lines were flushed with water.

5. Spent AP-DIL was processed through mixed-bed deionizers. The effluent, essentially deionized water, was used to flush and refill the reactor in preparation for the next step.

6. The deionized water was recirculated in the primary system to establish a temperature of 120°C and a pressure of 500 psi.

7. Concentrated ammonium citrate solution was injected into the primary system until the desired concentration (13 g/l $(NH_4)_2HC_6H_5O_7$) was attained.

8. The solution was recirculated for 24 hr at 120°C with periodic injection of AC to maintain concentration in the coolant at 13 g/l.

9. All spent AC-DIL was discharged through heat exchangers to a waste disposal tank.

10. Spent AC-DIL was processed through mixed-bed demineralizers. The effluent, essentially deionized water, was used as process water or was discarded.

11. Depleted ion exchange resins were discarded as solid radiation waste.

A 20-mesh strainer was located upstream of the charging pumps to prevent large particles from entering the pump. Two 200-micron strainers were located downstream of the charging pump to prevent small particles from entering the main coolant system.

Fifteen demineralizers were provided to treat the spent decontaminant. Each demineralizer contained 100 ft^3 of mixed-bed resin.

A mock run with carbonated flush water which lowered the pH to 5.0 released crud, with resultant high radioactivity levels measured in the water. After this run, radiation fields of 7 R/hr. were measured near the inlet of the demineralizer bed.

The actual decontamination began on February 29, 1964, and was completed in 14.6 days. The AP solution was not designed to remove activity, but rather to condition the film so that it could be removed with the contained activity by the subsequent AC acid solution. The AP solution did, however, remove a small portion of the radioactivity, primarily as ^{52}Cr.

The AC phase removed approximately 90-99% of the deposited corrosion product radioactivity from smooth surfaces, but it did not remove activity from crevices, low flow areas, dead legs,or crud traps.

Six and one-half days of flushing were needed after the AC step in order to remove chemicals from the system and to decrease the remaining radioactivity because of the low capacity of the resins and because of remaining undissolved crud particles. During the flushing, crud levels as well as the conductivity of the water decreased steadily.

The pipe walls of the steam generators were decontaminated at DF's of 49 while other areas either were not decontaminated at all or were more contaminated at the end of the procedure because of transport and redeposition of undissolved, sloughed crud. Levels in the main coolant flow venturies increased from 0.8 to 5 R/hr, in the main coolant pump increased from 0.9 to 9 R/hr, and in the safety injection line in loop D increased to 17 R/hr.

These "hot spots" were subsequently flushed with water to remove the crud. If this was not possible, lead shielding was placed around the area.

The degree of removal of radioactivity with a procedure such as the AP-AC process depends to a large extent on the velocity attainable in different portions of the reactor, and this in turn depends on the geometry of the reactor. A reactor designed with many "dead legs" or areas of low flow velocity requires treatment with procedures that are effective even at low velocities. The procedures must utilize reagents that dissolve the crud and do not form insoluble precipitates in the reactor.

The concentrated AP solution attacked several metals, including hard surface alloys, when in contact with them at 105°C for 16-24 hr. Examination of main cooling pumps, rod drive mechanisms, hydraulic and manual valves, and differential pressure cells revealed no adverse effects from the decontamination process.

Deionization of the AP-DIL solution required 850 ft^3 of resin, and treatment of the used AC-DIL solution required 990 ft^3 of resin. The volume of the Shippingport PWR primary system is 2,280 ft^3. Assuming an average solid concentration of 15 g/l for the AP and AC solutions, approximately 2,000 kg of chemicals were used. The required resin bed was almost as large as the primary system itself.

2.4.18 Decontamination of the SENA Power Plant in Chooz, France[17]

The SENA pressurized water nuclear plant located on the Meuse River in France began commercial operation in September, 1967. The plant has a rating of 825 MW thermal power and 250 MW electric power. The components of the nuclear steam supply system are housed in two caverns excavated from a hillside along the river.

The primary system of the SENA plant has four loops. The volume of an isolated loop of the plant is 350 ft^3. The pumps contain gaskets in which the main component is carbon. Above the thermal barrier of the main coolant pumps are two bearings and the thrust bearing of the motor. These bearings are primarily composed of graphite elements (GRAPHITAR[a]).

The reactor core is composed of 120 fuel assemblies, each containing a total of 208 fuel elements. The fuel element cladding is type 304 stainless steel. The rest of the primary system also is constructed of 300 series austenitic stainless steels.

In January, 1968, after about 2400 effective full power hours of operation, several pieces of metal, including

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[a] Trademark of Wickes Engineered Materials Division

bolts from the core barrel, were found detached and carried by the primary coolant to the inlet of the steam generators. The force of the water caused the loose metal pieces to hammer against the face of the tube sheets. After a brief visual inspection following plant shutdown, personnel decided to carry out an extensive examination and to perform repairs.

Radiation levels measured at the time of the plant shutdown near the steam generator tube sheet surfaces were approximately 1100 mr/hr for units 3 and 4 and approximately 1800 mr/hr for units 1 and 2. The latter had suffered extensive damage. The difference in radiation levels for the two pairs of units was attributed to the presence of activated metal fragments which had lodged in the tubesheet metal surfaces.

Six months after the shutdown, the plant was decontaminated in four steps, one loop at a time, on June 11-15, June 27-31, August 6-9, and September 9-12. A minimum of about 78 hours of continuous operation was required to decontaminate one loop. Manpower for the operation included a total of 12 operators: four equipment handlers for the laboratory, one analyst for sampling, one analyst to perform chemical analyses, one test engineer, local equipment operators for the drain valve and for the accumulator, and one to control the injection water of the motor, one senior operator and one operator in the control room of the plant.

A two-step method was selected to decontaminate the SENA plant. The first solution, alkaline permanganate, served as an oxidizer and preconditioner.

The second solution, Citrox served primarily as a complexing agent to dissolve metals which had increased oxidation states as a result of the AP pretreatment.

Extensive corrosion testing showed that major construction materials were not significantly attacked by this AP-Citrox process. However the primary pump bearing material, GRAPHITAR, showed excessive attack, and hence provisions for backflushing with deionized water were made.

The proprietary solutions, TURCO 4502 followed by TURCO 4521 were used. TURCO 4502 is a highly alkaline powder which contains potassium permanganate and a stable wetting agent. TURCO 4521 is a proprietary material which contains oxalic acid and citric acid as well as inhibitors and wetting agents.

Separate waste storage tanks had to be provided for the two solutions since they form precipitates and are incompatible when mixed.

The AP solution was prepared at a concentration of 240 g/l of the commercial product TURCO DECON 4502, and was applied at 176°F and 500 psi. The system was pressurized with nitrogen. Care was taken to expose the pumps as little as possible to the solution, and the pump bearings were purged with water.

The reactor coolant pump was jogged and connected to the bypass line where it could be vented in order to eliminate air pockets trapped at the top of the steam generator tubes. Each venting required several hours to perform. Heating was accomplished by operating the primary pumps which brought the temperature to 200°F. Excess heat input was controlled by bleed and feed operations at the secondary side of the steam generators.

After treatment was completed, the primary pump was stopped and the loop was depressurized, but the injection flow in the motor was maintained. The loop was completely drained and then rinsed with demineralized water by repeating the same operations used with the decontamination solution. Several rinsings were necessary.

The Citrox step was carried out with 60 g/l of solution of TURCO 4521 applied at 176°F by procedures similar to those used in the AP step. The times required to decontaminate each loop were as follows:

	Operation	Time Interval (Hours)
1.	Preheating of loop.	
2.	Heating of the water in preparation tank.	4
3.	Filling	1.5
4.	Venting	1
5.	Heating of metallic surfaces	3
6.	Draining	3
7.	Use of the first chemical solution (AP)	
8.	Preparation of solution performed during preheating of loop.	

	Operation	Time Interval (Hours)
9.	Filling	1.5
10.	Venting	1
11.	Heating and circulating of solution	4.5
12.	Draining	3
13.	Rinsings	
14.	Filling	1.5
15.	Venting	1
16.	Rinsing	1.5
17.	Draining	3
18.	Use of the second chemical solution (Citrox)	
19.	Preparation of solution	4
20.	Filling of loop	1.5
21.	Venting	1
22.	Heating and circulating of solution	3.5
23.	Draining	3
24.	Rinsings	21

Virtually all of the chromium and ^{51}Cr activity were removed from the contaminated surfaces during the alkaline permanganate step.

^{54}Mn was removed equally during the AP and AC steps. ^{60}Co and ^{58}Co were removed primarily in the oxalate/citrate step.

Although equal amounts of ^{59}Fe were found in both solutions, a preponderence of iron was found in the Citrox, solution 2, presumably because of removal of noncontaminated layers of corrosion film or because of disproportionately higher corrosion occurring during step 2.

Relatively low decontamination factors (DF = 14) were found for the inlets of the steam generators 1 and 2. Decontamination factors between 40 and 200 were found for generators 3 and 4 where virtually no neutron-activated base metal had been transported.

2.4.19 Decontamination of the PWR at Rheinsberg, DDR Germany[22, 23]

The volume of the primary system of the Rheinsberg PWR without volume compensators is 3333 ft^3. The exposed stainless steel surface is 1888 ft^2 and ZIRCALOY surfaces comprise 15,555 ft^2. The flow rate in the main system is 25.3 ft/second.

After 430 effective fullpower days, the radiation fields in the vicinity of the primary system at the Rheinsberg PWR reached levels of 1 R/hr. Decontamination of the reactor was indicated to permit modification and repair of the reactor primary system.

Preliminary laboratory studies showed that the radioactivity of the oxide layer in the primary system could be decreased only to 60% by acids or complexing agent, because of a chemically stable chromium oxide layer adjacent to the metal surface.

In the laboratory, decontamination factors of 30-60 were obtained at 90-120°C for oxidation of chromium oxide with a solution of 0.3-3 g/l of 30% hydrogen peroxide, 0.2-12 g/l aminosulfonic acid, 0.1-1 g/l hexamethylenetetramine, 0.3-5 g/l nitrilotriacetic acid (NTA), or 0.15-3.5 g/l EDTA, and 0.1-1.5 g/l acetanilide.

However an alkaline permanganate oxidation system was preferred, because of its lower corrosivity compared to the preceding acid solution. Oxidation was accomplished with a solution of 5-30% NaOH and 1-5% permanganate, and the resulting oxide layers were removed by treatment with 3-10% solutions of organic acids or their ammonium salts at 80°C. Oxalic acid was effective in this treatment but gave oxalates of low solubility. Because of the low solubility redeposition of radioactive materials occurred. Citric acid was less effective but gave reaction products which were more soluble. EDTA or NTA was added at

1-5 g/l to the organic acid solutions to maintain fission products in solution. Less concentrated solutions were chosen for actual decontamination of the Rheinsberg reactor. Laboratory experiments had shown that solutions of 0.1% NaOH and 0.1% $KMnO_4$ still would be effective. Acid concentrations in the Citrox solution can be reduced to 0.3-0.5% if enough excess acid is present to complex all of the iron.

Initial removal of the outer layer of the oxide deposit was necessary in order to oxidize deeper layers of chromic oxide and obtain decontamination factors of >10. Pretreatment was performed effectively with the organic acid solution described previously. Omission of this pretreatment presumably allowed manganic oxide hydrate to deposit in pores of the oxide layer during the alkaline permanganate step and thus result in incomplete oxidation of chromic oxide.

Use of only citric acid in the last step of the treatment gave decontamination factors of 10-15. Replacement of 30-50% of the citric acid by oxalic acid gave improved decontamination factors of 15-30.

Waste disposal experience with Citrox solutions indicated that iron could be maintained in the trivalent form by oxidizing it with hydrogen peroxide in order to avoid precipitation of FeC_2O_4.

Decontamination of the Rheinsberg primary system was carried out in August, 1968, three days into the outage for the second refueling.

The decontamination solutions were mixed in a 7 m^3 vat which had connections for condensate heating and recycling. The resultant solution was introduced into the primary system through the emergency core cooling system of the reactor. In order to reduce corrosion of the sensitive control and safety units, personnel introduced a continuous stream of condensate at a rate of approximately 5t(tonnes)/hr into the primary system during decontamination.

The Rheinsberg reactor is equipped for continuous work up of a partial stream of the primary coolant by evaporation. The continuous blowdown was handled by this system.

The procedure used to decontaminate the primary system was the following:

1. Citric acid (150 kg) and oxalic acid (100 kg) were introduced to give a solution 0.5% and 0.1% in these acids, respectively. The solution was recycled for 5 hrs at 103°C and 5-6 t/hr blowdown.

2. The solution was displaced with 18 t/hr condensate at 102°C for 17 hr to achieve dilution of the previous solution to 1%.

3. NaOH (150 kg) and $KMnO_4$ (200 kg) were introduced to give a solution 0.15% in alkali and 0.2% in permanganate. The solution was recirculated 4 hr at 105°C with 5-6 t/hr blowdown.

4. HNO_3 (63%, 300 l) was introduced in 5 tons of condensate to give a pH of 1.8-2. This acidic solution was recirculated for 2 hr at 101°C with a 5-6 t/hr blowdown.

5. Oxalic acid (300 kg) and HNO_3 (63%, 250 l) were mixed rapidly in 5 tons of condensate. This solution was recirculated for 1 hr at 105°C and 5-6 t/hr blowdown. The amount of acid used satisfied the demand of the redox reaction with the remaining $KMnO_4$.

6. Citric acid (350 kg) was added to give a solution 0.1% in oxalic acid and 0.3% in citric acid. This solution was recirculated for 6 hr at 100°C with 5-6 t/hr blowdown.

7. The solution was displaced at a rate of 18 t/hr with condensate for 30 hr to attain a residual concentration of 0.01% of the previous solution, with simultaneous purging of dead legs and other sensitive areas.

The following observations were made during this decontamination:

The ^{51}Cr activity reached a maximum after 1-2 hr, and about 30% of the $KMnO_4$ decomposed to MnO_2 during the alkaline permanganate treatment.

The specific activity of the solution increased rapidly after introduction of nitric acid (step d), but decreased after oxalic acid was added. Deposition of manganese hydroxide, which included some of the radioactivity, onto surfaces of the piping system would account for these results.

The amounts of radioactivity removed from the system during the three step procedure included 11,000 Ci of ^{51}Cr, 162 Ci of ^{60}Co, 48 Ci of ^{58}Co, 41 Ci of ^{59}Fe, 19 Ci of ^{54}Mn and 1.4 Ci of ^{95}Zr. Decontamination factors reached 27, and 70-80 kg of iron was removed.

Prior to decontamination, reactor materials were corrosion tested as follows:

1. Coupons were exposed to a solution of 0.067 wt% oxalic acid, 0.067 wt% citric acid, and 0.018 wt% ammonia at pH 3.1-3.7 and 100°C for 15 hr.

2. Coupons were exposed to a solution of NaOH (0.013 wt%) and $KMnO_4$ (0.13 wt%) for 6 hrs at 100°C.

3. Coupons were exposed to the same solution used in (2) for 6 hrs at 100°C but HNO_3 (3.8 g/l) and oxalic acid (2.05 g/l) were added to decrease the pH to 3.5-3.7.

4. The concentrations of the components of (3) were adjusted to 0.13 wt% oxalic acid, 0.13 wt% citric acid, and 0.01 wt% ammonia to establish a pH of 2.1-2.9 and the coupons were exposed at 100°C and for 15 hrs.

The coupons were measured for weight loss, and were microscopically inspected for intercrystalline corrosion, stress cracking, and pitting.

2.4.20 Boiling Water Reactor Decontamination

At the time of this writing no report on decontamination of a BWR piping system for an entire plant was known. Cleaning of the "A" loop at Dresden-1, which was carried out with limited success in 1968, was the only known approximation of an in-plant decontamination of a boiling water reactor. Other attempts at cleaning were more or less mechanical, and involved jetting or swabbing of piping. Thus, a lack of precedence for cleaning BWR's led to a review of PWR and LTWCR decontamination experience to use as guidelines for in-plant BWR procedures at Dresden-1.

Similar to the PWR experience, radiation levels also increased in BWR plants. Downcomers in the steam drum room at Dresden-1 showed levels of 45, 150, and 400 mr/hr when measured 7, 18, and 31 months, respectively, after startup of the plant.[24]

In the primary system at Dresden-1, the highest radiation doses were measured on the secondary steam generator bottoms where crud collected. The radiation level observed after 16,000 fullpower hours was about 2 R/hr. (More extensive radiation level data on this plant are given in other parts of this report.)

Twenty-seven months after start-up of Dresden-1, simple flushing reduced the steam generator B radiation levels by a factor of 2. Radiation levels associated with crud trapped at the bottom of the steam generator were decreased up to 10X. However, with increasing service life, radioactive deposits change composition and adhere more tightly, so that they can no longer be removed by flushing alone.

Commonwealth Edison Company's experience with chemical cleaning of conventional boilers led to the assumption that the Dresden-1 nuclear plant also would require cleaning. Therefore the plant was designed to accommodate such a process.

Films deposited on various components of BWR primary reactors have been examined and were reported in the literature by Ayres[3] (P. 533ff). Different oxides were found to predominate at different locations in the reactors. Two or more oxides usually were found in a given location, either in solid solutions or in phase layers. Magnetite (Fe_3O_4), α-Fe_2O_3, and $NiFe_2O_4$ were observed by x-ray diffraction and x-ray fluorescence analysis of samples from Dresden-1 after more than 10,000 fullpower hours. Principally, $NiFe_2O_4$ was observed in the steam drum, Fe_3O_4 in the low and intermediate pressure turbine, and α-Fe_2O_3 in the high pressure turbine. The chromium content of the oxides was generally low, and only occasionally exceeded 2 atomic %.

The first reagents tested to decontaminate parts from boiling water reactors had been developed to decontaminate pressurized water reactors. A two-solution treatment with alkaline permanganate followed by sodium bisulfate was inefficient. Decontamination factors up to 40 were obtained routinely for coupons from PWR's whereas decontamination factors of <2 were obtained for coupons from the General Electric Vallecitos BWR.

In other experiments, treatment with alkaline permanganate followed by ammonium oxalate removed 99% of the radioactivity from the surfaces of specimens which had been exposed in an operating BWR for about 2,000 hours. As little as 50% of the activity was removed from similar specimens exposed >10,000 hours. The review of these experiments by Ayres[3] (P. 594ff) Concludes "Many factors affect the performance of decontaminating agents, and additional development work must be done before a system-decontamination procedure, that will be both safe and effective, can be recommended for Boiling Water Reactors.

Decontamination of individual components of BWR's by pickling has been carried out, as opposed to decontamination of the entire reactor. Here undissolved oxide fragments which were detached from steel by the pickling solutions were cleaned from the surface by scrubbing, brushing or other direct measures.

A typical acid pickling solution for unsensitized stainless steels contained 6% $Fe_2(SO_4)_3$ and 1.5% HF, and was used at 75-80°C.

A more versatile approach to acid pickling is found in electrolytic cleaning. An inhibited 5-10% sulfuric acid or sodium bisulfate solution can be used as the electrolyte. The parts to be decontaminated are made cathodic, and a direct current of 1-2 $amps/in^2$ at 15-20 volts is applied at low temperatures.[26] This procedure has the advantage of providing a short defilming time due to the lifting action of the electrolytically produced gas, and decreases corrosion of the steel because of cathodic protection.

Several specimens from the BWR environment that resisted decontamination by complexing agents were successfully defilmed and decontaminated by such electrolytic cleaning techniques.

In 1963, eight months after criticality was achieved, several components of the Consumers Power Company's Big Rock Point plant were decontaminated by swabbing them with saturated $KMnO_4$ solution followed by dilute Na_2SO_3 solution, to give a decontamination factor of three.

The radioactivity associated with deposits in BWR's is presented typically by data obtained at the Northeast Utilities' Millstone-1 BWR. The highest radiation fields after 12,000 effective fullpower hours measured 150 mr/hr at the loop B discharge 66 days after shutdown. One specimen of the deposit contained 0.7 μCi/cm^2 ^{59}Fe, 2.0 μCi ^{58}Co, 1.5 μCi ^{54}M and 5.1 μCi ^{60}Co (Ayres[3], P. 597).

2.4.21 Decontamination of BWR Cleanup Loop at Dresden-1

The nuclear decontamination operation most closely related to the present project is the decontamination of the reactor cleanup loop "A" of Dresden-1 which was performed in 1968.[26] Commonwealth Edison Company's Dresden-1 Nuclear Power Station is a 200,000 kw dual cycle, boiling water reactor which was placed in commercial service in August, 1960. The reactor has duplicate cleanup loops which consist of heat exchangers and a mixed-bed demineralizer. In 1966, two of the regenerative heat exchangers developed gross tube-to-shell leakage. Twenty of the 84 U-tube bends had completely fractured transversely because of stress corrosion cracking. The high radiation fields associated with corrosion products in this system mandated that decontamination be performed before inspection and repairs were carried out.

The loop, with a volume of 2000 gal, consists of the following parts:

A 270 gpm capacity circulation pump which operated at the reactor pressure of 1005 psig.

Four regenerative heat exchangers connected in series with each having 205 ft^2 of effective heat transfer area.

One nonregenerative heat exchanger of horizontal U-tube type having 1404 ft^2 of effective heat transfer area.

A mixed-bed demineralizer 5' in diameter, with 6' vertical sides, and a hemispherical top and bottom.

All construction materials which come in contact with the reactor water are 304 stainless steel.

The radiation fields associated with the loop were measured as 0.5 R/hr at the doorway to the loop area, 4.5 R/hr at the head-end of the lower regenerative heat exchangers, and 8-10 R/hr at the head-end of the upper regenerative heat exchangers.

Extensive laboratory experiments were carried out in an attempt to identify an appropriate decontamination solvent for test specimens removed from the loop. The following solvents were ineffective:

1. 10% nitric acid and/or sulfuric acid at 180°F.

2. 7.5% or 15% phosphoric acid at 150°F.

3. Na-EDTA and HN_3, at various concentrations and temperatures.

4. Citric acid - oxalic acid plus NH_3 at 160°F at various concentrations.

5. (a) 5% ammonium persulfate plus 15% ammonium hydroxide at 100°F for 4 hrs followed by
   (b) 10% hydroxyacetic acid plus 5% formic acid at 200°F for 12 hrs; The sequence (a), 2 rinses, (b), and 2 rinses gave a decontamination factor of 34.

6. (a) citroc acid - oxalic acid plus EDTA at 190-210°F for 1 hr followed by
   (b) alkaline permanganate at 190-210°F for 1 hr (The sequence (b) alternating with (a), with adequate rinsings carried out 4 times, gave a decontamination factor of 50).

7. 5% sodium hydrosulfite at 180°F.

8. 10% H_2SO_4 plus 1% stannous sulfate at 170°F followed by 10% HNO_3 at 180°F.

9. 10% sulfamic acid at 180°F.

10. 4% hydroxyacetic acid plus 2% formic acid at 190°F.

11. 10% H_2SO_4 plus 0.1% sodium thiosulfate at 160°F for 2 hrs. Moderate etching and deep pitting occurred; the DF was 190.

12. 10% H_2SO_4 plus 2% sodium bisulfite at 160°F for 1 hr. The specimen was etched and deeply pitted; the DF was 100.

13. 10% sulfuric acid plus 1% hydroxylamine sulfate at 170°F for 3 hrs. Severe etching occurred with no pitting; the DF was 53.

14. 33% H_2SO_4 under a N_2 blanket at 250°F.

15. 80% H_3PO_4 at 220°F.

16. Ceric sulfate - H_2SO_4 (This treatment stripped film from the piping without dissolving it.)

17. Chromous sulfate - H_2SO_4 solution (No inhibitor was found for this corrosive solution.)

Concentrated inhibited phosphoric acid (procedure 15) appeared to be the most promising and was used for decontamination as follows:

1. The system was filled with low chloride, phosphoric acid based solvent and circulated at about 250°F for 2 hrs.

2. The nonregenerative heater of the cleanup loop was used to cool the solvent to about 100°F and to pump it to temporary storage.

3. Activity was removed from the solvent by ion exchange.

4. The system was alternately filled and emptied, with cleanup of solvent, until radioactivity in the solvent was low enough to allow it to be processed in the station's radwaste facility.

5. The system was rinsed with water.

This decontamination was carried out in August, 1968. Since considerable difficulties were encountered in an attempt to regenerate used solvent by ion exchange beds the procedure was used only twice with only partially regenerated phosphoric acid.

In spite of the extensive testing of representative samples in the laboratory, a procedure was used which dissolved only 75% of the actual reactor deposit. Thus, considerable solid crud accumulated in low flow regions of the piping, and caused increased radiation levels in certain areas.

The overall decontamination was sufficiently successful so that after the high level dead leg areas were covered with lead shielding, repair and maintenance work could be done on the unit.

Since cleanup of the solvent was not successful, 5,000 gallons of solvent and rinse water remained for packaging and disposal. The interiors of ten 1,250-gallon carbon steel tanks were painted with epoxy paint and were filled with a mixture of vermiculite and about 500 gallons of solvent per tank. These tanks were then transported and buried.

The report concludes with the following observation:

"The technology of decontamination of Nuclear Systems seems to be in its infancy. The "standard" decontaminating agents generate large volumes of liquid waste. Temporary storage and ultimate disposal becomes very expensive. It is to be hoped that a simple solvent system which will lend itself to some sort of concentration of activity will be found. This endeavor was an attempt at such a procedure. Perhaps, with further study, the problems which were encountered will be ironed out and a more successful operation will be possible."

2.4.22 Decontamination at the Lingen BWR in Germany

The kernkraftwerk Lingen (KWL) plant is a 256 MW(el) BWR. In 1971 the following parts of the steam-water cycle were decontaminated after they were removed from the main circuit: recirculation pump of Loop 1, primary cleaning system pump, and four steam valves from the main steam line.

Extensive preliminary studies resulted in the following insights:[28]

Oxidation layers present in the primary KWL system, where mainly chromium steels were used for construction, consisted of Cr_2O_3 adjacent to the metal, secondly a layer of Fe_3O_4, and finally Fe_2O_3. Attempts to remove the radioactivity in the oxide layers with acids or complexing agents verified a previous report which stated that a maximum of 60% of the oxide layers can be removed by such solutions. Apparently these solutions dissolve only the outer Fe_2O_3 and Fe_3O_4 layers of the deposit. However, oxalic acid based solutions were especially useful in this application. Citric acid was added to prevent redeposition of dissolved metal oxalates.

Decontamination solutions based on oxalic acid - citric acid, ammonium citrate - citric acid, aminosulfonic acid - EDTA - ammonium peroxide, and NaOH - $KMnO_4$ were considered, and the following were chosen:

Solution 1: 0.25% oxalic acid, 0.25% citric acid; 95°C, 3-5 hrs.

Solution 2: 0.2% NaOH, 0.2% $KMnO_4$; 95°C, 2-6 hrs.

A three-step procedure was followed whereby treatment with solution 1 was followed by treatment with solution 2 and subsequent retreatment with solution 1.

The first step reduced the dose rate very little and the second had no effect. The third step effected a decontamination factor of 6. The remaining activity on the specimen was contained in an oxide layer which was attached very loosely to the metal, and could be removed by rubbing it with filter paper. In this way, bare metal was exposed to achieve a decontamination factor of 32.

The loosely adhering oxide layer was obtained only after a thorough oxidation of chromic oxide by the alkaline permanganate solution. Experiments showed that treatment with hydrogen peroxide did not accomplish oxidation at temperatures below 95°C.

The readily sloughable residual oxide layer had to be kept moist or its mechanical removal was considerably impeded.

The actual procedure used to decontaminate the reactor components was adversely affected by precipitation of iron oxalate which carried some of the activity. Thus the entire procedure had to be repeated in order to decontaminate the dismantled components. Decontamination factors ranging between 3 and 200 were obtained after the mechanical sloughing step.

2.4.23 Decontamination of a BWR Coolant Pump[28].

The decontamination of a reactor coolant pump removed from a reactor in Japan has been reported. The following procedure was used:

1. Treatment was made with alkaline permanganate solution, TURCO DECON 4502, at 25% concentration for 2-4 hr at 70-80°C.

2. A demineralized water rinse was performed until the pH was <9.

3. Treatment was made with a mixture of oxalic acid and ammonium citrate, TURCO DECON 4521, at 6% concentration for 2-4 hr at 70-80°C.

4. A water rinse was performed until the pH was >5.5.

These steps were repeated until no further reduction in radiation levels was observed. Several treatments decreased the activity on the internal surfaces of the pump from 5-20 R/hr (before decontamination) to <300 mr/hr (after treatment).

2.5 COMMENTS ON THE STATE OF THE ART

Although this review of the state of the art and the literature is not all inclusive, it nonetheless illustrates the approaches applied to the removal of radioactive deposits from nuclear power plants. These approaches served as the starting point for the research and development contained in other portions of this report. Although the literature which was reviewed does not discuss copper redeposition during chemical cleaning, solving this problem was a major effort in the procedure proposed for decontamination of Dresden-1.

2.6 CANADIAN EXPERIENCE WITH NUCLEAR POWER PLANT DECONTAMINATIONS: EVALUATION OF THE CAN DECON PROCESS

2.6.1 Introduction

Nuclear plant reactors in Canada are fueled entirely with natural uranium, and are operated with small primary loops filled with heavy water. The primary coolant loops of Canadian deuterium-uranium (CANDU) reactors consist only of piping, and the fuel is not bathed in the coolants in large pressure vessels as is done in light water reactors.

The in-core surfaces of CANDU reactors consist of carbon steel, MONEL, INCONEL 600, and INCOLOY[a] 800.

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[a] Trademark of Huntington Alloys, Inc.

2.6.2 Decontamination of Douglas Point Reactor

When radiation fields reached undesirable levels in 1970, the Atomic Energy of Canada, Ltd (AECL) began planning remedial action. In August, 1971, the Douglas Point plant radiation fields reached 3 rem/hr, and procedures were initiated in an attempt to loosen the radioactive deposits and collect them in filter beds. The techniques were based on the general observation in power plants that changes in operating conditions are always accompanied by "crud-bursts," i.e., the dislodging of radioactive corrosion material into the coolant. Techniques to deliberately induce such crud-bursts were:

> Temperature cycling: lowering and raising of the coolant temperature by operating the reactor at different power levels.
>
> Hydraulic cycling: Changing the water velocity and pressure in the system.
>
> Redox cycling: changing from reducing conditions (excess dissolved hydrogen) to oxidizing conditions by addition of oxygen.
>
> pH cycling: adjusting the water chemistry from slightly basic to slightly acid.

Filters installed in the system efficiently removed solid particles from the coolant.

These procedures reduced the radiation fields at Douglas Point to about 0.6 rem/hr, but were effective only on MONEL surfaces.

The above decontamination procedures are based on "sloughing" the corrosion deposit from the interior surfaces of the reactor. Sloughing occurs when the bond at the interface between the deposit and the metal becomes weakened, and the scale forms flakes which are carried away by the stream. This weakening of the interface can be brought about either by forced movement of the metal substrate relative to the deposit or by chemically undermining the scale by dissolution of the metal surface. Forced mechanical movement is effected through temperature cycling. The coefficients of expansion between the metal and the scale differ, causing relative movement between the two phases and weakening of the bond. The scale cracks and paths open for chemical undermining. Hydraulic cycling also effects mechanical action on the deposit, causing weakly attached particles to leave the surface.

During chemical changes, such as redox and pH cycling, the material forming the bond between the deposit and the metal surface undergoes a transformation and may no longer support bonding. Involved in these transformations may be dissolution by hydrogen ions which penetrate the scale and attack the metal, formation of a different oxidation state, or formation of a crystal type which is thermodynamically more stable under the new conditions.

The above mechanisms will cause suspended solids to be dislodged into the coolant. Although some of these solids can be removed by filtration, the remainder collect in "crud-traps" where radiation fields can build up to multiples of the initial levels, making this approach to decontamination less than ideal. At its best, this procedure is limited to removing spallable scale at decontamination factors of 3-7, and appears to work well only on MONEL surfaces.

2.6.3 The CAN DECON Process

Chemical decontamination was evaluated in an attempt to reduce radiation levels at other CANDU plants. The precedent for chemical decontamination of nuclear plants was established in the United States with LWR's and involved use of large amounts of protonated solvents. These solvents, if used in a D_2O system, probably would undergo proton-deuteron exchange reactions with the D_2O and degrade it. Thus a decontamination process requiring minimum amounts of organic acids was chosen in which the low-acid solvent would be regenerated in a deuterated cation exchange bed.

An acid concentration was chosen to maintain a minimum pH of about 3, a compromise between decontamination effectiveness and low corrosivity to the metals in the system.

The resulting Canadian decontamination (CAN DECON) process involves addition of dilute acids to the system to be decontaminated and circulation of the acids through a filter and an cation exchange bed. The former collects the sloughed material, while the latter retains the dissolved metal ions and returns the reconstituted acid to the system. At the end of the operation, the acid is removed by passing the solvent through a mixed bed demineralizer, and the treated reactor coolant is returned to the system.

This process was first used to decontaminate the Gentilly reactor. Decontamination factors of 3-5 were achieved, and about 40 curies of ^{60}Co was removed from the heat transport system. Similar results are reported for subsequent applications at NPD and Douglas Point.

Although CANDU reactors and LWR's operate under different conditions, consideration of the CAN DECON technique and its effectiveness on specimens from LWR primary systems seemed desirable prior to developing a method for decontamination of Dresden-1 for the Commonwealth Edison Company.

The following details of the CAN DECON process were obtained:

> "... tests proved that a mixture of EDTA, oxalic acid and citric acid was equal to phosphoric acid as a decontaminant..."[29]
>
> L-106, a modified polyfunctional organic compound used at low concentrations, was regenerated on, and removed by, ion exchange resins.
>
> Large-scale demonstrations were performed successfully on the complete heat transport system of the Gentilly-I CANDU-BLW reactor at Quebec Hydro.
>
> L-106 was used at low concentrations of about 0.5 g/kg, at a pH of 3.0 ± 0.25 at 25°C.
>
> An 0.1 wt% solution dissolved 300 ppm polyvalent metal oxides at 100°C.
>
> One liter of 50/50 anion/cation ion exchange resin, Amberlite IRN-150, had sufficient capacity to process 100 liters at 40°C and 2 $ml/min/cm^2$ before effluent conductivity exceeded 25 μmhos.
>
> The total halogen concentration of an 0.1 wt% solution of L-106 was <<0.1 ppm.[30]

2.6.4 Evaluation of CAN DECON Approach to Dresden-1

Evaluations were based on the following assumptions:

1. The test solution would contain a mixture of citric acid, oxalic acid and EDTA at a concentration of 0.5% w/w.
2. Decontamination would be performed at 100°C and completed within 100 hr.
3. The ability of EDTA for form complexes would exist only during the initial stages of decontamination since EDTA is not regenerated from iron complexes by cation exchange. Also, the action of EDTA at the low concentrations used would be insignificant. (Use of excess solvent for a stationary test would not be representative of the action of EDTA in the actual CAN DECON solvent system.)
4. More conservative testing would be accomplished at higher temperatures.
5. In tests without a loop and without regeneration of acids in the treatment solution, residual acidity would decrease, thus restricting such tests to use of small specimens and large excesses of solvent in order to avoid significant changes in the test conditions, such as exhaustion of the solvent.

Preliminary tests showed that 5 g/kg solutions of pyruvic acid, citric acid, oxalic acid, and a 1:1 mixture of 2.5 g/kg of each of the latter two acids had pH values of 2.4-3.0. The solutions were buffered with salts of the acids.

Small specimens cut from hand hole covers in the Dresden-1 secondary steam generators were tested under static conditions. The initial radioactivity present on each specimen was determined. Four specimens were incubated in glass lined bombs at 115-125°C for 100 hours with the solvents described above. These solutions at 350 ml each provided four to ten-fold excesses of available acidity relative to the amount of corrosion deposit present on the small specimens.

The specimens were removed from the bombs after approximately 100 hours and were rinsed with distilled water. The remaining radioactivity was determined. The specimens were reincubated in fresh solvents for 100 hours at 115°C. The results are given in Table 2.6.4.

The first citric acid-oxalic acid treatment appeared to give anomalous results. Treatment of a fresh specimen with the mixed acids gave results which were more consistent with the other data.

Results from these experiments indicated the CAN DECON process could be expected to remove deposits at Dresden-1 with an effectiveness similar to Canadian experience at Gentilly-I; i.e., decontamination factors of one order of magnitude might be achieved at most.

2.6.5 Test at Chalk River Laboratory, Canada

In October, 1975, four specimens were prepared at Midland, MI and shipped to the Chalk River Laboratory where they were decontaminated with the CAN DECON process. Two of the specimens, one of which was cleaned ultrasonically prior to shipment, were from the Dresden-1 primary reactor; one of the specimens was from a manhole cover in a PWR plant; and one specimen was from steam generator tubing from a second PWR plant.

Table 2.6.4

Experimental Evaluation of CAN DECON Process

Origin of Specimen	Solvent	pH Initial	pH Final	DF After First Treatment 100 hr 115-125°C	DF After Second Treatment 100 hr 115°C
Dresden-1	0.5% citric acid	2.9	3.5	1.3	1.3
Dresden-1	0.5% oxalic acid	2.4	2.6	4.5	5.5
Dresden-1	0.25% citric and 0.25% oxalic acid	2.6	9.1?	11.2	15.5
Dresden-1	0.5% pyruvic acid	2.9	3.25	1.3	1.4
Dresden-1	0.25% citric and 0.25% oxalic acid	2.6	2.6	4.3	---

Note: The specimens tested were cut from handhole covers removed from Dresden-1 secondary steam generators.

The radioactivity due to ^{60}Co associated with the deposit on each specimen was determined prior to shipment. The specimens were subjected to the CAN DECON process in the experimental loop at the Chalk River Laboratory of AECL for 48 hours each, and were rinsed and returned to Midland. The remaining gamma radioactivity from ^{60}Co was redetermined. The decontamination factors are presented in Table 2.6.5.

The effectiveness of the CAN DECON treatment with respect to decontamination of BWR scale specimens correlated reasonably well with results given in Table 2.6.4 for static bomb tests.

Significantly, the CAN DECON treatment did not decontaminate the PWR specimen, as predicted from previous experience at Dow with these deposits, and thus did not meet the objectives of the Dresden-1 decontamination project.

Table 2.6.5

Decontamination of PWR Specimens for 48 hrs By CAN DECON Process at AECL Lab at Chalk River

Origin of Specimen	Solvent System	DF	
		Dow Measured	AECL Measured
Dresden-1	CAN-DECON	3.15	3.01
Dresden-1 (ultrasonically cleaned)	CAN-DECON	3.06	3.06
PWR Manhole Cover	CAN-DECON	1.04	1.1
PWR SG Tubing	CAN-DECON	1.03	1.1