Decontamination Handbook

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REPORT SUMMARY

Decontamination has played a key role in reducing collective exposures at U.S. nuclear power plants over the last decade. Today's challenges are to decrease costs and minimize the impact of decontamination activities on outage duration. This handbook compiles lessons learned from sub- and full-system decontaminations as well as decontamination after plant shutdown. It provides critical information about dilute solvents, corrosion issues, the effect of coolant chemistry on decontamination effectiveness, recontamination rates, and waste disposal issues. The handbook synthesizes the most important utility information for performing quick, efficient decontaminations that meet plant-specific needs.

Background

Nuclear utilities widely apply dilute chemical solvents (weak acids) to remove deposited radioactivity and thereby lower exposure of plant personnel to ionizing radiation. Since the first version of this handbook (NP-6433) was issued some 10 years ago, significant advances and industry milestones have occurred. New and improved decontamination solvents have been developed, decontamination of reactor subsystems are now performed at the rate of about 10 per year, and the first full-system decontamination of a large commercial U.S. PWR (Indian Point 2) with fuel removed took place in 1995. Decontaminations to remove deposited activity from shutdown LWR plants (Big Rock Point, Maine Yankee, and Connecticut Yankee) have also been performed since 1998.

Objectives

- To compile current information about decontamination technology.
- To present it in a format that provides critical guidance for utilities familiar with the technology and a good introduction to the topic for all others.

Approach

The principal investigator synthesized information from proceedings of EPRI decontamination and radiation field control seminars, recent EPRI technical reports documenting utility decontamination experiences, and discussions with personnel providing decontamination services to the nuclear power industry.

Results

This comprehensive review of dilute chemical decontamination addresses

- Solvents used to perform sub- and full-system decontaminations of plants that will return to service as well as those used in decontamination of permanently shutdown plants
- The effectiveness of each type of solvent in plant decontaminations

- The impact of chemical decontamination and oxidation processes on corrosion of plant materials
- Recontamination rates, with data showing that recontamination following decontamination is generally slower than expected, indicating benefits will last longer
- Worldwide experience with full-system decontaminations
- Results of four decontaminations of permanently shutdown plants, with a review of the EPRI DFD and CORD D UV processes
- Disposal of decontamination wastes, now a routine process where solubilized material is removed from solution by using ion exchange resin that is later transferred to high-integrity containers (HICs), dewatered, and transported to a radioactive burial site for disposal

EPRI Perspective

EPRI has been at the forefront of developing decontamination solvents and helping utilities implement plant demonstrations. EPRI recommends that utility staff involved with planning future decontaminations review lessons learned from sub- and full-system decontaminations as well as decontamination after plant shutdown. Recent technical advances include the improved LOMI-2 decontamination solvent (report TR-108740), which EPRI plans to demonstrate in an operating plant. In addition, EPRI-sponsored research has resolved technical issues associated with performing a full-system decontamination at a PWR with the fuel in place in the reactor core, with key results reported in TR-107986 and TR-112145. EPRI is available to assist utilities interested in demonstrating the most recent advances in decontamination technology.

TR-112352

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ABSTRACT

Dilute chemical decontamination of reactor subsystems is now a mature, well-defined technology. The LOMI, CITROX, and CAN-DEREM processes employed for these decontaminations are described. The AP and NP oxidizing process required for removal of chromium from high-chromium deposits in PWRs and BWRs on HWC, are also described. Worldwide experience with full system decontaminations is reviewed. Results of four decontaminations applied to permanently shutdown plants prior to decommissioning activities are presented. These applications involved two new processes, EPRI DFD and CORD D UV, which are described. The effects of zinc addition and hydrogen water chemistry on decontamination, and the possible effects of noble metal chemical addition, are discussed. Recontamination data from two BWRs that have undergone numerous decontaminations over a period of up to 15 years, is presented. Data from Indian Point 2 two years after a full system decontamination is also presented. Recontamination has been less than expected which means that the benefits of the decontamination will be longer lasting than predicted. Recent issues with respect to corrosion and waste disposal are discussed. Lessons learned from operational (subsystem) decontaminations, full system decontaminations, and decontaminations applied prior to decommissioning are reviewed.

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EXECUTIVE SUMMARY

Dilute chemical decontamination (DCD) of subsystems and components of operational nuclear power plants is now a mature, well-established technology. Since the first such application in 1979, the industry has grown to the point where about 10 decontaminations are now performed each year in the USA. DCD is, in part, responsible for the average radiation dose per reactor being reduced from about 1,000 rem for BWRs and about 600 rem for PWRs in the early 1980s, to about 100 rem per reactor in 1998. Three DCD processes have been employed for the vast majority of these decontaminations. They are:

1. LOMI (used for 46% of all USA operational decontaminations since 1990, and essentially 100% of the BWR recirculation piping decontaminations)
2. CITROX (36%)
3. CAN-DEREM (18%)

Detailed technical descriptions of these processes are presented. Chemical reactions are given, where appropriate, to assist in understanding the technology involved. These processes bring about decontamination by dissolving the deposits found on the interior surfaces of pumps, valves, pipes, heat exchangers, etc., and releasing the entrapped radionuclides that are responsible for the external radiation fields. All solubilized material is removed from solution by ion exchange resin. The resin is transferred to high integrity containers (HICs), dewatered, and transported to a licensed radioactive waste disposal site for burial.

These processes will dissolve most iron and nickel-based deposits found in LWRs, but are ineffective on high-chromium deposits such as those found in PWRs and BWRs operating under hydrogen water chemistry (HWC). To dissolve such deposits, the chromium must first be removed. This is done with an oxidizing step based on the use of potassium permanganate. Potassium permanganate oxidizes the chromium in the deposit from the insoluble +3 valence state to the highly soluble +6 valence state. Once the chromium is removed, the decontamination process is applied as described above. Two dilute chemical oxidizing processes have been developed – alkaline permanganate (AP), and nitric permanganate (NP). Detailed technical descriptions of each are provided.

The history of chemical decontamination is reviewed. One chapter of the report is devoted to describing the formation of oxide films, and how they incorporate radioactivity, a process referred to as activity transport. Numerous references are provided for the reader interested in a more thorough description.

Worldwide experience with full system decontaminations (FSD) is reviewed. In the USA, the LOMI process has been qualified for FSD in BWRs, while the AP/LOMI and AP/CAN-DEREM processes have been qualified for PWR FSDs. The sole FSD in the USA was performed at Indian Point 2 in 1995 with the AP/CAN-DEREM process. The development work leading up to that application, and the results obtained, are briefly reviewed.

Four plants that are permanently shutdown and are to be decommissioned, were decontaminated in 1998. To reduce radiation exposure ALARA during decommissioning, management personnel at three of the plants elected to perform chemical decontaminations of all major systems prior to the start of major decommissioning activities. Selective subsystems were decontaminated at the fourth. Higher levels of radioactivity removal are required than for operational-type decontaminations. While a decontamination factor (DF) of 10 is generally considered adequate for operating plants, a target DF of 100 or more is not unreasonable for decontamination prior to decommissioning. To achieve such a high DF, removal of a thin layer of underlying base metal is required in addition to removal of the oxide film. Operational-type process are, by design, too “mild”. They have been specifically developed not to remove base metal. Two new process have recently appeared on the market that are designed to remove a small amount of base metal and give the high DFs required for decontamination prior to decommissioning. They are the DFD process developed by EPRI, and the CORD D UV process developed by Siemens. Both are described in detail. The four applications, three with EPRI DFD and one with CORD, are reviewed.

The effect on decontamination of zinc addition to BWRs is discussed. Many plants are using zinc addition and several of these have been decontaminated. No effect on the ability of the operational DCD processes to achieve the required DF has been observed.

The effect of hydrogen water chemistry on decontamination in BWRs is also discussed. It has been found that the oxide film in plants on HWC is converted to a high-chromium film similar to that found in PWRs. The film also contains a high proportion of nickel ferrite. The NP/LOMI process is very effective on films of this type. There is also evidence that the HP/CORD process is effective on HWC films.

Disposal of ion exchange resins from decontaminations is reviewed. Generally, they are dewatered in a high integrity container (HIC) and buried at a licensed radioactive waste disposal facility. The potential exists for creating a mixed waste due to the presence of chromium. However, all wastes to date have passed the toxic characteristic leach procedure (TCLP) and thus are classified as non-hazardous. The potential also exists for creating a waste form that is greater than Class C due to the presence of transuranic (TRU) radionuclides. Such a waste form would be unacceptable for burial at any currently available site. In plants with TRU as the result of fuel failures, the ion exchange resin is taken off line during the decontamination based on TRU loading as opposed to chemical loading. This usually generates more waste, but none of it is greater than Class C.

Recontamination following operational subsystem decontaminations and FSD applications is reviewed. Data from the Brunswick and Quad Cities plants are presented. These plants have performed numerous decontaminations over the last 15 years and provide a good indication of what a plant undergoing its first decontamination can expect. Data two years following the

Indian Point 2 FSD is also presented. In general, recontamination rates are lower than expected. The original DF of 7.8 was reduced to 6.4, where as a reduction to about 2 had been predicted.

Major lessons learned from the three types of decontaminations covered in this report – operational (subsystems), full system decontaminations, and decontamination prior to decommissioning – are reviewed. References to more comprehensive lists of lessons learned also are provided.

GLOSSARY

A large number of acronyms are used throughout this report. For the convenience of the reader, this Glossary of all acronyms has been prepared. Acronyms are not defined in the body of the report. Rather, the reader is referred to this section.

AECL	Atomic Energy of Canada Limited. Developed the CAN-DECON and CAN-DEREM processes, initially for CANDU reactors but the technology was later extended to all water-cooled reactors.
AC	Ammonium Citrate. Usually employed as about a 10% solution. An inhibitor such as phenylthiourea is added if carbon steel is present.
ACE	Ammonium Citrate plus EDTA. Similar to AC with the addition of about 0.04% (400 ppm) EDTA.
AMDA	Automated Mobile Decontamination Appliance. The name given by Siemens to their portable decontamination equipment.
AP	Alkaline Permanganate. A mixture of sodium hydroxide and potassium permanganate used to oxidize chromium in the oxide lattice from the insoluble +3 valence state to the soluble +6 state. Originally developed as a concentrated process (up to 10% total reagent concentration), but later modified to a dilute version with a maximum concentration of about 1,100 ppm (0.11%).
Bradtec	A company based in the UK specializing in decontamination research.
BWR	Boiling Water Reactor
CAN-DECON	A mixture of EDTA, citric acid, and oxalic acid developed by AECL for use in CANDU-PHWRs but the technology was later extended to PWRs and BWRs. The name was derived from CANDU decontamination.
CAN-DEREM	Similar to CAN-DECON but does not contain oxalic acid. This totally eliminates IGA/IGSCC on heavily sensitized austenitic steels.
CANDU	Canadian Deuterium Uranium. A Canadian designed reactor employing separate cooling and moderator circuits. It is fuelled with natural uranium.

CEGB	Central Electricity Generating Board in the United Kingdom. Developed the LOMI and NP processes.
CERT	Constant Extension Rate Test. An aggressive test with metal specimens to determine if exposure to decontamination solvents will cause IGA or IGSCC.
Chelate	Defined in 10CFR61.2 as "amine polycarboxylic acids (e.g., EDTA, DPTA), hydroxy-carboxylic acids and polycarboxylic acids (e.g., citric acid, carbolic acid and gluconic acid".
CITROX	A concentrated (~8%) mixture of citric and oxalic acids originally developed in the 1960s for the PRTR and Shippingport reactors. Modified by PN Services for dilute, regenerative applications (0.2%) in BWRs and PWRs.
CONAP	A two-step decontamination process based on the use of NP and oxalic acid or citric acid. Concentrations are higher and pHs are lower (0.5-1.0) than those usually associated with DCD processes. Used extensively by Westinghouse European Service Center.
CORD	Chemical Oxidation Reduction Decontamination. A dilute process based on the use of HP and oxalic acid. Developed by KWU/Siemens in Germany. Mainly used in Europe and Asia.
CORD UV	A modification of the basic CORD process employing UV light during the cleanup step to decompose oxalic acid to CO_2 and H_2O. This significantly reduces the amount of IX resin required for cleanup.
CORD CS UV	A modification of the CORD process to make it suitable for use with carbon steel. UV refers to the use of UV light for oxalic acid destruction during the cleanup phase. See CORD UV.
CORD D UV	A modification of the basic CORD process employing UV light during the decontamination step. This makes the process more aggressive and it is suitable for decommissioning applications. The UV option is also employed (usually) during the cleanup step for oxalic acid destruction.
DCD	Dilute Chemical Decontamination. Generally means <1% total reagent strength.
DF	Decontamination Factor = Radiation field before decon ÷ Radiation field after decon. Generally refers to shielded contact readings on pipes and is a measure of process efficiency. Compare with DRF.
DRF	Dose Reduction Factor = General area radiation field before decon ÷ General area radiation field after decon. DRF pertains to actual work areas and so more accurately reflects the expected reduction in radiation exposure to workers as a result of a decontamination. Compare with DF.

DPS	Decontamination Processing System. A term coined to describe the equipment built for the Indian Point 2 FSD in 1995.
EBWR	Experimental Boiling Water Reactor. 100 MW (t). Operated 1956-1967.
ECP	Electrochemical corrosion potential. The difference in potential (or voltage) measured between a component and a reference electrode. In BWRs under NWC, the typical ECP of stainless steel components is +0.1 to +0.3 V (versus standard hydrogen electrode, SHE). IGSCC may occur at this potential. Under HWC, the ECP drops to –0.3 to –0.4 V. Under NMCA it drops to about –0.5 V. GE has determined that the ECP must be below –0.23 V to ensure that IGSCC is mitigated.
EDTA	Ethylenediaminetetraacetic acid. A chelating agent used in many decontamination solvents.
EPA	Environmental Protection Agency. Defines solid wastes, hazardous wastes, toxicity characteristics, etc. in 40CFR261.
EPRI DFD	A decontamination process developed by Bradtec and EPRI that is applied prior to decommissioning. Based on the use of AP, oxalic acid and fluoroboric acid.
FSD	Full System Decontamination. Refers to decontamination of all major plant systems simultaneously. The RPV may be included or bypassed, and the reactor may be fueled (“fuel-in”) or defueled (“fuel-out”). RCPs are usually run to provide adequate flow.
DZO	Depleted Zinc Oxide. When zinc oxide is added to BWRs for radiation field control (see GEZIP), Zn-64 (48% of natural zinc) becomes activated to Zn-65 thus partially negating the benefits of zinc injection. DZO contains <1% Zn-64.
GEIS	Generic Environmental Impact Statement. Pertains to decommissioning of nuclear power plants.
GEZIP™	General Electric’s trademark for its zinc oxide injection process for BWRs. Zinc ions preferentially fill the voids in the oxide lattice and reduce pickup of Co-60. This reduces radiation fields.
HIC	High Integrity Container. A polyethylene (usually) container for radioactive waste disposal. It must not contain any free-standing water so dewatering (usually by applying a vacuum for several hours) is standard. Used for IX resins wastes from decontaminations. Available in a variety of sizes with 100 ft^3 being typical. Transported in a heavily shielded shipping cask.

HP	Permanganic Acid. Used for oxidizing chromium in oxide deposits. The term was coined for analogy with AP and NP. Used by Siemens as part of the CORD process.
HWC	Hydrogen Water Chemistry. The constant addition of hydrogen to BWR water to lower the chemical potential and reduce (or eliminate) IGA/IGSCC on large diameter pipe. Slowly changes BWR oxide deposits so that they have more of a PWR characteristic (i.e., higher chromium content and less hematite). Promotes formation of nickel ferrite. “Low” HWC (0.5-1 ppm H_2 in feedwater) has little effect on deposits over several years. “High” HWC (1-2 ppm) has a more rapid and pronounced effect.
IGA	Intergranular Attack. A type of localized corrosion that may occur when certain metals are contacted with certain decontamination solvents.
IGSCC	Intergranular Stress Corrosion Cracking. A type of localized corrosion that may occur when certain metals are contacted with certain decontamination solvents. Usually preceded by IGA.
LN Technologies	The first of the modern decontamination vendors. Most active in the 1980s. Original licensee of AECL for CAN-DECON technology. Sold to Westinghouse in 1989.
LOMI	Low Oxidation State Metal Ion. Based on the use of vanadous picolinate as a dilute (0.7%) decontamination reagent. Developed by the CEGB.
LOMI-2	A modification to the basic LOMI process is which picolinic acid is recycled thus making LOMI effectively a regenerative process.
LPCI	Low Pressure Coolant Injection. Injection points on BWR discharge risers that can be adapted for decontamination use.
LWR	Light Water Reactor. A generic term covering both BWRs and PWRs.
NITROX	A dilute version of Conap (NP + oxalic acid) employed by PN Services, mainly for decontamination of pump impellers.
NobleChem™	Trade name for the noble metal chemical addition process (NMCA) developed by General Electric.
NMCA	Noble Metal Chemical Addition. The addition of trace amounts of Pt and Rh (40-150 ppb) to BWRs to enhance the beneficial effect of HWC. Also appears to work synergistically with zinc injection to keep radiation fields low. Still in the testing/evaluation stage by GE and a few utilities as of this writing (May 1999).

NWC	Normal Water Chemistry. Applies to BWRs that operate without hydrogen addition. See HWC.
NZO	Natural Zinc Oxide. See DZO and GEZIP.
NP	Nitric Permanganate. Developed by the CEGB as an alternative to AP. Operates faster at a lower reagent concentration. Contains nitric acid and potassium permanganate.
OWC	Optimum Water Chemistry. Specifications by General Electric for BWR water chemistry. Strategy is to keep all impurities to a minimum except the feedwater additives iron, zinc, and hydrogen, which are controlled to optimum values for beneficial effects.
OZOX	A decontamination process employed in Europe by Siemens that used OZone and OXalic acid. No longer in use.
PHWR	Pressurized Heavy Water Reactor. Usually refers to CANDU reactors.
PN Services	A decontamination vendor specializing in CITROX, LOMI and EPRI DFD. Acquired by Westinghouse from Vectra in 1995.
PRTR	Plutonium Recycle Test Reactor. A 70 MW PHWR. Went critical in 1960.
Quadrex	The original USA licensee of the CEGB for LOMI technology. Equipment sold to Bechtel in the mid-1980s.
RCP	Reactor Coolant Pumps. Used to provide high flow during FSD and decontaminations prior to decommissioning work. Cast impellers can be difficult to decontaminate. Siemens uses HP/CORD while PN Services uses NITROX, both with good results.
RCRA	Resource Conservation and Recovery Act.
RCS	Reactor Coolant System. Main coolant recirculation system. This term is usually applied to PWRs.
RPV	Reactor Pressure Vessel. There are special concerns with decontamination of this component: • potential for crack propagation in stainless steel-clad low alloy steel; • potential for localized corrosion in Inconel 182 shroud welds; • potential for removal of large quantities of radionuclides from activated surfaces that would complicate waste disposal with little or no benefit in reduction of personnel radiation exposure.

RRS	Reactor Recirculation System. Refers to the external pumps and large diameter piping in BWRs. Also called the reactor water recirculation system.
RWCU	Reactor Water Cleanup System. The filtration and ion exchange system in BWRs.
RWR	Reactor Water Recirculation system. This term is usually applied to the main coolant recirculation system of BWRs.
SCrP	Stabilized Chromium Process. A chromium plating process developed by EPRI. Cast materials such as pump impellers and casings are characterized by porous surfaces that are significant "sinks" for deposited activity. The SCrP should render such surfaces more resistant to activity deposition.
SGHWR	Steam Generating Heavy Water Reactor. A unique reactor design typified by the Winfrith plant in the UK.
TCLP	Toxic Characteristic Leach Procedure. A test used as the basis in 40CFR261 for determining whether or not a waste form is hazardous. The TCLP (Method 1311) is described in EPA Publication SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods".
TRU	Transuranic radionuclides. Officially defined as "alpha-emitting transuranic nuclides with half-life greater than 5 years".
VBWR	Vallecitos Boiling Water Reactor. 33 MW(t) experimental prototype. Operated 1957-1963.
VECTRA	Vectra Technologies, Inc. Owner of PN Services until its sale to Westinghouse in 1995. Prime contractor for the FSD at IP-2 in 1995.
WOL	Wedge Open Loaded. An aggressive corrosion test with metal specimens to determine if exposure to decontamination solvents will cause IGA or IGSCC.

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1
INTRODUCTION

Objective

The last comprehensive review of chemical decontamination technology was the EPRI Decontamination Sourcebook prepared in 1989 (1). Since then, dilute chemical decontamination has become a mature, fully developed technology for operational decontaminations of component and subsystems in both PWRs and BWRs. In addition, some DCD processes have been qualified for full system decontaminations, also in both PWRs and BWRs. This work culminated in the FSD of Indian Point 2 in 1995. Although this decontamination has been discussed at various decontamination conferences, and described in detail in an EPRI report (2), certain details of the application are provided in this report.

Another recent development is the use of somewhat more aggressive decontamination processes for use in retired plants prior to decommissioning. Higher levels of radioactivity removal are required than for operational-type decontaminations. While a DF of 10 is generally considered adequate for operating plants, a target DF of 100 or more is not unreasonable for a decommissioning application. To achieve such a high DF, removal of a thin layer of underlying base metal is required in addition to removal of the contaminated surface film. Operational-type processes are, by design, too “mild”. They have been specifically developed not to remove base metal. In 1998, there were four decontaminations of retired plants prior to decommissioning work. They have been described in the literature. Some details of the applications are included in this report.

The objective of this report is to provide detailed descriptions of the various DCD processes that are commercially available in the above categories, i.e., subsystem/component operational decontaminations, full system decontaminations, and decontaminations of retired facilities prior to decommissioning work. A comprehensive list of references for each process is given. In addition to generic descriptions and summary tables, detailed chemical reactions are provided for each process. Thus, the report is apropos for both chemists and utility personnel with a non-chemical background

Application techniques for all three types of applications are briefly described. Those for subsystem and component decontaminations are described in EPRI’s Decontamination Sourcebook (1) and have not changed much since then.

Corrosion issues, particularly as they relate to operational decontaminations and FSD applications, are also discussed. Corrosion is not really an issue with decontamination of retired plants since the processes used in these applications are designed to remove some base metal. Nevertheless, the amount of base metal removed during a typical application is reviewed.

The current situation with respect to disposal of decontamination wastes, principally highly, contaminated ion exchange resins, is reviewed. This section is relevant to all three categories of decontamination listed above since the wastes from each are similar.

Sources of Information

As previously mentioned, this report builds on the Decontamination Sourcebook. While that report was used as a starting point, for the most part information contained therein is not repeated here. Principal sources of information for this update include:

- proceedings of EPRI decontamination seminars that have been held every year or two since 1985;
- reports from the EPRI chemical decontamination program;
- EPRI radiation field control manuals;
- licensing reports submitted to the NRC by Westinghouse and General Electric for full system decontaminations of PWRs and BWRs, respectively;
- papers and presentations at technical conferences and meetings;
- personal contact of selected personnel within the decontamination industry;
- the author's personal knowledge from first-hand field experience.

A total of 249 references from the above sources are listed in Chapter 16 of this report. This provides a comprehensive bibliography for all major publications relating to dilute chemical decontamination since 1980, and to chemical decontamination in general since the 1950s.

Organization of the Report

Chapters 2-5 provide background information on the history of the decontamination industry in the United States, oxide film formation in LWRs, and a description of some of the early (1950-1970) decontaminations. The development of dilute chemical decontamination processes, the type that is used almost universally today, is discussed.

Chapter 6 reviews the current situation with respect to operational decontaminations in the U.S. For most of the 1990s, about 15-20 such decontaminations were performed each year. However, over the last 2-3 years there has been a noticeable downward trend. The reasons for this are discussed. Guidelines are provided to assist utilities in deciding whether or not an operational decontamination is justified.

Chapter 7 describes all major dilute chemical decontamination processes in use today. Detailed descriptions and chemical reactions are given.

Chapter 8 discusses the issues associated with corrosion, particularly with respect to operational decontaminations and FSD applications in plants that will be going back into service. Corrosion is not really a concern in decontamination of a retired plant since the plant will not be going back into service, and such processes are designed to remove a small amount of base metal to give the much higher decontamination factors and field reduction required for decommissioning activities.

Chapter 9 discusses the current situation with decontamination wastes. For the most part, these are ion exchange resins that are routinely handled by placing them in a HIC, dewatering, and eventually burial in a licensed waste disposal facility. Problems associated with mixed wastes and wastes that are greater than Class C, are also discussed.

Chapters 10 and 11 review the effects of hydrogen water chemistry and zinc injection, respectively, on chemical decontamination. Possible effects of noble metal chemical addition on decontamination are also discussed.

Chapter 12 reviews worldwide experience with full system decontaminations using modern dilute chemical methods. There have been numerous such applications in Canada, England and Europe, but only a single application in the U.S.

Chapter 13 reviews decontamination of retired plants prior to major decommissioning activities. This is becoming an increasingly important aspect of decontamination as older plants shut down, their operation having become uneconomic in the deregulated power industry. There are two competing processes for this type of decontamination. Both are described in detail and application experience is presented.

Chapter 14 describes recontamination in plants that have undergone repetitive decontaminations over a number of years. This information will be of interest to utilities that may be planning a decontamination and are trying to project future benefits. Recontamination data from the sole FSD in the U.S. is also presented.

Chapter 15 summarizes major lessons learned from the three types of dilute chemical decontaminations described in this report – operational decontaminations of subsystems and components in temporarily shutdown plants, full system decontaminations in temporarily shutdown plants, and decontaminations in plants permanently shutdown for decommissioning. Several references are provided for the reader who is interested in a more detailed list of lessons learned.

Chapter 16 gives a list of 249 references covering all aspects of decontamination. They cover chemical decontamination and related topics from the 1950s up until April, 1999.

2
BACKGROUND

Definitions

Contamination is defined as radioactive material where it is not wanted. Decontamination is the removal of this material to a place where it can be controlled, stored, or disposed. Just about any object that becomes contaminated can be decontaminated. In the nuclear industry a list of such objects includes walls, floors, tools, clothing, machinery, scaffolding, hoses, pipes, pumps, and the human body, both internal and external. The list could go on and on.

For the purposes of this report, decontamination will mean the removal of contaminated metal oxide films, or metal oxide deposits, (the terms tend to be used interchangeably) from the interior surfaces of pipes, pumps, valves, heat exchangers, etc., located in the various circuits of water-cooled nuclear reactors. The definition will be further restricted in that only methods employing dilute chemical solutions will be described. Other methods employing strong chemical solutions, mechanical and electrical techniques will be mentioned but will not be described.

Reasons for Decontamination

Starting in 1969, all commercial nuclear power plants in the United States were required to submit radiation exposure data for all personnel to the Nuclear Regulatory Commission. This data is published annually by the NRC and is readily available to the general public. From 1969 to the early-1980s, the total annual collective exposure increased rapidly but the average dose per worker remained essentially constant. This meant that many more workers were being exposed each year.

Apart from the physiological concerns with such rapidly increasing cumulative exposure, there was also the practical concern of whether there would be a large enough pool of workers to service nuclear power plants in the future if such trends continued. Thus, there was considerable pressure on the nuclear industry to reduce radiation exposure. The dose per worker can be reduced by using more workers to perform a particular job, but detailed audits have shown that this tends to increase the collective dose, exactly the opposite of what is desired. Since any effects of the exposure to the group as a whole are proportional to the collective dose, this procedure has no net benefit and in fact is detrimental. The only way to benefit the group as a whole is to reduce the collective dose. This conclusion is based on:

1. linear extrapolation from high dose exposures where both the dose and effects can be measured (e.g. survivors from the atomic bomb explosions in Japan), and,

2. the assumption that there is not a threshold value below which there is no effect on the human body (i.e. any exposure to ionizing radiation will have some effect).

The efforts of the nuclear industry in this regard have been remarkably successful. The average annual dose per reactor is shown for the period 1970 to 1998 in Figure 2-1. For PWRs it has dropped from a high of 640 rem in 1981 to 69 in 1998. For BWRs the reduction is even more dramatic dropping from a high of 1,120 rem per reactor in 1980 to 126 in 1998. There has been a corresponding reduction in the cumulative dose to all nuclear workers from a high of 50-55,000 rem per year in the early 1980s to about 13,000 in 1998. Decontamination has been responsible for a significant portion of this decrease. Figure 2-2 shows the average radiation exposure of all nuclear workers in the period 1983 to 1998 as function of power produced. Again, the downward trend during this period is obvious.

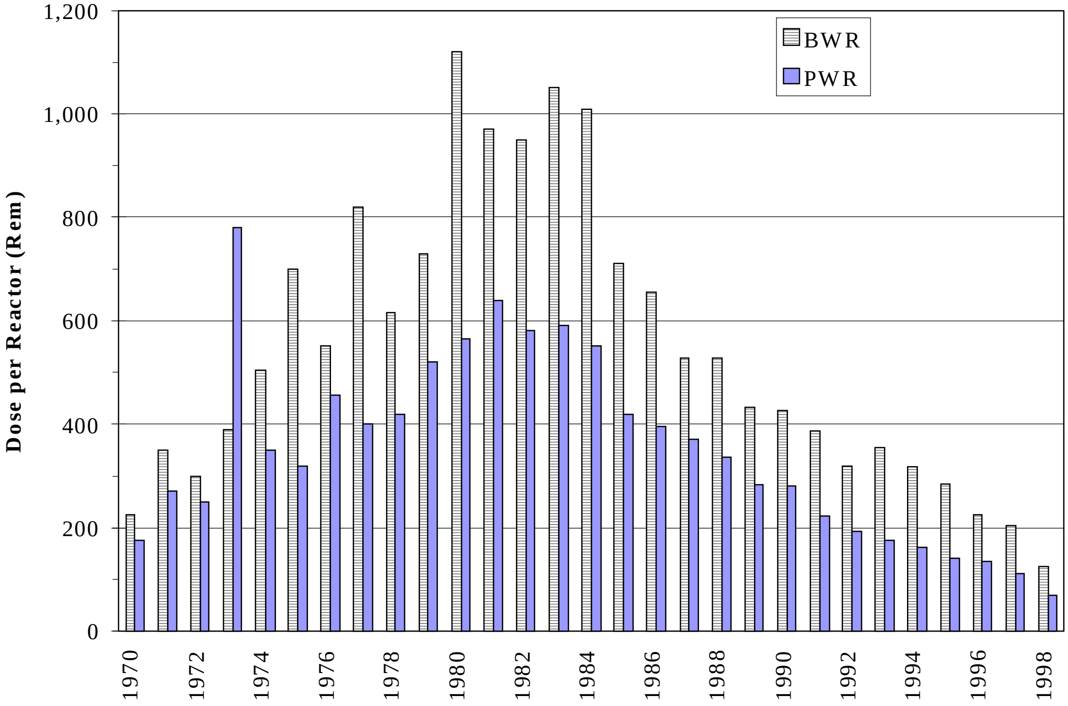

Figure 2-1
Annual Average Radiation Exposures at PWRs and BWRs – 1970 to 1998

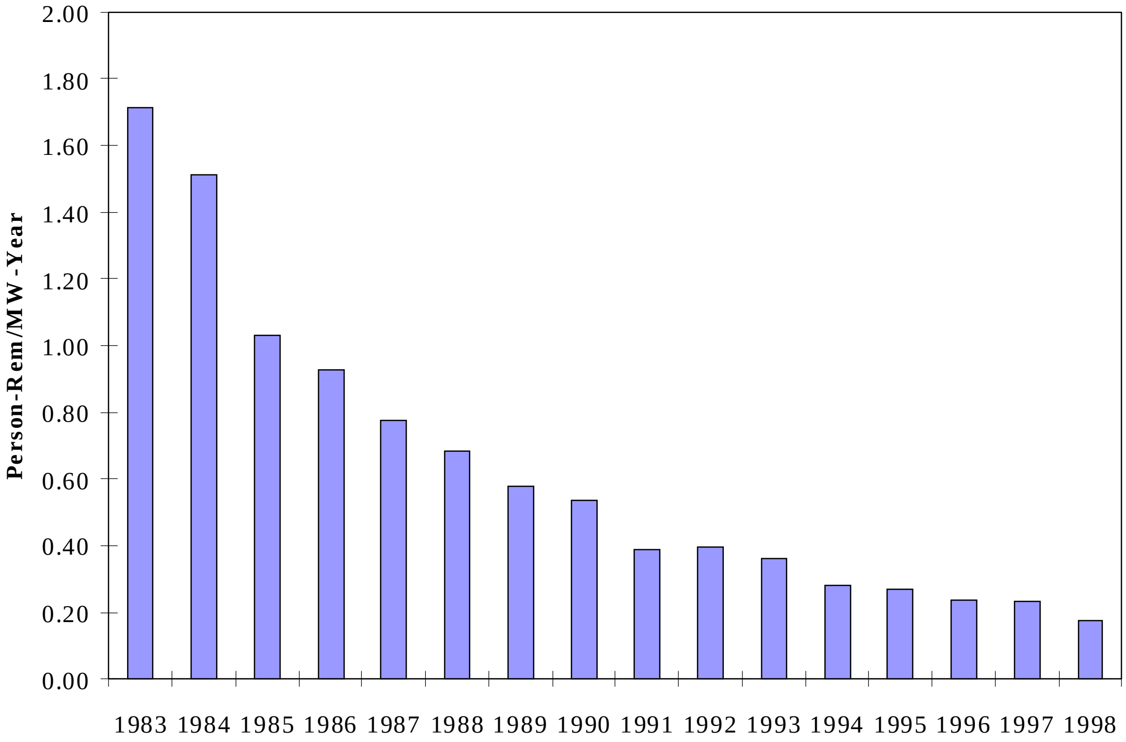

Figure 2-2
Radiation Exposure as a Function of Power Produced – 1983 to 1998

The ALARA Principle

The International Commission on Radiation Protection (ICRP), reflecting practices and trends in countries involved in the peaceful uses of atomic energy, has published recommendations to limit the radiation doses arising from ionizing radiation to workers and to the general public. In addition to recommending dose limits, the Commission has also insisted that efforts be made to follow radiation protection practices that result in doses not exceeding a fraction of the said limits. This idea has been expressed in several forms. For example, the term of keeping doses *"as low as possible"* (ALAP) was used for a period of time. This term became very controversial because technically it was *"possible"* to reduce doses to very low levels, but the associated costs became very high. Hence people were not receiving a benefit commensurate with the money being spent. Other expressions such as *"as low as practical"* were tried with similar results.

In 1971, the ICRP recommended the following:

"As any exposure may involve some degree of risk, the Commission recommends that any unnecessary exposure to ionizing radiation be avoided, and that all doses be kept as low as readily achievable, economic and social considerations being taken into account."

In that recommendation, the ICRP specifically indicated that economic and social aspects must be considered. In 1973, the ICRP commission issued additional explanations and gave some examples of cost per unit dose.

In 1977, the ICRP introduced new recommendations and expressed the same idea with the following words:

"The limitation of stochastic effects is achieved by keeping all justifiable exposures as low as is reasonably achievable, economic and social factors being taken into account, subject always to the boundary condition that the appropriate dose equivalent limits shall not be exceeded."

This practice is now known commonly as the ALARA principle. The ICRP also addressed the question of what is reasonably achievable in the following manner:

"For this purpose, the question is whether or not the activity is being performed at a sufficiently low level of collective dose equivalent, so that any further reduction in dose would not justify the incremental cost required to accomplish it. In making this determination, the cost-benefit analysis shifts from a consideration of the <u>total</u> benefit of the activity to the <u>change</u> in net benefit."

It also proposes some general cost-benefit formulations. The ALARA principle has been adopted by virtually all countries engaged in peaceful uses of atomic energy. The way in which the principle is applied, however, may vary from country to country.

The most recent report on the Biological Effects of Ionizing Radiation (BEIR V) by the USA National Academy of Sciences (NAS) and the (USA) National Research Council (NRC), concludes that the risk of developing cancer from exposure to "low level" radiation may be 3 to 4 times higher than was formerly recognized. However, the level they consider to be "low" is 10 Rem exposure to the whole body, received instantaneously. The study points out that spreading out the exposure over time would be expected to reduce the cancer risk by a factor of two or more. The NAS/NRC does not recommend radiation standards. The (USA) National Council on Radiation Protection and Measurements (NCRPM) is reviewing these recent findings. Based on this study and any new recommendations made by the ICRP, the NCRPM may submit a new set of recommendations to the USNRC which has the authority to make them law.

For a number of years, USA regulations limited nuclear plant workers to a whole body exposure of 3 Rem/quarter and 5 Rem/year. Most utilities adopt much lower administrative limits, partly to minimize individual exposures, and partly to maximize the probability that they will not exceed the federal limits. The average annual exposure of nuclear workers in recent years in the USA has been less than 0.5 Rem/year. Starting January 1, 1994 the annual occupational radiation exposure limit remained at 5 Rem/year but now includes both internal and external exposure. The total dose equivalent of internal exposure (TDE) is estimated for each individual and subtracted from 5 Rem to give the allowable external exposure. The sum of external and internal exposures is referred to as the total effective dose equivalent (TEDE).

Methods of Decontamination

There are many methods available for reducing radiation exposure. Some general categories are:

- shielding;
- remote handling;
- robotics;
- removal of item requiring maintenance from a high dose area to a low dose area;
- decontamination.

Figure 2-3 shows some specific decontamination methods. As previously mentioned, the subject area for this report is decontamination, principally dilute chemical decontamination.

There are many methods of decontamination, but each can usually be assigned to one of three major types as shown in Figure 2-3: Electrical, Chemical, or Mechanical.

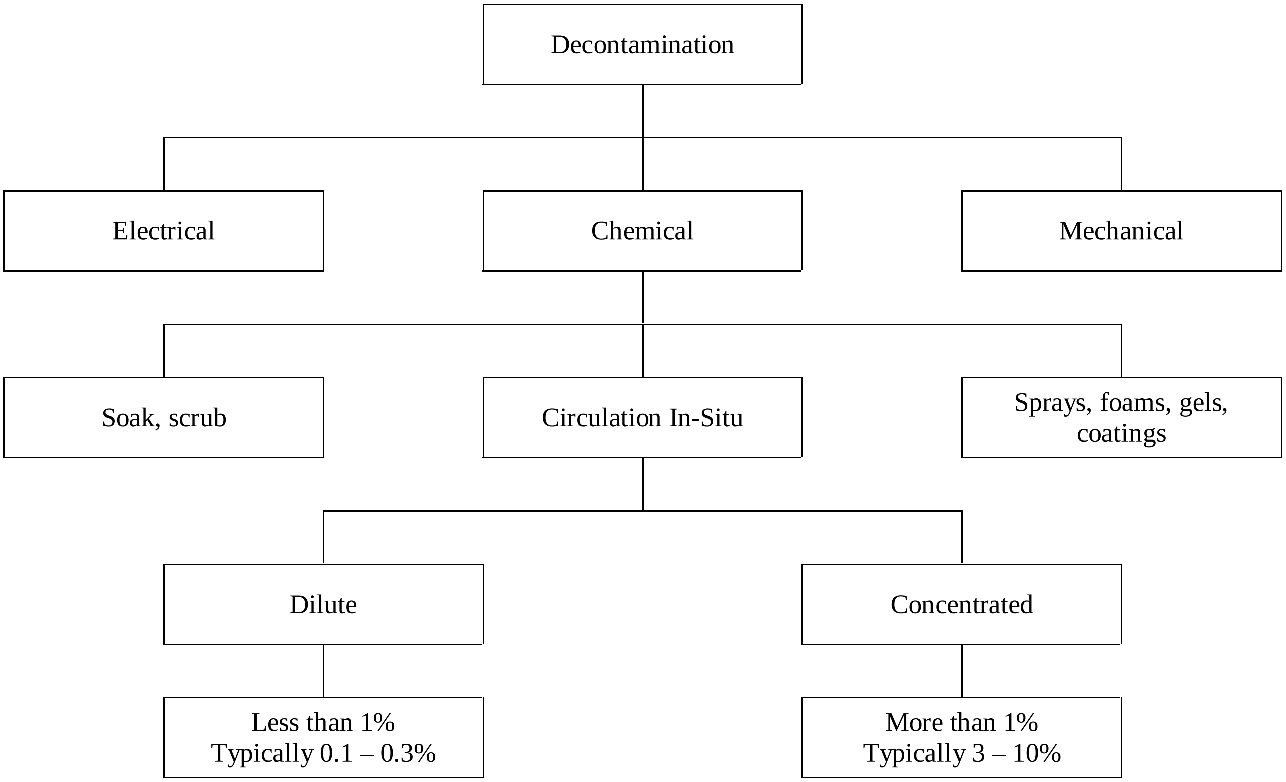

Figure 2-3
Decontamination Methods

Electrical decontamination is typified by electropolishing (anodic) and electrolytic cleaning (cathodic).

Mechanical decontamination refers to methods such as hydrolazing (or jet cleaning), abrasive (or grit) blasting (dry or wet), filing, and scrubbing, either by hand or with power brushes.

Chemical decontamination involves dissolution of the radioactive contaminants themselves, or the matrix in which they are entrapped. This matrix is usually a metal oxide film or deposit. Typical oxide films found on PWR and BWR stainless steel (SS) surfaces are described below. Note that chemical decontamination methods fall into two categories – dilute and concentrated. The emphasis of this report will be on dilute methods.

Small components can be chemically decontaminated by dipping them in a vat containing chemical solutions in a decontamination center. For larger components, the chemicals can be applied in the form of a spray, foam, or gel or other type of coating. Reactor coolant pumps can be decontaminated in specially constructed tanks. Strippable coatings are used for large, flat surfaces such as walls and floors. For process systems where the contamination is on the internal surfaces of pipes and components, the chemicals can be circulated in solution through the system. This type of chemical decontamination is the subject of this report.

3

OXIDE FILMS IN WATER COOLED REACTORS

Formation of Oxide Films in Water-Cooled Reactors

The basis of all chemical decontamination processes, including DCD processes, is chemical dissolution of the contaminated oxide films from the interior of pipes and components of nuclear reactor systems. To understand how a specific process works, it is necessary to know how the films are formed as well as their morphology, structure, and composition. This section deals with formation; the following sections discuss morphology and composition.

Oxide films are formed by two fundamentally different mechanisms. An adherent inner layer next to the base metal is formed in-situ by corrosion of the base metal. It is also referred to as a grown-on oxide layer. Its composition is determined by the composition of the base metal and the chemical and physical conditions that exist in the water that flows over it. This layer forms quickly during the initial weeks of reactor operation, but as the base metal becomes shielded from the water, the rate of formation slows down. For all practical purposes formation of this inner layer essentially stops. The corrosion rate is said to be parabolic in nature, i.e., it is rapid initially but then slows down to essentially zero. If this inner layer is removed for any reason (i.e., mechanical or chemical decontamination), the corrosion rate will increase until it reforms.

The outer layer of the oxide film is formed by a combination of deposition of circulating crud and by precipitation of dissolved metals from the water flowing over the surface. Its composition is determined by the composition of these impurities. In PWRs, the source of these impurities is mainly from the in-situ corrosion process. During this process, some material is released to the water; it is not all transformed into a corrosion product layer. This released material may accumulate in crud traps or on in-core surfaces until it is re-released through a combination of dissolution and erosion. It then forms the outer layer by precipitation.

In BWRs, there is a source of impurities in addition to corrosion products from the base metal. This is the feed water system. Although every attempt is made to minimize the concentration of impurities in this water by techniques such as condensate polishing, a significant amount of impurities still enter the reactor from this source and contribute to the deposited layer of oxide.

Formation of films is shown schematically in Figure 3-1 and Figure 3-2 for PWRs and BWRs, respectively. More detailed information on the formation of oxide films can be found in the three editions of the EPRI Radiation Field Control manual (3, 4, 5), and in several other EPRI reports (6, 7, 8).

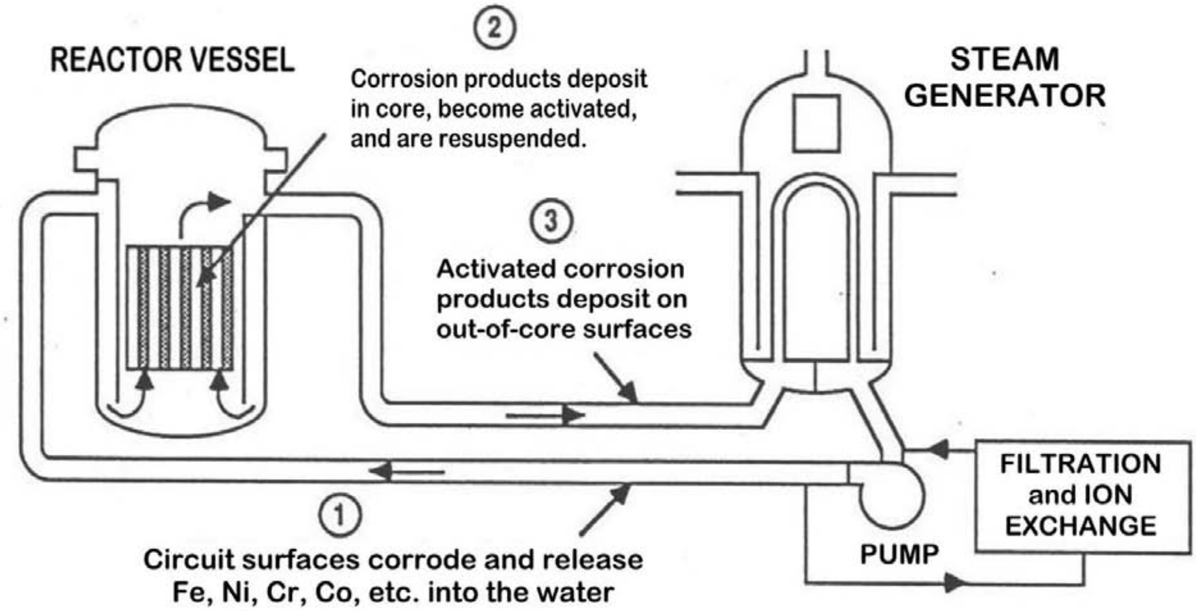

Figure 3-1
Schematic Representation of Formation of Radioactive Deposits in PWRs[1]

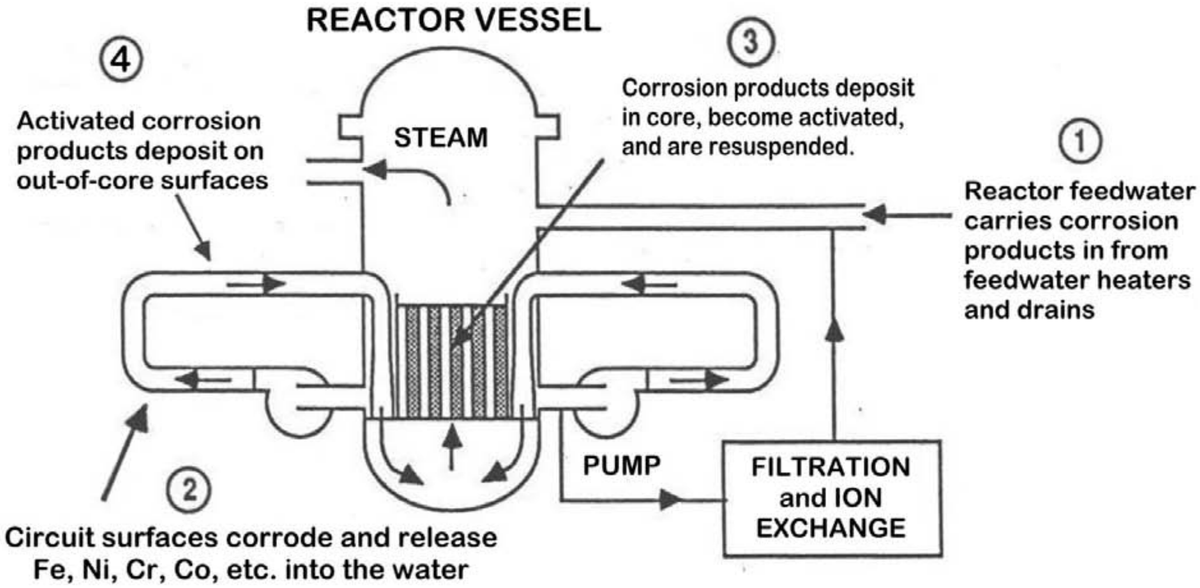

Figure 3-2
Schematic Representation of Formation of Radioactive Deposits in BWRs[2]

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[1] Copied from EPRI NP-3177 (91)

[2] Copied from EPRI NP-3177 (91)

Thickness and Density of Oxide Films

Oxide films in PWRs tend to be much thinner than those in BWRs for two reasons:

1. the high pH reducing conditions that exist in PWRs minimize in situ corrosion and the release of corrosion products;

2. there is no continuous ingress of impurities as there is with the BWR feedwater system.

Typical film thicknesses on PWR stainless steel surfaces are 2-3 μm while those on Inconel surfaces are closer to 1-2 μm. This is partly due to the lower general corrosion rate of Inconel and partly due to the higher velocities over the Inconel surfaces, which tend to limit deposition. Hydrodynamic conditions at the surface are not conducive to particles settling and adhering to the surface. The majority of these films are grown-on oxide. Deposited oxide accounts for <25% of the film. This is because of the inherently clean nature of PWRs, as previously alluded to. The densities of these films are in the range 3.0-5.0 g/cm^3 with 4.0 being a typical average. This is about 75% of the theoretical density of 5.2 g/cm^3.

Another method that is commonly used to express deposit thickness is the specific weight, i.e., mg/cm^2. In many cases, this is a more practical unit of measure since it is obtained directly by scraping or descaling a known area of pipe or fuel. It does not depend upon knowledge of the film thickness and density, both of which require sophisticated laboratory techniques to measure. The specific weight is simply the product of the thickness and density, with the appropriate corrections for units. For the stainless steel deposits referred to above, the specific weight is:

$$3\ \mu\text{m} \times 4\ \text{g/cm}^3 \times 10^{-4}\ \mu\text{m/cm} \times 10^3\ \text{mg/g} = 1.2\ \text{mg/cm}^2$$

For the Inconel deposits, the specific weight is 0.8 mg/cm^2.

Be aware that some authors use the unit mg/dm^2 to express specific weight, which gives values that are 100 times higher than mg/cm^2 (e.g., 1.2 mg/cm^2 = 120 mg/dm$^{2)}$, while still others use g/m^2 which gives values that are 10 times higher than mg/cm^2 (e.g., 1.2 mg/cm^2 = 12 g/m^2).

Deposits on cooler heat transfer surfaces such as heat exchangers in the letdown or purification system may be much thicker than the values given here. The thickness of such deposits will be dependent upon local conditions and it is difficult to make general statements. The majority of the additional deposit will be of the deposited type as opposed to grown on oxide.

BWR deposits tend to be much thicker than those in PWRs and vary more from one reactor to the next than do PWR deposits. Typical deposit thicknesses on system surfaces vary in the range 5 to 20 μm. Densities are similar to those of PWR deposits i.e. 3 to 4 g/cm^3. Specific weights are in the range 2 to 6 mg/cm^2 since the thicker deposits tend to have the lower densities. Deposits on cool heat transfer surfaces such as the RWCU heat exchangers may be as high as 35 mg/cm^2, but more typical values are in the range 10 to 20 mg/cm^2.

Deposits in CANDU-PHWRs tend to be much thicker than those in PWRs. This is because of the use of carbon steel as the primary system piping. It does not have the same corrosion resistance as does stainless steel and builds up a relatively thick protective layer. Typical thickness is 75 µm, or 30 mg/cm^2. Deposits on steam generator tubes also tend to be thicker because of the large source of corrosion products available on the carbon steel surfaces. These deposits may be as much as 10 times as thick as those on PWR steam generator surfaces.

Although the use of carbon steel pipes in CANDUs results in thicker deposits, the amount of activity in the deposit is substantially less than in either PWRs or BWRs. This is because there is negligible cobalt impurity in carbon steel compared to stainless steel where it is difficult to separate it from the nickel. There is some cobalt in the CANDU boiler tubes but very stringent specifications on its concentration and good water chemistry control have minimized the amount that is released.

All the information discussed above is summarized in Table 3-1 below.

Table 3-1
Typical Deposit Parameters for PWRs, BWRs and CANDU-PHRWs

Reactor Type	Deposit Thickness µm	Deposit Density g/cm^3	Specific Weight mg/cm^2
PWR - Pipe	3	4	1.2
- SG	2	4	0.8
BWR - Pipe	10	3.5	3.5
- HX	50	3.5	17.5
CANDU - Pipe	75	4	30
- SG	25	4	10

Composition of Oxide Deposits

The composition of the oxide film found in various types of reactors is determined, in part, by the composition of the base metal and the water chemistry conditions used. PWRs are constructed mainly of stainless steel type 304 (pressure vessel and piping) and Inconel 600 (steam generator tubes). BWRs are constructed almost exclusively of SS 304 but recent pipe replacement projects have used nuclear grade SS 316 since it less susceptible to localized corrosion such as intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC) which have plagued BWRs. The composition of the two is almost identical (18% Cr, 8% Ni, 74% Fe). The small amount of molybdenum in SS 316, the only difference between the two, has negligible effect of the composition of the film. Nuclear grade means that the carbon content is at the low end of the acceptable range, i.e., <0.03%. This will also have a negligible effect on film composition but does have major implications as far as IGA and IGSCC are concerned.

CANDU reactors are constructed mainly of A106-B carbon steel with either Monel 400 (Pickering), Inconel 600 (Bruce) or Incoloy 800 (Darlington) steam generator tubes. There is some stainless steel 410 and 403 on each endfitting, but this has no effect on film composition other than the grown-on film on the stainless steel itself.

All reactors use significant amounts of zirconium alloys in the core section but they are coated with the highly refractory ZrO_2. It has a negligible corrosion rate under normal reactor conditions and does not contribute to the oxide films found throughout the system nor does it contribute to the corrosion product loading in the reactor. The fuel elements and other core components may become coated with a thin deposited layer of crud, but this is a function of the water chemistry of the system itself and not of the zirconium alloy.

Literally hundreds of other materials are used in nuclear reactors, but they have little, if any, effect on chemical composition of the oxide films. There are several reasons for this:

1. the majority of them are simply different grades of stainless steel or nickel alloys, so their principal components are still Fe, Ni and Cr;

2. their surfaces areas are very small when compared to the major materials used;

3. they release metal ions that do not readily incorporate themselves into the oxide film lattice (a detailed discussion on this topic is given latter in this section).

Typical chemical operating parameters for the three major types of water-cooled reactors are shown in Table 3-2. Hydrogen is added to PWRs and CANDUs to maintain reducing conditions. Radiolytic decomposition of the water occurs in core, but the large excess of hydrogen causes the oxygen to recombine almost as fast as it is produced. In BWRs, hydrogen is not added (except for those plants that are on hydrogen water chemistry – HWC)[3] so its concentration is much less than in PWRs. As hydrogen and oxygen are formed through radiolytic decomposition in-core, both are carried with the steam to the turbine. Hydrogen is preferentially removed due to its lighter mass resulting in an excess of oxygen and thus chemically oxidizing conditions. This has a profound effect on the composition of the oxide films as compared to PWRs. In both PWRs and CANDUs lithium is added to raise the pH to reduce corrosion. Apart from this beneficial aspect, the presence of lithium does not affect the composition of the oxide films.

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[3] The effect of HWC on decontamination of BWRs is discussed in Chapter 10 of this report.

Table 3-2
Typical Chemical Operating Parameters in PWRs, BWRs and CANDUs

Parameter	PWR	BWR	CANDU
Dissolved O_2	<10 ppb	200 ppb	<10 ppb
Dissolved H_2	2000 ppb	40 ppb	2000 ppb
pH (25°C)	10	7	10.3 - 10.6
pH (300°C)	7.5	5.5	7.5
Lithium	1 ppm	0	1 ppm
Boron	0 - 1000 ppm	0	0

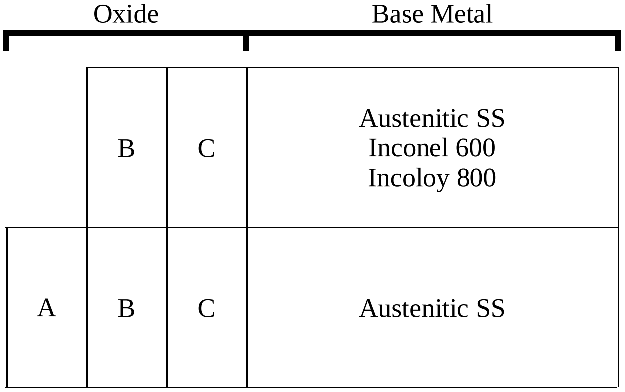
In PWRs, boron is added for reactivity control. Its concentration is about 1000 ppm at the beginning of a fuel cycle but slowly decreases to 0 ppm at the end of the cycle. It does not appear to have any effect on the composition of the oxide films. Boron is not used in either CANDU reactors or BWRs.

The composition of the films found in PWRs, BWRs and CANDUs is shown in Table 3-3 where the individual chemical compounds are listed. Data for PWRs and BWRs is shown in a different format in Figure 3-3. Differences between the inner and outer layers are shown. These are idealized descriptions and in practice the distinction between the inner and outer layers is not as clear-cut as suggested in Table 3-3 and Figure 3-3. In general, the compounds are listed in order of their concentration but it must be remembered that inner layer compounds on Inconel will be higher in concentration in nickel than those on SS 304. Most of the compounds listed are inverse spinels. This is a complex crystal structure having the general formula $M^{2+}M_2^{3+}O_4^{2-}$. The oxide ions are arranged in a cubic close packed structure that creates tetrahedral and octahedral interstices or "holes". In a normal spinel the M^{2+} ions occupy the tetrahedral sites and the M^{3+} ions the octahedral sites. In an inverse spinel the M^{3+} ions occupy the tetrahedral sites and half the octahedral sites and the M^{2+} ions occupy the remaining octahedral sites. Through the use of X-ray diffraction techniques, crystallographers can distinguish the presence or absence of the individual compounds listed. Since most of the deposits are spinel-type structures, only those metals ions that have the correct electron configuration can occupy a site and become incorporated into the deposit. These metals include Fe, Co, Ni, Cr, and Mn. Excluded are Li and B and this is the reason these elements do not form part of the PWR or CANDU deposits even though they are present in the water in significant concentrations. Cu is also excluded so it does not form part of the deposit found in CANDU reactors even though it is a major constituent of Monel 400, the boiler tube material used in the Pickering reactors.

Table 3-3
Principal Compounds in Oxide Films in PWRs, BWRs and CANDUs

Reactor Type	Inner Layer	Outer Layer
PWR	Cr_2O_3 $Ni_XFe_{1-X}OFe_YCr_{2-Y}O_3$	$NiOFe_2O_3$ Fe_3O_4
BWR	$Ni_XFe_{1-X}OFe_YCr_{2-Y}O_3$ Fe_3O_4 Fe_2O_3	Fe_2O_3
CANDU	Fe_3O_4	Fe_3O_4 $NiOFe_2O_3$

Of particular interest Table 3-3 and Figure 3-3 is the much lower proportion of Cr in BWR deposits even though it is a major component of SS-304. The oxidizing conditions that exist in BWRs result in chromium that is released from the surface being oxidized to the +6 state. In this state it is in the CrO_4^{2-} form. Chromium in this form is highly soluble and cannot assume a place in the spinel lattice. Therefore it remains in solution until removed by the ion exchange resin in the RWCU. When SS-304 corrodes in a reducing PWR environment, it releases chromium in the Cr^{3+} form where it can be readily incorporated into the spinel to form iron chromite, ($FeCr_2O_4$), or the highly insoluble oxide chromium trioxide, (Cr_2O_3). A thin, grown-on, inner layer may form on stainless steel in BWRs where access of oxygen is restricted. In this case the conditions are more like those in PWRs and chromium becomes incorporated. This aspect is shown in Figure 3-3.



PWR:
Activity in both B & C
Probably need to remove both layers for reasonable decontamination

BWR:
>90% of activity in A & B
Reasonable decontamination if only A & B removed

Layer A – Deposited oxide (Fe as Fe^{3+}) containing predominantly:
Fe_2O_3 and FeOOH

Layer B – Deposited oxide (Fe as Fe^{3+} and Fe^{2+}) containing predominantly:
Fe_3O_4, $NiFe_2O_4$ and $Ni_xFe_{3-x-y}Cr_yO_4$ ($y<1$)

Layer C – Grown-on oxide (Fe as Fe^{2+}, higher Cr) containing predominantly:
$Ni_xFe_{3-x-y}Cr_yO_4$ ($y>1$), $FeCr_2O_4$, $NiCr_2O_4$ and Cr_2O_3

Figure 3-3
Summary of Film Composition in PWRs and BWRs

The composition of the circulating crud in BWRs is generally hematite or red iron oxide Fe_2O_3. Thus this is the main constituent of the outer layer and is responsible for the reddish color of BWR deposits.

In PWRs the circulating crud is mainly nickel ferrite, $NiFe_2O_4$, which is black. Thus it is the main constituent of the outer layer in PWRs and is responsible for the black appearance of PWR deposits.

In CANDUs the circulating crud is mainly magnetite, Fe_3O_4, formed by releases from the relatively heavy deposits on carbon steel surfaces. The contribution of nickel from the boiler tubes is small. Since the inner layer on carbon steel surfaces is also magnetite, there is not a definitive junction between the inner and outer layers. The composition is more or less uniform across the deposit. The stainless steel endfittings on each pressure tube build up an in-situ layer that is chromium rich, similar to the inner layer in PWRs. Although the stainless steel area is small, the location of these endfittings on the reactor face results in these deposits having a significant effect on reactor face fields. Since most CANDU decontaminations are aimed at reducing reactor face fields, these chromium rich deposits must be considered. Sometimes a separate step in the decontamination process is required to deal with them. This aspect is discussed further in Chapter 3, Oxidation Processes.

Figure 3-4 and Figure 3-5 show idealized compositions of PWR and BWR films in cross section. In PWRs there is an enrichment in Cr to 30 - 40% in the inner layer but it drops to 10% at the surface as nickel ferrite becomes the dominant deposit. Ni constitutes about 25% of the deposit throughout, its approximate concentration in nickel ferrite and nickel chromite. Iron comprises about 15% of the inner layer and about 45% of the outer layer. Note that oxygen comprises about 30% of the film, its contribution to iron, nickel and chromium based spinels. Some authors refer to oxide deposits in terms of metals only. Such numbers will have to be divided by 0.7 to convert them to weights of oxide film.

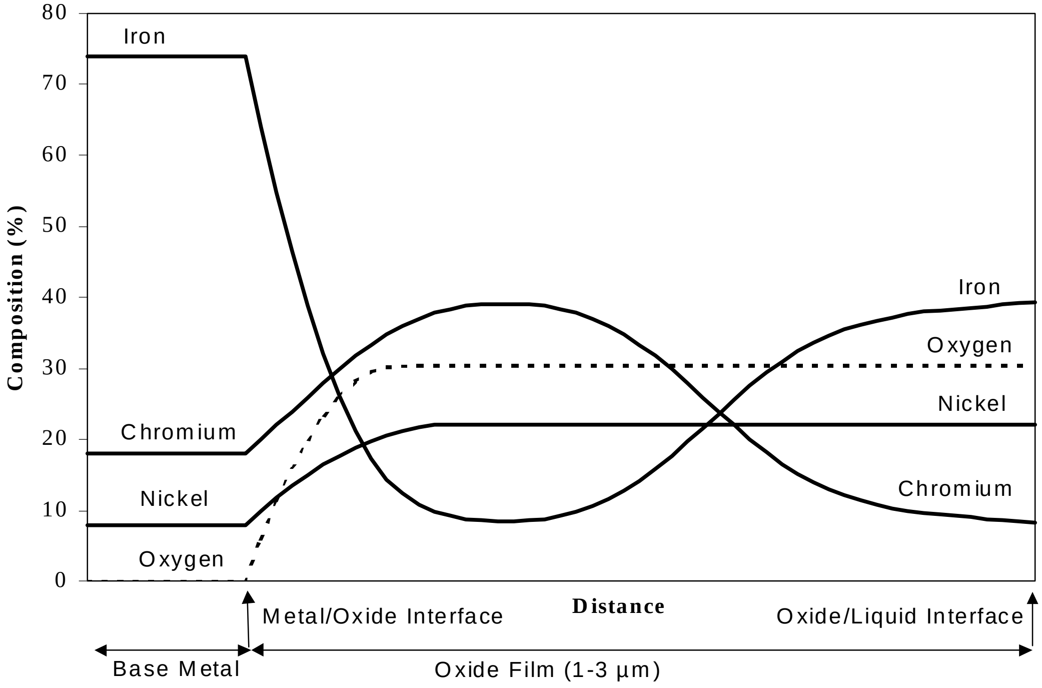


Figure 3-4
Idealized Composition of PWR SS Oxide Film as a Function of Film Thickness

In BWRs there is some chromium in the inner layer but usually it is less than 10%. It may slowly increase as the reactor ages since as the film builds up, the slow in-situ corrosion will take place under anaerobic conditions and chromium will become incorporated into the film in a similar manner to PWR films. Both chromium and nickel are very low in the outer layer, which is predominantly hematite.[4]

Deposits on carbon steel surfaces in CANDUs are almost exclusively magnetite, as previously mentioned. The inner layer on the steam generator tubes is enriched in nickel and/or chromium, depending on the tube composition. The inner layer on stainless steel surfaces will also be enriched in chromium, as discussed above.

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[4] This discussion refers to BWRs operating under NWC. For those operating under HWC, there is a large increase in the amounts of Cr and Ni in the film. See Chapter 10.

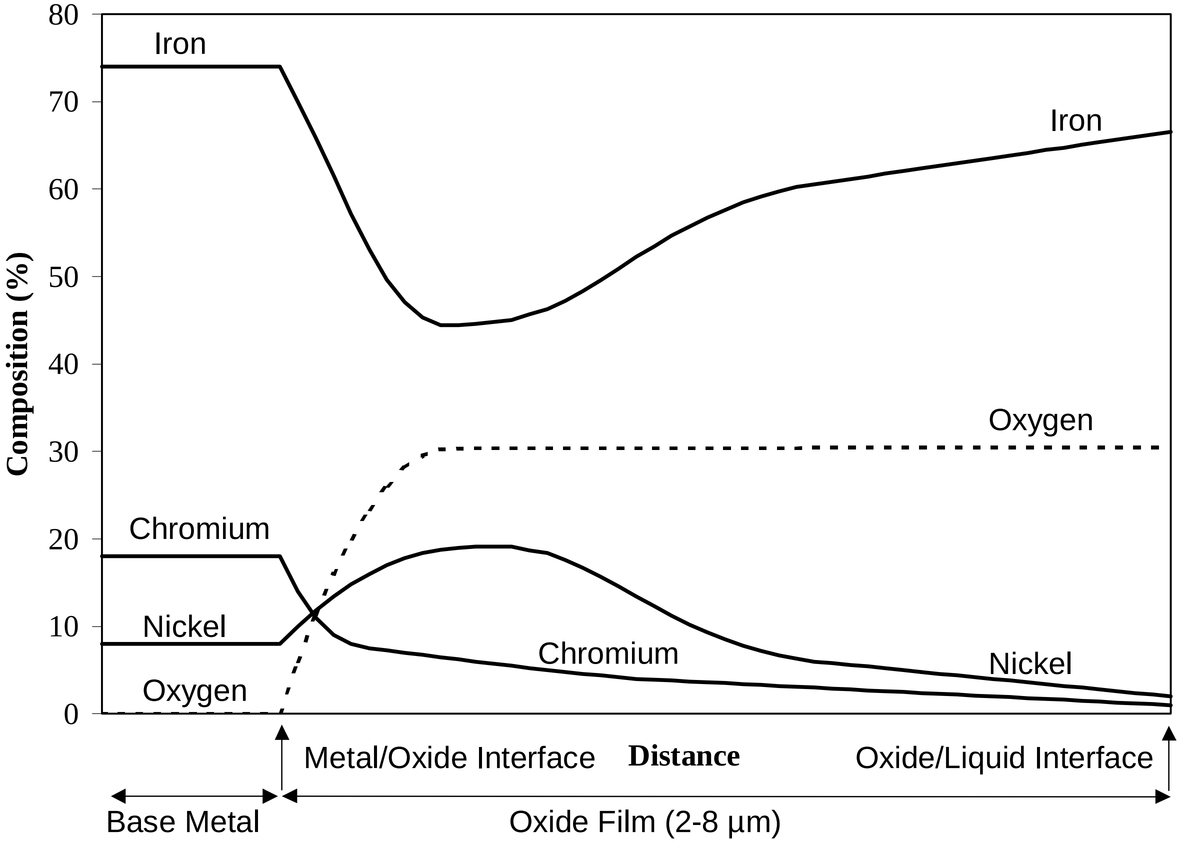

Figure 3-5
Idealized Composition of BWR SS Oxide Film as a Function of Film Thickness

Radionuclides Encountered in Decontaminations

A list of radionuclides commonly encountered in decontamination of water-cooled reactors is shown in Table 3-4. These radionuclides are either fission products from fuel failures, or are formed by activation of the parent that is released to the water by corrosion. This list is not meant to be exhaustive, but it does contain most of the radionuclides that are found in LWRs and CANDU-PHWRs. Information on half-life, gamma energy, and method of formation is also given.

In BWRs, Co-60 is the radionuclide of primary concern for several reasons:

1. it emits two high energy g-rays (1.17 and 1.33 MeV);
2. its abundance (>70% of all radionuclides on out core surfaces);
3. its long half life (5.5 years);
4. on a curie for curie basis, it results in more radiation exposure than most other radionuclides (see below and Table 3-5).

Table 3-4
Radionuclides Commonly Found in Water Cool Reactors

Nuclide	Half Life	Energy	Formation
Cr-51	27.7 days	0.32 MeV	Cr-50 (n,γ)
Mn-54	312 days	0.83 MeV	Fe-54 (n,p)
Fe-55	2.7 years	Soft X-ray	Fe-54 (n)
Co-58	70.9 days	0.81 MeV	Ni-58 (n,p)
Fe-59	44.5 days	1.10 MeV 1.29 MeV	Fe-58 (n,γ)
Co-60	5.3 years	1.17 MeV 1.33 MeV	Co-59 (n,γ)
Zn-65	244 days	1.12 MeV	Zn-64 (n,γ)
Zr-95	64 days	0.72 MeV 0.76 MeV	Zr-94 (n,γ) & Fission Product
Ru-103	39 days	0.50 MeV	Fission Product
Sb-122	2.7 days	0.56 MeV	Sb-121 (n,γ)
Sb-124	60 days	0.60 MeV 1.69 MeV	Sb-123 (n,γ)
Sb-125	2.76 years	0.43 MeV	Sb-124 (n,γ)
I-131	8 days	0.36 MeV	Fission Product
Cs-137	30 years	0.66 MeV	Fission Product
Ce-141	32.5 days	0.15 MeV	Fission Product

In PWRs, Co-58 is the radionuclide of major concern when a reactor is new (<10 years old) since it builds up more quickly than Co-60 and reaches equilibrium much sooner, and there is a large source of the parent, Ni-58, in the steam generator tubes. As the reactor ages Co-60 becomes of concern and together with Co-58 is responsible for >80% of the radiation in PWRs.

Fe-55 is of concern from a waste disposal point of view. It is present in large quantities in some BWRs and may be the dominant radionuclide in waste shipments. It presents no external hazard since it emits neither beta nor gamma rays. It does emit a soft X-ray that is not detectable by standard counting equipment. Specialized counting equipment normally not found at nuclear power plants is required to measure it. If waste shipments are limited based on curie content, this nuclide may make shipment very difficult, or at the very least delay shipment until an accurate measure of Fe-55 is obtained.

Sb-124 and Sb-125 are also of concern since they are not usually removed by dilute chemical decontamination methods. They may be mobilized, transported around the system, and redeposited in different areas, but are not effectively removed. Antimony is best removed with a process based on hydrogen peroxide. Such a process is available from Siemens/KWU and was applied successfully at the three Palo Verde units in 1987-88 (9). Despite the passage of 12 years since that application, the technology remains the best available for removal of antimony.

Table 3-5 gives a comparison of the inventory of several of the more common radionuclides compared to Co-60. This data shows, for example, that a curie of Mn-54 yields only 33% of the radiation exposure of a curie of Co-60. This is another illustration of why Co-60 is the radionuclide of most concern.

Table 3-5
Conversion of Radionuclide Inventories to Equivalent Inventory of Co-60

Radionuclide	Equivalent Co-60
Cr-51	0.013
Mn-54	0.33
Co-58	0.33
Fe-59	0.47
Co-60	1.00
Zn-65	0.21
Sb-124	0.71

Contamination Mechanisms and Activity Transport

Exactly how interior pipe surfaces become radioactive has been the subject of dozens of scientific investigations in several countries, and has resulted in the publication of dozens, if not hundreds, of scientific papers. A representative cross-section of these papers can be found in the following references (6–8, 10–33). In its simplest terms, corrosion of out-core piping in the primary circuit releases both dissolved and particulate material to the circulating water. Wear of hardfacing alloys such as Stellite™ in valve seats can also contribute particulate material. Some of these materials deposit on the fuel cladding in the reactor core and become activated. Cobalt in the form Co-59 is the isotope of principal concern since it readily forms Co-60. However, other isotopes also become activated, as shown in Table 3-4.

The deposits on the core are not fixed but slowly dissolve, or spall, and release the now active material to the water which carries it to out of core surfaces where it becomes incorporated in the outer layer of the oxide film. Experiments have shown that the average residence time of a cobalt atom in-core is of the order of a few weeks. All of these processes are shown schematically in Figure 3-6.

The inner layer also contains activity. It incorporates radioactive ions during the early days of reactor operation while it is rapidly growing and before a protective outer layer has been built up. However, even after the film is established the inner layer continues to assimilate radioactive ions by a combination of solid state diffusion from the outer layer and direct incorporation from the water through the pores in the outer layer. There is no doubt that things happen much more slowly in the inner layer and that it is “older” than the outer layer. Measurements of PWR films have shown decreasing amounts of Co-58 relative to Co-60 in moving from the outer surface in towards the base metal. In the “older” inner film, some of the Co-58 has decayed.

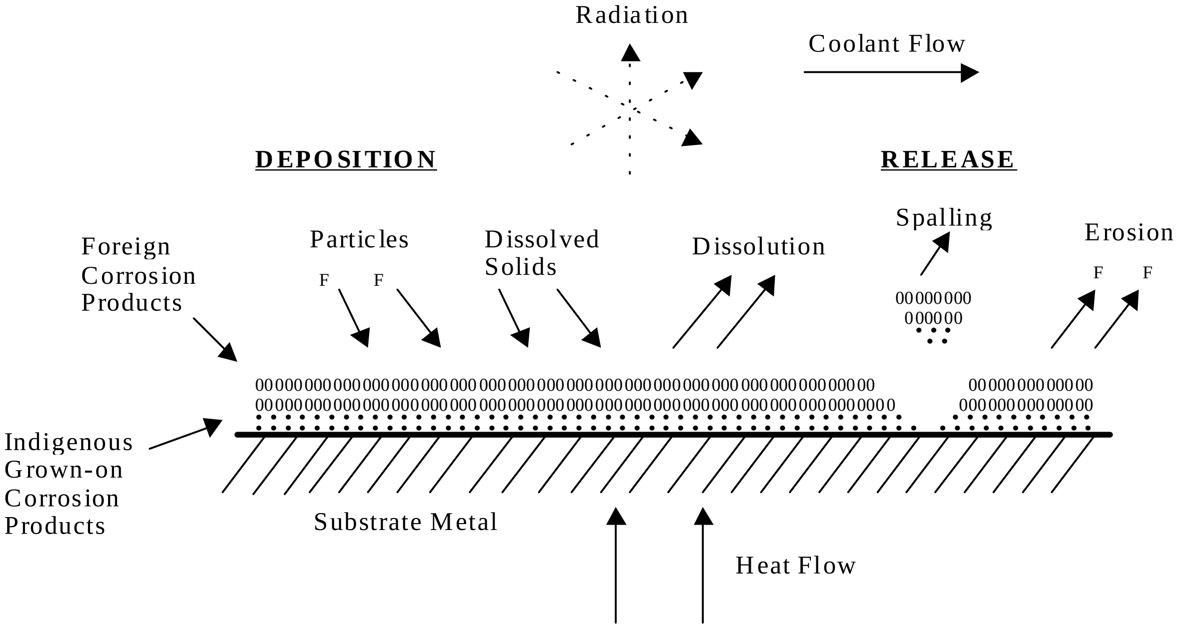

Figure 3-6
Schematic Representation of Process Involved in Activity Transport

Radioactive ions can also diffuse into the pores between grains thus limiting the amount of decontamination that can be achieved with dilute processes. More aggressive processes that remove a few microns of base metal give higher DFs than do dilute processes, which, by design, do not attack the base metal.

Several mathematical models have been developed to explain and predict corrosion product transport and radiation field growth around the primary systems of nuclear power plants. A brief summary of work on activity transport is given in below. A detailed discussion of these models is outside the scope of this report but some of the conclusions drawn from the models will be listed.

1. Cobalt as an impurity in steam generator tube material is the major source of Co-59 in PWRs. Significant reductions in the cobalt source term can be realized by reducing the cobalt content of the SG tube material.

2. Cobalt is released preferentially to other elements. In other words, cobalt has a reluctance to become incorporated directly in the oxide film.

3. Under PWR conditions, chromium remained in the oxide and was barely released at all. Under oxygenated conditions it was released almost totally.

4. High cobalt alloys such as Stellite release particulate material to the system and increase the cobalt source term. They should be replaced with low cobalt alloys.

5. Disturbances in coolant chemistry cause release of corrosion products from Inconel and other surfaces.

6. Increasing the primary side pH in PWRs by increasing the Li to 2 ppm results in much thinner fuel deposits. This means that less material is being deposited in-core and becoming activated.

7. Increase demineralization/filtration to reduce the concentration of soluble and insoluble material in the coolant.

8. Partial system decontamination is a short-term solution since the removed deposit will rapidly reform and incorporate radionuclides from other parts of the system. Complete system decontamination with the fuel in place performed in conjunction with materials replacement where possible, and improved coolant chemistry, are the long term solutions.

Many of these conclusions may seem intuitively obvious, but it is important that a fundamental understanding of the processes involved in activity transport be obtained before committing to changes in the reactor. This stage has now been reached and changes to reactor design and method of operation are being made based on these conclusions.

Radioactivity Inventory in LWRs

Typical values for the amount of radioactivity found in various types of water-cooled reactors are given in Table 3-6. The values in the first two rows for PWRs and BWRs are calculated estimates for a newly shut down reactor and include a large contribution from short lived radionuclides. If the reactor is shut down for months or years, these values will be much lower. Two estimates are given for BWRs; one is based on data available in 1990 (34), while the other is based on more recent unpublished data (35). The large reduction in the estimated activity is due to a combination of factors:

- improved water chemistry
- improved feedwater quality

- reduction in the cobalt source term through gradual replacement of high cobalt alloys such as Stellites with low cobalt equivalents
- use of Optimum Water Chemistry, as recommended by GE, in most plants

In 1990, the large amount of activity estimated to be on BWR fuel made it seem very unlikely that a full system decon with the fuel in place would ever be done. However, more recent estimates are almost an order of magnitude lower and such a decontamination is now considered feasible.

The full system decontamination of Indian Point 2 in 1995 removed about 3,900 curies from the entire primary system. The RPV was in the flow path, but was empty. To date, this is the only FSD performed in an operational PWR in the USA using dilute chemical techniques. It is described later in this report. European and Asian experience with FSDs, which is also described later in this report, indicates that the values given in Table 3-6 for USA PWRs and BWRs are far too high. Their experience shows “hundreds” rather than “thousands” of curies on out core surfaces. This is attributed, in part, to very tight specifications on cobalt impurity limits in the original materials of construction.

Note that CANDU-PHWRs tend to be at the low end. These values are based on actual measurements, not calculated estimates. The lower values are attributed to two major factors:

1. Separate moderator and heat transport systems.
2. Limited use of alloys that contain cobalt, and restrictions on the concentration where such use is unavoidable.

The decreasing trend experienced at the Winfrith SGHWR prior to its shutdown in 1990, is attributed to several factors, which are listed below. Note that the values for activity inventory at Winfrith are also based on measured values, not calculations.

1. Regular, annual decontamination of the entire primary system, including fuel.
2. Gradual replacement of high cobalt alloys such as Stellite valve faces and pump wear rings.
3. Improved water chemistry (lower average conductivity).
4. Improved ion exchange system (higher throughput).
5. Replacement of feed water heaters with more corrosion resistant material.

This demonstrates how the source term, and resulting radiation fields and personnel doses, can be reduced through a combination of chemistry, materials replacement, and decontamination. A further discussion on Winfrith experience is given in Chapter 14 – Recontamination.

Table 3-6
Typical Radionuclide Inventory of Various LWRS and PHWRs[5]

Reactor Type	In-Core	Out-Core	Total
Calculated Values			
PWR (USA)	1,000-2,000	4,000-6,000	~7,000
BWR (USA) (1990 est) BWR (USA) (1999 est)	~128,000 ~16,000	2,000-3,000 ~1,000	~130,000 ~17,000
Measured *Values*			
PWR (IP-2)		*3,900*[6]	
PWR (Europe)		*1,000*	
BWR (Europe & Asia)		*100-300*	
CANDU	*50-100*	*100-200*	*~300*
1980 *Winfrith SGHWR 1986* *1990*			*~3,500* *~1,000* *~400*

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[5] Entries in italics are based on measurements made during FSD applications. Other entries are calculated or estimated values.

[6] This value is not strictly out-core surfaces. The RPV was in the flow path but it was empty. Deposits on the RPV surface are included in this value.

4
HISTORY OF CHEMICAL DECONTAMINATION

Introduction

Decontamination techniques employing concentrated chemical solutions were developed at a number of research centers in the 1950s and 1960s. Extensive programs were undertaken at Oak Ridge, Hanford, Bettis, Knolls Savannah River, General Electric, General Atomics, etc. Much of this work was in support of the nuclear navy for decontamination of reactors on submarines and aircraft carriers. All of this work was, and still is, classified. However, the techniques were applied to a number of experimental land-based reactors and the results were published. The CITROX process and the alkaline permanganate (AP) oxidation process evolved from this work, which has been thoroughly covered by Ayres (36).

Following this splurge of activity in the 1950s and 1960s, there was a slowdown in chemical decontamination. The navy had methods that they could use, and the reactor vendors thought that their reactors would have very low rates of contamination and would never require decontamination over the operational life of the plant. That type of thinking is evident in the design of the plants, most of which have no facilities for decontamination.

Interest in decontamination was rekindled in the 1970s when extensive steam generator maintenance at the Indian Point 1 plant in 1973 resulted in "every welder east of the Mississippi being burned out". The spike in the BWR data in Figure 2-1 at 1973 is due to the work at IP-1. DOW Chemical took the early lead and developed the NS-1 solvent specifically for the Dresden 1 decontamination. Canada got into decontamination when radiation fields around the Douglas Point plant started rising rapidly in the late 1960s. If the same sort of phenomenon occurred with the larger Pickering units, which were under construction at that time, there would be major exposure problems. This work eventually led to the development of the CAN-DECON and CAN-DEREM process, which are described in detail in subsequent chapters. In England, the CITROX process was used for some time at the Winfrith plant, but concerns with corrosion led to the development of a fundamentally different process – LOMI. It is described in detail later in this report. Workers at the Central Electricity Generating Board (CEGB) in England also developed the nitric permanganate (NP) oxidation process.

We tend to think of decontamination as relatively recent development that is confined to the few companies who are in the business commercially today. However, it is a science that is almost as old as the nuclear reactor itself and the modern, dilute techniques that we employ today have their beginnings in the 1950s and 1960s. To fully understand chemical decontamination, it is necessary to be acquainted with the history of the subject and the developments that lead to the methods in use today. The following sections provide some of this background from the perspective of PWRs and BWRs.

Early Experience in Pressurized Water Reactors

A list of PWRs that were decontaminated in the period 1960 to 1980 is given in Table 4-1. Most of these involve concentrated chemical processes, except for the CAN-DECON and LOMI applications towards the end of the table. Three PWRs were decontaminated in the early 1960s - PRTR (twice), Hanford N reactor, and Shippingport. PRTR was a pressure tube type reactor and had stainless steel piping. In 1962 it was decontaminated with alkaline permanganate and oxalic acid (AP-OX) followed by AP and ammonium citrate plus EDTA (AP-ACE). The full primary system with the fuel removed was decontaminated. Decontamination factors in the range 4 - 16 were obtained. The system was again decontaminated in 1965 using the AP-CITROX process. An average DF of 24 was obtained.

Table 4-1
Early PWR Decontaminations

Plant	Process	Results
PRTR	AP-OX, AP-ACE	DF of 4-16. Precipitate with oxalate
PRTR	AP-CITROX	DF 24.
N-Reactor	AP-Sul	DF 4 -10 on SG.
N-Reactor	Phosphoric	DF 3-6 on carbon steel. Annually 1967-1983 .
Shipping-	AP-AC	DF up to 49 but a lot of crud was generated
Various	Hydrolazing	DF 2-3 but rapid recontamination
Surry (Retired SG)	AP/CAN-DECON	Contact DF 50-80. Area DF 5-15.
Surry (Retired SG)	NP-LOMI	Similar results
Ginna SG	AP/CAN-DECON	DF 3-10.

Hanford N-Reactor is also a pressure tube reactor but with carbon steel pipe and stainless steel steam generators. In 1965 the steam generators were decontaminated with the AP and sulfamic acid (AP-Sul) process. DFs in the range 4 - 10 were obtained. In 1967 the carbon steel piping was decontaminated with phosphoric acid in a once-through operation taking about 20 minutes. It was decontaminated almost annually until its shutdown in 1984 using this same technique. DFs in the range 3 - 6 were routinely obtained. World wide, it was second only to the Winfrith plant (see Chapter 12) in the number of lifetime decontaminations.

Shippingport was a more typical PWR with a pressure vessel and steam generators. The primary circuit was decontaminated in 1964 using the AP-AC process. The operation was less successful than hoped. DFs of up to 49 were obtained on the pipes and steam generators, but a lot of crud was generated and in some areas the fields actually went up.

Apart from many loop tests and the continuing annual decontaminations at N-Reactor, these were the last major decontaminations in PWRs until the 1980s. Many experimental reactors were decommissioned in the 1960s and 1970s and the new generation of full-size power reactors did not require decontamination – at least not at that time. Westinghouse, the major PWR vendor was so confident that decontamination would never be required in a PWR that absolutely no provisions were included in the design to facilitate decontamination. This decision was to have a major impact on utilities, maintenance personnel, decontamination vendors, as well as the reactor vendor when replacement of steam generators became necessary in the 1980s. It was at this point that decontamination of PWRs again became a major issue.

A great deal of radiation exposure was being absorbed by workers inside the channel heads taking measurements, effecting repairs, etc. Because of concerns about additional corrosion, many utilities were reluctant to use chemical decontamination techniques to reduce fields. A variety of hydrolazing and grit blasting techniques were used with marginal success. These techniques limit the available DF to a maximum of 5 since they have no effect on shine from the tubes. In practice, they achieved DFs of 2-3. In some cases the fields increased rapidly following start of operation due to an increased roughness (and hence an increased surface area) of the channel head surface. In one case the field increased to more than the original field within one reactor cycle.

In the late 1970s Dow developed a solvent NS-3 specifically for PWR decontamination. It was the sister solvent to NS-1 used in BWRs. It is a two step process, each step taking 100 hours at 250°F. It was never used commercially.

In 1982, the United States Department of Energy agreed to fund two demonstration decontaminations on the retired Surry steam generator, which had been moved to the Battelle laboratories in Richland, Washington for testing and eventual destructive examination (37). The CAN-DECON process with a dilute AP oxidizing pretreatment was used on the cold leg. The LOMI process with a dilute NP oxidizing process was used on the hot leg. LN Technologies (then called London Nuclear) applied CAN-DECON, and Quadrex applied LOMI. Results on both sides were comparable. Contact readings on the stainless steel walls were reduced by factors of 50 - 80, while general radiation fields in the head were reduced by factors of 5 - 15.

Based on this experience LN Technologies obtained a contract to decontaminate the steam generators at the Ginna Station in 1983 using the CAN-DECON PWR process, and Quadrex obtained a contract to decontaminate the Monticello plant using LOMI. Results from both of these applications have been published in the open literature (38, 39). The former was the first commercial application of a dilute process to an operational PWR, while the latter was the first commercial application of the LOMI process in the USA. Both were significant milestones in the development of the decontamination industry.

Early Decontamination Experience in Boiling Water Reactors

A list of the early BWR decontaminations is given in Table 4-2. Most decontamination experience at these units consisted of steam cleaning, brushing, scrubbing and detergent cleaning. Very little of what we think of today as chemical decontamination was performed. This is partly because radiation fields were generally low and partly because there was very little maintenance required in the areas that did have high fields.

Table 4-2
Early BWR Decontaminations

Plant	Process	Result
EBWR	Scrubbing	Reduced fields sufficiently to allow mods.
VBWR	Scrubbing	Similar results.
Dresden-1	Hydrolazing	DF of 100 in refueling canal.
Humboldt Bay	Washing	Reduced fields on pump from 35 R/hr to 200 mR/hr.
Big Rock Point	AP-BiSulf	DF of 2. Smearable reduced by factor of 100.
Vermont Yankee	CAN-DECON	DF of 4 in RWCU.
Dresden-1	NS-1	DF of 11. Pipe fields <10 mR/hr.

In the early 1970s, the Dow Chemical Company was awarded a contract to decontaminate the entire primary system of the Dresden 1 BWR. Radiation fields were rising and maintenance was becoming more difficult. The project was partially financed by the USA government, which foresaw that decontamination might have a role to play in reducing radiation exposure in the future. Tests with available solvents (AP-CITROX and AP-ACE) gave poor results on the BWR oxide film, so Dow developed a new solvent, NS-1, especially for Dresden. Details of the composition of the solvent are proprietary and have never been released. It is known that the solvent contains about 7% solids and is thought to be composed of chelating agents (principally EDTA), reducing agents, and corrosion inhibitors. It is a concentrated chemical decontamination process and required that an extensive waste treatment facility be built on-site at Dresden to handle the large amount of liquid waste that was generated

The decontamination was originally scheduled for the mid-1970s but delaying tactics by various environmental groups were successful in having it postponed many times. It was eventually performed in September 1984 (40). A total of 840 lbs. of iron oxide containing 779 Ci of Co-60 was removed from the reactor. DFs around the reactor varied from 1.4 to 27 with an average of 11.3. Most piping doses were reduced to <10 mR/hr.

The process generated about 600,000 gallons of active, liquid waste. It was concentrated to about 15,000 gallons at which point it was to be solidified using a urea formaldehyde process developed by Dow especially for the NS-1 solvent. Unfortunately, the waste product was shown to have properties that made it unacceptable for burial. It was stored at site for several years. The waste was eventually solidified in concrete and buried.

Prior to its use at Dresden 1, the NS-1 process was tested in a loop at Dresden and in the reactor water cleanup systems at Peach Bottom 2 and 3. After Dresden, a dilute version of NS-1 was offered by Dow. It used NS-1 at 10% of its original strength or 0.7% reagent strength. It was used at Pilgrim where both the primary recirculation piping and the RWCU system were decontaminated (40). It was also used at Dresden 2 where the same systems were decontaminated. Following these applications, the process competed unsuccessfully several times against LOMI, CITROX and CAN-DECON. Finally, in 1987, IT Corporation, who had bought the rights to the process from Dow in the early 1980s, decided to withdraw from the decontamination business. NS-1 has not been used or offered since then.

The Decontamination Industry in the USA

In 1979, London Nuclear, the predecessor of LN Technologies, performed the first commercial dilute chemical decontamination in the United States at Vermont Yankee using the CAN-DECON process (41, 42). Many other decontaminations were performed in succeeding years. In 1984 Quadrex performed the first North American LOMI application at Monticello (39). Since then this process has been applied many times and has become the process of choice for most BWR decontaminations. Both of these processes will be discussed in detail in the following chapters.

Beginning in 1983, other decontamination vendors appeared on the scene. Bechtel, Combustion Engineering, General Electric, and Westinghouse all made brief forays into the decontamination business. Pacific Nuclear, offering a dilute CITROX process, PNS CITROX-A, and LOMI, has performed many decontaminations. In 1988 they acquired a license from AECL for the CAN-DECON and CAN-DEREM processes. Pacific Nuclear is now a wholly owned subsidiary of Westinghouse and is currently the only USA-based company active in the chemical decontamination business.

Bechtel performed a major decontamination of the steam generator channel heads at Indian Point 3 in 1985, the first commercial application of LOMI to a PWR (43–46). It then joined forces with KWU of Germany to offer a variety of decontamination processes and other services to the nuclear industry. The Alliance terminated its interest in the decontamination business in the USA in 1989. KWU continues to be a major player in Europe and Asia, and as part of Siemens has recently reentered the North American market in the area of decontamination for decommissioning. This aspect of decontamination is discussed later in the report.

Westinghouse made a brief foray into the decontamination business in the early 1980s with its DCD process, a modified form of AP-AC (47). Although this process was aimed primarily at PWRs, it was also effective on BWR deposits but was not applied to a plant. In the fall of 1989 Westinghouse purchased LN Technologies and along with it the rights and licenses to the LOMI, CAN-DECON and CAN-DEREM processes. In 1995 they also purchased PN Services from

Vectra, combined it with their in-house capabilities as a result of their purchase of LN Technologies several years earlier, and set it up as a wholly owned subsidiary operating under the name PN Services. As of this writing, that company is now the only North American vendor for chemical decontamination services. PN Services has licenses for all major decontamination processes, including the recently developed EPRI DFD process. See Chapter 13 for a description of this process. They have also developed NITROX, a combination of NP followed by oxalic acid for use on pump impellers. See Chapter 7.

5

CONCENTRATED AND DILUTE PROCESSES

Dilute Chemical Decontamination Techniques

Several of the authors involved in the development of decontamination techniques in the 1950s and 1960s refer to dilute versions of some of the solvents - principally the AC process where a concentration of 1% is referred to as dilute when compared to a more typical 7 or 8% solution. However, true dilute methods, those employing reagent concentrations of <1%, were developed in Canada in the late 1960s and early 1970s. The CANDU reactors use heavy water and a decontamination method was required in which draining of the heavy water would not be necessary. Addition of concentrated reagents to the heavy water would downgrade it from its normal 99%+ D_2O to some lower value at which the reactor could not operate. Draining would require defueling the reactor and even then downgrading would occur because of light water remaining in deadlegs, etc. Therefore a solvent was required that could be added directly to the heavy water without significant addition of hydrogen ions, H^+. The initial solvent considered was P_2O_5, which could be added to the heavy water to form phosphoric acid with no downgrading whatsoever. However, problems with formation of ferrous phosphate films and degradation of some types of valve packing eventually ruled out its use.

The next solvent tested was NUTEK L-106, a proprietary mixture of organic acids and chelating agents sold by the Nuclear Technology Corporation. It is a crystalline solid that could be added as a slurry in heavy water directly to the reactor system where it would dissolve and form the acids in-situ. A concentration of 0.1% was found to be optimum. The only downgrading would result from the protons associated with the acids and any water of hydration. Hydrogen atoms attached to the organic molecules are usually non-labile and do not exchange. Calculations showed that the amount of downgrading was small and would not affect subsequent reactor operation.

The amount of deposit in a CANDU system is more than can be dissolved by an acid of strength 0.1%. Rather than replenish the acid as it was consumed, the concept of regeneration of the acid by ion exchange resin was developed. It is an integral part of dilute processes and is now used by all vendors. It will be described in detail when the CAN-DECON process is discussed.

Since one of the requirements for a decontamination process in CANDU reactors was that the system not be drained, a method had to be developed for removing the reagent and dissolved contaminants at the end of the process. In-situ ion exchange was used. For CANDU applications, the beds were deuterated (converted from the H-OH to D-OD form) before use, but such a procedure is not necessary in LWRs.

The process was highly successful and was applied at the NPD, Douglas Point and Gentilly-1 reactors in Canada in the mid-1970s (48). There was so much international interest, especially because of the environmental and waste concerns being raised over the Dresden decontamination with NS-1, that AECL, the developers of the process, decided to license a private company to market, exploit, and apply the technology, now known as CAN-DECON, on a worldwide basis. Thus was born London Nuclear, the first of the modern decontamination companies. Its history has been described in the preceding sections.

Advantages of Concentrated Chemical Decontamination Processes

- There is a lot of experience with the processes, which have been in use since the 1950s.
- A large number of solvents have been tested so it is easy to pick the appropriate solvent for the particular conditions that exist. Factors to be considered are type of contaminant (fission products or activated corrosion products), type of reactor (PWR or BWR), and type of base metal (carbon steel, stainless steel, or Inconel or a mixed system).
- High DFs are possible (greater than 200 in laboratory tests), but in practical applications the DFs are typically in the range 10 to 50.
- Most processes for dissolving fission products and fuel rupture debris are of the concentrated type.

Disadvantages of Concentrated Chemical Decontamination Processes

- Large tanks are required for mixing the chemicals, and also for draining the system.
- Usually two rinses are required after each step, so a two-step process such as AP-CITROX will produce 6 system volumes of waste. This must be concentrated or solidified prior to disposal since the high concentrations of chemicals usually make processing by ion exchange resin uneconomic.
- Although concentrated chemical solutions are invariably inhibited, corrosion can still be a problem. An extensive materials compatibility program must be performed prior to any application.
- The actual decontamination time may be only one or two days, but the large number of steps in the complete operation generally mean a total time of two to three weeks or more.
- During the oxide dissolution step, all the dissolved activity remains in solution. The specific activity of the liquid may be as high as 3 mCi/ml, resulting in high radiation fields from pipes and equipment. This can present a hazard to station staff and personnel involved in the job.

Advantages of Dilute Chemical Decontamination Methods

- There are no liquid wastes.
- No large tanks are required for either reagent mixing or draining and rinsing, which are unnecessary.
- The entire process can be applied in a short time; typically a few days.

- The low reagent concentration results in low corrosion rates even on mild steels.
- Nuclear fuel is completely unaffected by the reagents, so it can be left in the reactor if a full system decontamination is to be performed. This has been done routinely in Canada and the UK.
- Radiation exposure to personnel during the decontamination is low, since the radioactive impurities are continuously removed from the circulating fluid by ion exchange resin as they are released from the system surfaces. Their concentration in the circulating fluid never reaches a level such that there is a significant radiation field emanating from the system piping.
- When a post-decontamination passivation step is performed, the rate of recontamination is sufficiently low that the benefits can still be realized several years after the decontamination. Even without passivation, recontamination is still low, since the surface is not stripped of all protective oxide.

Disadvantages of Dilute Chemical Decontamination Methods

- Historically, dilute processes have been thought of as giving low DFs in the range of 2 to 5. When AECL started development of the CAN-DECON process, the initial goal was for a process that would give a DF of 2. However, it was soon realized that a much higher DF than this could easily be achieved. Modifications and improvements have resulted in DFs of 5 to 20 being routinely obtained and DFs of 50 being occasionally reported. Dilute processes can no longer be automatically associated with low DFs. Therefore, low DF is not listed as a disadvantage.
- Localized corrosion is possible, since acidic conditions are used in most dilute processes. However, through judicious selection of reagents and conditions, localized corrosion need not be a cause for concern. The large number of successful applications of the LOMI, CAN-DECON and CITROX processes, followed by years of successful operation of the reactor or system without any evidence of corrosion due to the decontamination, is proof of this. Therefore, localized corrosion has not been listed as a disadvantage.
- The end product of most dilute processes is radioactive ion exchange resin. This requires processing and disposal or storage. The volume of resin generated by dilute processes is not large (10 to 30% of the volume of the system being decontaminated). Most nuclear power plants already have facilities for handling ion exchange resins, or the necessary equipment and technology is readily available from several waste processing contractors.
- Most dilute reagents contain chelants. In the USA, the NRC has proposed regulations that would prohibit the burial of chelants with radioactive wastes. There are already limits on the upper concentration of chelants in waste. If new, more stringent regulations come into force, it may require that the reagents be modified or that the chelants be broken down before burial. The newer decontamination processes applied to retired plants prior to decommissioning (described later in this report), in fact, employ such technology. Chelants are a concern because they form highly soluble complexes with most heavy metals and radionuclides. If ground water should enter the disposal site, the possibility of heavy metals and radionuclides being carried into the water supply is significantly greater when chelants are present in the waste.

- Most dilute reagents are based on organic chemicals. These tend to decompose at high temperature and in a high radiation field. Thermal decomposition can be limited to an acceptable rate by maintaining the temperature below 150°C (300°F). Radiolytic decomposition is only of concern if the reactor core with the fuel in place is being decontaminated. In that case, there are inhibitors that can be added to the reagent to reduce the decomposition rate to an acceptable value.

Comparison of Concentrated and Dilute Processes

The features of concentrated and dilute processes are compared in Table 5-1. The newer dilute processes have significant advantages compared with the older concentrated processes. The main argument against dilute processes in the past has been low DFs. Technological advances have improved the processes so that DFs of greater than five are consistently obtained, and DFs of greater than 50 are occasionally obtained. For all practical purposes, modern dilute processes remove the same fraction of activity as the concentrated processes.

The development of dilute oxidizing reagents has made dilute process applicable to all types of light water reactors and heavy water reactors. There have been many applications of dilute processes to BWRs, PWRs and CANDU-PHWRs.

Chemical decontamination processes have been used in the nuclear industry since the late 1940s. Initially, strong acid solutions were employed, but within the last 20 years dilute processes have been more widely used. Concentrated chemical processes will continue to be used for specific decontamination requirements of items that can be moved to a decontamination center. Almost without exception, processes applied to complete reactors and reactor subsystems over the last 20 years, have been, and will continue to be, based almost exclusively on modern, dilute methods.

Table 5-1
Comparison of Concentrated and Dilute Processes

Parameter	Concentrated	Dilute
Waste	Liquid, 3-6 system volumes	IX resin, 0.1-0.3 system volumes
Tanks	Mixing & waste	None required
Rinse steps	Always	Seldom
Precipitation	With certain chemicals	With certain chemicals
Corrosion	High with some materials	Generally low
Inhibitor	Always	Seldom
Activity removal	90 - 99% (DF of 10-100)	80 - 98% (DF of 5-20)
Applicability	LWRS only	LWRS & CANDUS

6

CURRENT SITUATION

Overview

The electric power industry has directed considerable resources at the problem of minimizing radiation exposure in both routine and special maintenance work during outages, and, more recently, prior to decommissioning activities. Reducing out-of-core radiation fields by decontamination represents one of the most cost-effective methods for achieving this and it is not surprising that the use of this technology on commercial plants has grown rapidly, particularly the use of dilute chemical decontamination (DCD)[1] processes. The first "modern" DCD was of the reactor water cleanup system (RWCU) at Vermont Yankee in 1979 (41, 42). Following that initial application, the industry grew rapidly and is now a mature, fully developed technology suitable for:

- component and sub-system decontaminations in both PWRs and BWRs;
- full system decontaminations (FSD) in both PWRs and BWRs, either with the fuel in place or fuel removed;
- decontamination of retired PWRs and BWRs prior to decommissioning work.

The status of DCD technology for both BWR and PWR applications was reviewed by Battelle for EPRI in the early 1980s (49, 50). A more general review of plant decontamination methods was performed for EPRI in 1981 (51), and updated in 1988 (52). The subject has been reviewed in EPRI's decontamination sourcebook published in 1989 (1) and in the three editions of EPRI's Radiation Field Control Manual (3, 4, 5). In addition, technological updates and state-of-the-art reviews have been presented at EPRI decontamination seminars which have been held every year or two since 1985. As of this writing, the most recent seminar was held in Greenville, SC in May, 1998 (53).

In this report, DCD technology is described in detail, and developments since 1989 are presented. These developments are mostly associated with full system decontaminations and decontamination of retired facilities prior to decommissioning work. In 1991, the LOMI process was qualified for FSD applications in BWRs, both with the fuel out the fuel in (54, 55), but to date there have been no applications. The AP/LOMI and AP/CAN-DEREM processes were also qualified in 1991 for FSD applications in PWRs with the fuel removed (56–60). Off-normal, or "fault" conditions were also analyzed (61, 62). This work culminated in an FSD at Indian Point 2 in February 1995 (2, 63). This application is described later in the report. Work to qualify

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[1] All process acronyms are defined in the Glossary at the front of the report.

PWR FSD applications with the fuel in place is currently underway (64–68). Some details are provided in Chapter 12.

There have been four recent decontaminations of retired plants in the USA, one in late 1997 and three in 1998. The processes employed, and the method of application, are described later in the report. There have also been several applications of this type in Europe and Asia. These are also briefly described.

Operational Decontaminations

Although the FSD application at Indian Point 2 and the four decontaminations at permanently shutdown plants were by far the most significant events in the evolution of DCD technology for several years, component and subsystem operational decontaminations continue to be performed at a steady rate. The number of U.S. plants performing operational chemical decontaminations since 1990 is shown graphically in Figure 6-1. The numbers in this graph do not include decontaminations performed by U.S. vendors in countries such as Canada, Korea, Mexico and Taiwan nor those performed by off-shore vendors (principally Siemens/KWU and Électricitϑ de France) in Europe and Asia. The number of U.S. plants performing decontaminations had stabilized at about 10 per year, but in recent years appears to be dropping off. This decrease in operational decontaminations is partially offset by the rise in the number of decontaminations of retired plants, which are discussed in Chapter 13. Of the operational DCDs, about 75% are BWR plants and 25% PWRs. Decontaminations are more cost effective in BWRs since outage maintenance workers tend to spend more time in radiation fields than do PWR workers, e.g., in the drywell, in RWCU heat exchanger rooms, etc. Most plants perform more than one decontamination during an outage so the total number of applications is higher than suggested by Figure 6.1. For example, a BWR plant might use the LOMI process for the reactor recirculation system (RRS) piping and then a dilute organic acid process such as CAN-DEREM or CITROX for the reactor water cleanup system (RWCU). Either application might include an oxidizing step such as alkaline permanganate (AP) or nitric permanganate (NP). Reasons for employing an oxidizing step are discussed later in this report.

A breakdown of U.S. operational decontaminations by process type in the period 1990 to 1998 is given in Figure 6-2. Multiple decontaminations at a given plant are counted separately unless they were all part of a continuous flowpath. For example, LOMI on the recirculation piping, followed by CAN-DEREM on the RWCU, followed by CITROX on a pump, would count as three applications. The most popular process was LOMI (46% of all U.S. decontaminations, but essentially 100% of the BWR recirculation piping decontaminations), followed by CITROX/NITROX (36%) and CAN-DEREM (18%). Oxidizing steps such as AP and NP were employed in every PWR application and in some BWR applications depending upon factors such as:

- composition of the film (was it high in chromium?);
- had the plant been on HWC;
- was a high DF required (i.e. >10), or was the plant satisfied with a DF in the 5-10 range;
- allotted time;

- amount of waste that could be tolerated.

Prior to 1995, when an oxidizing step was required, AP was used in >90% of the applications and NP in <10%. However, since 1995 NP has become the preferred oxidizing step for BWRs on HWC, and for pump impeller decontaminations employing the NITROX process. The reasons for this are discussed in the following chapters of this report.

With few exceptions, the non-regenerative, strongly reducing LOMI process was the process of choice for decontamination of large diameter primary system piping, while the regenerative, mildly reducing organic acid processes were favored for smaller subsystem, heat exchangers, pumps, etc. There are sound technical justifications for this division of the processes. These will also be discussed in the following sections of this report.

In Europe the CORD process continues to be used on a regular basis for both subsystem and full system decontaminations (69, 70, 71). The process is described in the following chapters of this report and some details of the seven FSD applications to date are presented.

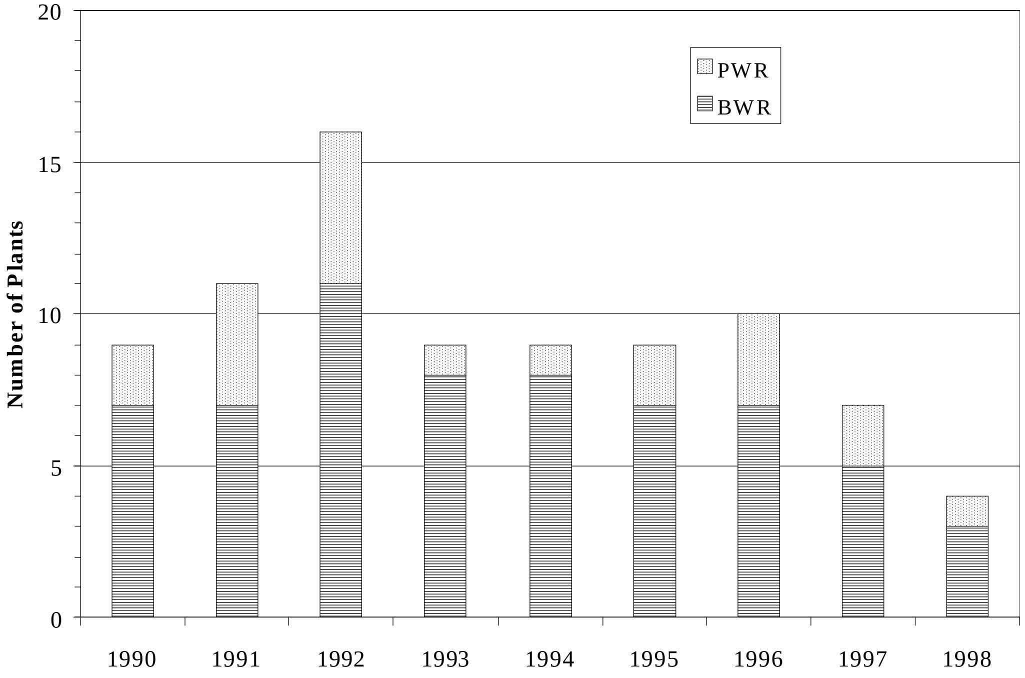

Table 6-1
Number of U.S. Plants Using Operational Chemical Decontaminations

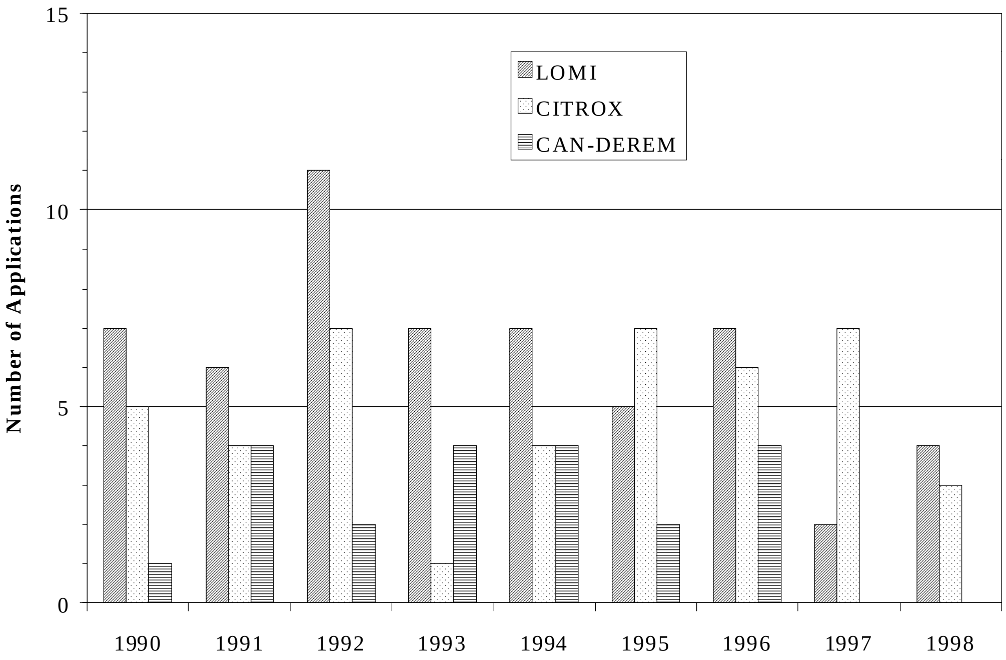

Table 6-2
Number of Operational Decontaminations in U.S. Plants by Process Type[2]

Guidelines for Performing an Operational Decontamination

Reactor Subsystems

Operational decontaminations of reactor subsystems (e.g., RRS, RWR, RWCU, letdown system, etc.) are always performed for ALARA considerations. A cost/benefit analysis is usually performed by the utility prior to the application. For example, it is hardly worthwhile spending several hundred thousand dollars on a decontamination if only 1-2 person-rem are going to be avoided. A general rule-of-thumb that has evolved, is that a major subsystem operational decontamination is only justified if at least 100 person-rem will be avoided in the outage in which the decontamination is performed. This is based, very loosely, on the premise that a major decontamination will cost the utility about $1M, when all is said and done. This includes vendor's charges, waste disposal costs, in-house costs, etc. Assuming a person-rem is "worth" $10,000, the breakeven point is 100 person-rem. Values for a person-rem used by utilities range from $5,000 to $20,000. Obviously, a different value changes the breakeven point. Smaller decontaminations such as an RWCU or a letdown heat exchanger cost much less to perform. For decontaminations of this type, the breakeven point may be as low as 10 person-rem.

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[2] Commencing in 1996, CITROX values include NITROX applications.

Another reason for performing operational decontaminations is to assist a utility in meeting pre-established targets for radiation exposure. If a utility has committed to operation below a certain number of person-rem and major maintenance must be performed, then a decontamination may be required to meet the target, regardless of the results of a cost-benefit analysis.

Yet another reason for performing operational decontaminations is to minimize the radiation exposure of maintenance specialists. They may not be able to work in even moderate radiation fields at several different plants and remain within their annual exposure limit. In cases such as these, a cost-benefit analysis is not relevant.

BWRs

Another rule-of thumb that has evolved for BWRs, is that a decontamination of the RRS is only worthwhile if the average contact radiation field with the recirculation piping is >400 mR/hr. Several utilities have determined that this is the breakeven point for a decontamination to be cost beneficial. However, a partial RRS decontamination of the pumps and isolation valves may be performed for specific maintenance activities regardless of the radiation fields on the upper level piping.

PWRs

An equivalent rule-of-thumb for PWRs is that a decontamination of the RCS is justified if general area fields in the vicinity of the RCS loops are >50 mR/hr. Usually they will be closer to 100 mR/hr. These general area fields can typically be reduced by factor of about 4 (i.e., a DRF of 4) by a decontamination. Note that this rule-of-thumb only applies to those plants with loop stop valves. Decontamination of the RCS loops is not feasible in plants without them.

It is very difficult to assign a radiation field value to other components such as SG channel heads, letdown systems, heat exchangers, etc., above which a decontamination is justified. The value is very site-specific and depends upon the amount of work that is to be done in the vicinity of the component. For these cases, the utility is usually better off performing a cost/benefit analysis of the type described above under Reactor Subsystems.

Reactor Coolant Pumps

For the RCPs, the main reason for the decontamination is to minimize the radiation exposure of specialists who perform the maintenance, not the actual dollar savings. These specialists work both in the plants and at fixed base facilities where the decontaminations are performed. They can't pick up dose in both places and expect to last the year without exceeding regulatory limits.

RCPs typically have contact radiation fields in the range 3-20 R/hr. Chemical decontaminations have resulted in contact DFs in the range 3-100, with 50 being about average (72–75). General area fields about 3 ft away from the pump are typically reduced from about 1,000-3,000 mR/hr to <100 mR/hr. These dose reductions have resulted in exposure savings of 5-50 person-rem per pump. In one sense these reported savings are academic, since the utility would not have permitted such a large dose expenditure on a single maintenance item. On the other hand, chemical decontamination enabled the required maintenance work to be performed with acceptably low radiation exposure.

NITROX is the process mainly used in the USA for RCP decontaminations. It is described in Chapter 7.

EPRI is currently developing a chromium coating process for the internals of pipes, pumps, valves and other components. It is known as the EPRI Stabilized Chromium Process, SCrP. Laboratory work has shown that chromium-plated surfaces pick up activity at a much lower rate than as-received material. SCrP can be applied to complex shapes. It has been used successfully to deposit chromium on the internals of small valves. New York Power Authority's FitzPatrick BWR and PECO's Peach Bottom 3 BWR plan to participate in projects that will lead to the installation of piping and valves with chromium-coated internals either at the fall '99 outage of the spring '00 outage. Because Peach Bottom 3 will later implement NMCA (see Chapter 11), these plant demonstrations will serve to provide data about the effectiveness of SCrP in such an environment.

New work is planned for 2000 that will show that SCrP can be used to treat the surfaces of pump components, such as impellers and casings. As discussed above, maintenance personnel must contend with very high radiation fields when repairing or refurbishing pumps because these components are made from castings that are characterized by porous surfaces that are significant "sinks" for deposited activity. The SCrP should render such surfaces more resistant to activity deposition.

Other Circumstances

An operational chemical decontamination should also be considered under the following circumstances:

- prior to the implementation of DZO so the protective zinc-rich film can form with minimum incorporation of radioactive ions;
- prior to the implementation of HWC to minimize post-HWC dose rates;
- specialized maintenance work is required in a region of elevated dose rates, even if the rule-of-thumb values given above are not met;
- elevated dose rates are present at locations outside containment which result in non-outage exposures (this would normally apply to fuel pool cleanup and residual heat removal systems);
- to remove deposits from fouled heat exchanger heat transfer surfaces and thereby restore heat transfer efficiency.

7
OPERATIONAL DECONTAMINATION PROCESSES

CAN-DEREM

CAN-DEREM is a modification of the CAN-DECON process (from CANDU decontamination) which was developed in Canada by Atomic Energy of Canada Ltd. in the 1970s for use in CANDU reactors (48). The concept of using very dilute reagents (typically 0.1 wt %) and regenerating them on ion exchange (IX) resins, originated with the CAN-DECON process. Minor modifications have made it suitable for use in both BWRs and PWRs (76). The first commercial LWR application was to the RWCU at Vermont Yankee in 1979 (41). Since that time there have been well well over 100 applications of the technology to LWRs in the U.S. by licensees of AECL.

CAN-DEREM is a variant of CAN-DECON. The only difference between the two is that the CAN-DEREM reagent does not contain oxalic acid while the CAN-DECON reagent does. Under aggressive laboratory conditions, CAN-DECON may cause IGA, which can lead to IGSCC on heavily sensitized SS 304. IGA/IGSCC has never been observed in field applications, but concerns of utilities dictated that the process be modified. CAN-DEREM does not cause IGA/IGSCC even under the most extreme conditions (77-81), nor is the effectiveness of the process on LWR oxide films significantly diminished by the elimination of oxalic acid (82). CAN-DEREM is based on a mixture of citric acid and EDTA. The CAN-DEREM concept is summarized in Table 7-1.

The chemicals circulate through the system dissolving the oxide deposits and releasing contaminants from the surfaces. Once in the liquid the contaminants are removed by purification. Dissolved metals and radionuclides are removed by ion exchange resins while particulate material is removed by filtration. The decontamination is terminated by valving out the cation resin and placing on line a mixed bed of cationic and anionic resins. The anionic resins removes the chemical reagents themselves, and the cationic resin removes any remaining dissolved metals. Normal system chemistry is then restored and the system returned to service.

Table 7-1
The CAN-DEREM Concept

Feature	Advantages
Low reagent concentration – typically 0.1 wt %	Minimizes corrosion Inhibitor only required when carbon steel present Permits cleanup with IX resins
Reagent added directly to water in system	Simplifies operation No tanks required for draining of system
Reagent is a soluble powder	Dissolves insitu to form decon solution No need for large chemical mixing tanks
Reagent is a mixture of citric acid and EDTA	EDTA forms a very strong complex with ferric ions eliminating ferric ion corrosion
For full system application, reactor does not necessarily have to be defueled	Simplifies operation Fuel is decontaminated Reduces rate of recontamination
Regeneration of reagent by cationic resin	Continuous removal of dissolved contaminants so radiation fields remain low around equipment Reagent is, in effect, reused Effective concentration much higher than low initial concentration suggests
Removal of reagent by anionic resin	Solid wastes only (ion exchange resins)
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors but pretreatment required if chromium present
Decontamination factors of 5-20	Removal of 80-95% of the deposit and outer oxide film, but <u>does not</u> remove thin, inner protective film

Chemical decontamination involves the dissolution of metal oxides from the system's surfaces. The principal non-chromium containing oxides found in LWRs (chromium oxides are discussed later) are magnetite (Fe_3O_4), nickel ferrite ($NiFe_2O_4$) and hematite (Fe_2O_3). During CAN-DEREM these dissolve by simple acidic dissolution.

<u>Acidic Dissolution of LWR Deposits</u>

$$\underset{\text{acid}}{8H^+} + \underset{\text{oxide}}{Fe_3O_4} \rightarrow \underbrace{Fe^{2+} + 2Fe^{3+}}_{\text{metal ions in solution}} + 4H_2O$$

The EDTA and citric acid prevent redeposition of the metal ions by forming highly soluble chelate complexes.

Formation of EDTA Chelate Complex

$$\underset{\text{metal ion}}{Fe^{2+}} + \underset{\text{chelate}}{EDTA^{4-}} \rightarrow \underset{\text{chelate complex}}{Fe{:}EDTA^{2-}}$$

These chelate complexes breakdown when passed through strong acid cation resin (H:R). The resin breaks the chemical bond between the metal ion and the chelating anion, captures and retains the metal ion, and releases the chelating agent and a hydrogen ion. These are returned to the system to dissolve more deposits.

Reagent Regeneration by Cation Resin

$$\underset{\text{chelate complex}}{Fe{:}EDTA^{2-}} + \underset{\text{cation resin}}{2H{:}R} \rightarrow \underset{\text{captured metal}}{Fe{:}R_2} + \underset{\text{acid}}{2H^{+}} + \underset{\text{chelating agent}}{EDTA^{4-}}$$

Anion resin is used to remove the EDTA and citric acid. Either strong base anion resin or weakly basic Ionac-A365 may be used. The latter has about twice the capacity of the former so only one-half as much is required. Removal of EDTA and neutralization of the acid by anion resin is shown in the following reaction.

Reagent Removal by Anion Resin

$$\underset{\text{acid}}{4H^{+}} + \underset{\text{chelate}}{EDTA^{4-}} + \underset{\text{resin}}{4R{:}OH} \rightarrow \underset{\text{captured chelate}}{R_4{:}EDTA} + \underset{\text{water}}{4H_2O}$$

CITROX

CITROX is an acronym for citric plus oxalic acids. It is a decontamination reagent that was originally developed at Hanford by R.D. Weed (83) for use in the plutonium recycle test reactor (PRTR) (84). At that time it was described as "*the most effective procedure for removing corrosion product films from stainless steel*" (85). The original formula was 0.3 M (25,000 ppm) citric acid plus 0.2 M (58,000 ppm) oxalic acid representing a total reagent concentration of 8.3 wt%, plus inhibitors. In the early 1980s Pacific Nuclear Systems modified the process to produce a dilute version with a total reagent concentration of 0.2%. PNS CITROX A is applied without inhibitors while PNS CITROX B contains an inhibitor for use in carbon steel systems. Both versions are classified as dilute, regenerative, organic acid decontamination processes similar to CAN-DEREM. Although the reagent concentration is double that of CAN-DEREM, most of the features listed in Table 7-1 apply equally well to CITROX. The process tends to be a little more "aggressive" than CAN-DEREM due to the higher reagent concentration and the use of oxalic acid. Approximately double the amount of anion exchange resin is required for cleanup due to the higher reagent concentration. This process remains very popular and was second only to LOMI in the number of applications in the period 1990 to 1998. It is suitable for all LWR main systems, subsystems and components, but has not been qualified for FSD applications.

The most significant difference from CAN-DEREM is the absence of EDTA. This means that ferric ions that are released from the deposit are available to cause ferric ion corrosion since the citrate:ferric chelate is far less stable than the EDTA:ferric chelate. This effect is minimized by ensuring a large enough regeneration flow through cation resin to maintain the ferric ion concentration at <10 ppm. Experience has shown that corrosion is very low below this concentration.

The chemistry of deposit dissolution, chelate formation, reagent regeneration and reagent removal is almost identical to that previously described for CAN-DEREM. The major difference is that citrate ion rather than EDTA is the principal chelating agent.

Formation of Citrate Chelate Complex

$$\underset{\text{metal ion}}{Fe^{2+}} + \underset{\text{chelate}}{Citrate^{3-}} \rightarrow \underset{\text{chelate complex}}{Fe{:}Citrate^{-}}$$

CORD

CORD is an acronym for Chemical Oxidation Reduction Decontamination. It evolved from the OZOX process (from OZone/OXalic acid) in which the original concept was to employ ozone as the oxidizing agent, but because of technical difficulties alkaline permanganate was used for all field applications (86). In the mid-1980s permanganic acid was substituted for alkaline permanganate and the name was changed to CORD. In the early 1990s a UV option was added to decompose the residual oxalic acid and thus reduce the volume of ion exchange resin required (87). This modification is discussed further below. In the mid 1990s a D option was added to make the process suitable for decontamination of retired plants prior to decommissioning work (88-90). This modification is discussed in Chapter 13. CORD is a regenerative, DCD process that consists of four blended steps:

1. Oxidation step. Addition of permanganic acid (HMnO4 or more simply HP for analogy with AP and NP) at a concentration of 50-300 ppm and a temperature of 190°F. This step typically takes 3-6 hours. Permanganic acid is produced by cation exchange of a solution of potassium permanganate as shown in the reaction below. It only exists in solution.

   Production of Permanganic Acid from Potassium Permanganate by Cation Resin

   $$\underset{\text{potassium permanganate}}{KMnO_4} + \underset{\text{cation resin}}{H{:}R} \rightarrow \underset{\text{captured potassium}}{K{:}R} + \underset{\text{permanganic acid}}{HMnO_4}$$

   Oxidation of the chromium in the oxide film by permanganic acid is shown in the reaction below. The chromium is converted from the insoluble Cr_2O_3 form to the highly soluble $HCrO_4^-$ form

Oxidation of Chromium Oxide in Permanganic Acid

Cr_2O_3	$+ 2MnO_4^-$	$+ H_2O$	$\rightarrow$	$2HCrO_4^-$	$+ 2MnO_2$
chromium oxide	permanganate			bichromate	manganese dioxide

Some decomposition of the permanganate also occurs as shown in the following reaction. The manganese dioxide that is formed by these reactions is insoluble and deposits on system surfaces.

Decomposition of Permanganate in Acid Solution

$4H^+$	$+ 4MnO_4^-$	$\rightarrow$ $4MnO_2$	$+ 3O_2$	$+ 2H_2O$
acid	permanganate	manganese dioxide	oxygen	water

2. Reduction step+. Addition of a stoichiometric amount of oxalic acid to reduce the remaining $HMnO_4$ to Mn^{2+}. The chemical reaction involved is shown below. The oxalic acid also dissolves deposited MnO_2 as shown in the second reaction below. If 300 ppm of $HMnO_4$ was used, approximately 550 ppm of oxalic acid would be required. There is no cleanup of the water at this point. Step (iii) follows directly.

Dissolution of Residual Permanganic Acid With Oxalic Acid

$2MnO_4^-$	$+ 5H_2C_2O_4$	$+ 6H^+$	$\rightarrow$ $2Mn^{2+}$	$+ 10CO_2$	$+ 8H_2O$
permanganate	oxalic acid		manganous ion (soluble)	carbon dioxide	water

Dissolution of Deposited Manganese Dioxide With Oxalic Acid

MnO_2	$+ H_2C_2O_4$	$+ 2H^+$	$\rightarrow$ Mn^{2+}	$+ 2CO_2$	$+ 2H_2O$
manganese dioxide	oxalic acid		manganous ion (soluble)	carbon dioxide	water

3. Decontamination step. Addition of an excess of oxalic acid to perform the actual decontamination step. The chemical reaction for dissolution of magnetite in oxalic acid is shown below. Typically about 1,500 ppm is used. In practice, steps (ii) and (iii) are performed as one by the addition of 2,000 ppm of oxalic acid. Indeed, they must be performed as one since the additional hydrogen ions (H^+) required in the above reactions are supplied by the excess oxalic acid.

Dissolution of Magnetite by Oxalic Acid

Fe_3O_4	$+ 4H_2C_2O_4$	$\rightarrow$ $3FeC_2O_4$	$+ 4H_2O$	$2CO_2$
magnetite	oxalic acid	ferrous oxalate	water	carbon dioxide

After all MnO_4^- has been converted to Mn^{2+} by the oxalic acid, a cation exchange column is placed on line. This serves two functions. Firstly, it removes the Mn^{2+} ions produced by reduction of the $HMnO_4$. Secondly, it removes cationic metal species such as Fe^{2+}, Ni^{2+}, Co^{2+}, etc., which are formed as the oxalic acid dissolves the deposit. These chelate complexes breakdown when passed through strong acid cation resin (H:R). The resin breaks the chemical bond between the metal ion and the chelating anion, captures and retains the metal ion, and releases the chelating agent (oxalate) and a hydrogen ion, which are returned to the system to dissolve more deposits. The oxalic acid is regenerated as shown below.

Regeneration of Ferrous Oxalate by Cation Resin

$$FeC_2O_4 + 2H{:}R \rightarrow Fe{:}R_2 + H_2C_2O_4$$

ferrous oxalate	cation resin	captured metal	oxalic acid

4. Decomposition/Cleanup step. Removal of the oxalic acid on anion exchange resin, or decomposition of the oxalic acid by hydrogen peroxide and UV light. The original CORD process used ion exchange resins for the cleanup step, but a recent innovation by KWU/Siemens is the use of hydrogen peroxide and intense UV light to decompose the oxalic acid to carbon dioxide and water (87). The chemical reactions involved for both methods are shown below. The carbon dioxide generated in the second reaction is vented off leaving only the metal cations to be removed by IX resin. This greatly reduces the amount of resin required for reagent removal. A small amount of mixed bed resin is required for final polishing. For a 10,000 gallon system using 1,500 ppm of oxalic acid, this technology results in the saving 25 - 60 ft^3 of anion resin depending on whether high capacity weak base resin or lower capacity strong base resin is used. For a FSD of an 80,000 gallon system involving multiple CORD cycles, it can result in saving approximately 700 ft^3 of ion exchange resin. Not only is significantly less waste IX resin generated, but also the problem of chelates in the waste is avoided.

Removal of Oxalic Acid by Anion Resin

$2H^+$	$+ C_2O_4^{2}$	$+ 2R{:}OH$	$\rightarrow$ $R_2{:}C_2O_4$	$+ 2H_2O$
acid	oxalate anion	resin	captured oxalate	water

Decomposition of Oxalic Acid by Hydrogen Peroxide and UV Light

H_2O_2	$+ H_2C_2O_4$	$\rightarrow$	$2CO_2$	$+ 2H_2O$
hydrogen peroxide	oxalic acid	UV	carbon dioxide	water

The process described above is a single CORD cycle. Most applications employ three to five such cycles. A typical CORD cycle takes 4-16 hours if IX cleanup is employed, and 10-36 hours if H_2O_2/UV decomposition is used. For the first CORD cycle, the oxidizing step with permanganic acid may be omitted if there is known to be an outer layer of deposit that contains very little chromium. This is typically the case in BWRs on NWC.

The CORD UV concept is summarized in Table 7-2 below. Descriptions are also available in the literature (88-90). The only three chemicals the vendor brings to site for a decontamination are permanganic acid (2-4 wt% aqueous solution), oxalic acid dihydrate (solid), and hydrogen peroxide (30-50 wt% aqueous solution). For some applications solid potassium permanganate is brought to site from which permanganic acid is produced in a separate IX module prior to addition to the system.

Table 7-2
The CORD/UV Concept

Feature	Advantages
Four blended steps: Oxidation (of Cr by $HMnO_4$) Reduction (of $HMnO_4$ by oxalic acid) Decontamination (with oxalic acid) Decomposition (of oxalic acid by H_2O_2/UV)	No need to cleanup or drain system between steps Simplifies operation Shorter time Less waste Oxidation step can be omitted for first cycle if low Cr. (Sometimes the case in BWRs)
Oxidation step uses permanganic acid	Faster and more efficient than AP and NP Less waste since lower concentration and no additives such as NaOH or HNO_3. Also no K.
Reduction step performed in-situ with oxalic acid, the same chemical used for the decontamination step	Avoids contact of IX resin with permanganate ion Stoichiometric calculation unnecessary since large excess added so that decontamination step begins as soon as reduction of $HMnO_4$ is complete
Decontamination step is regenerative using continuous flow through cationic IX resin	Mn^{2+} ions from reduction step are removed Continuous removal of dissolved contaminants so radiation fields remain low around equipment Reagent is, in effect, reused. Effective concentration much higher than low initial concentration suggests
For full system application, reactor does not necessarily have to be defueled	Simplifies operation. Fuel is decontaminated Reduces rate of recontamination
Decomposition of oxalic acid by H_2O_2 and UV light	Decomposition products are innocuous (CO_2 and H_2O) No anion exchange resin required for reagent removal No chelates in waste
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors Separate pretreatment step not required - it is integral in the process
Each CORD cycle is independent	Number of cycles can be adjusted according to final dose rate or DF required
Decontamination factors range from 10 to >100, depending on number of cycles	Mildly contaminated components can be cleaned to free release limits

LOMI

LOMI is an acronym for low oxidation state metal ion. It is a chemical decontamination process that was developed by the Central Electricity Generating Board in the U.K., with financial support from EPRI, in the early 1980s (91). It is fundamentally different from the regenerative organic acid processes, CAN-DEREM and CITROX. LOMI employs a strong reducing agent, vanadium (II) tris picolinate, or, more simply vanadous picolinate, to reduce the cations (principally Fe^{3+}) in the oxide lattice by electron transfer from the low oxidation state metal ion, V^{2+}. This process destabilizes the oxide film and it rapidly dissolves in excess picolinic acid.

This process is known as reductive dissolution. It is much faster than simple acidic dissolution and is usually complete within a matter of minutes. However, practical considerations involving reagent addition, transfer of the reagent to all parts of the system, and reagent removal, usually mean that it takes up to about six hours. This is still much faster than the organic acid processes which can take 12 hours, or more.

The LOMI concept is summarized in Table 7-3. The reagent is formed insitu by the simultaneous (preferred) or sequential addition of sodium picolinate and vanadous formate. Although the process is non-regenerative, the total concentration of all chemicals is <1% (typically 0.6-0.7 % or 6,000-7,000 ppm as shown in Table 7-4) so it is still classified as a dilute process and is amenable to reagent removal by ion exchange resins. LOMI will dissolve all iron and nickel based deposits found in water-cooled reactors, but, like the organic acid processes, will not dissolve high-chromium deposits. This aspect is discussed in the section entitled Oxidation Processes.

Table 7-3
The LOMI Concept

Feature	Advantages
Dissolves LWR deposits by reductive dissolution	Much faster than simple acidic dissolution Strong reducing conditions minimize corrosion Higher pH than organic acid processes thus lower corrosion
Reagent is a two-part concentrated liquid (vanadous formate and sodium picolinate) which is added directly to water in system	Simplifies operation No tanks required for draining of system No need for large chemical mixing tanks
Total reagent concentration is <1% so process is classified as dilute	Permits cleanup on IX resin Solid waste only
For full system application, reactor does not necessarily have to be defueled	Simplifies operation Fuel is decontaminated Reduces rate of recontamination
No ion exchange columns online during deposit dissolution	Simplifies operation
Removal of dissolved deposits and spent reagent by cation and anion ion exchange resins in series	Solid wastes only (ion exchange resins)
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors but pretreatment required if chromium present
Decontamination factors of 5 - 20	Removal of 80 - 95% of the deposit and outer oxide film, but does not remove thin, inner protective film

LOMI chemistry is summarized in the reactions below. More detailed descriptions of the process are available (91, 92, 93)

Reduction of Fe^{3+} by Single Electron Transfer

$V(Pic)_3^-$	$+ Fe^{3+}$	$\rightarrow V(Pic)_3$	Fe^{2+}
vanadous picolinate	iron(III)	vanadic picolinate	iron(II)

The ferrous ion is stabilized in solution by complexation with excess picolinic acid. Other ions such as Zn^{2+}, Ni^{2+}, Co^{2+}, etc., which are released into solution as the oxide breaks down, are similarly complexed. The complete reaction for reduction, dissolution and complexation of nickel ferrite is shown below.

Reductive Dissolution of Nickel Ferrite

$NiOFe_2O_3$	$+ 2V(Pic)_3^-$	$+ 9HPic$	$\rightarrow 2V(Pic)_3$	$+ Ni(Pic)_3$	$+ 2Fe(Pic)_3^-$	$+ 4H_2O$	$+ H^+$
nickel ferrite	vanadous picolinate	picolinic acid	vanadic picolinate	nickel picolinate	ferrous picolinate	water	proton

Similar reactions can be written for other ferrites as well as hematite. LOMI will dissolve deposits found in BWRs, CANDUs and the outer layer of PWRs. Like the organic acid processes, it is not effective with deposits which contain >10-15% chromium, i.e. most PWR deposits. A pretreatment step is required to remove the chromium. This technology is discussed later in this chapter.

Ion exchange resins are not used during the reductive dissolution phase (LOMI is not a regenerative process), but are used for cleanup at the end of the process. The absence of an ion exchange column during the actual deposit dissolution process simplifies operations but has the disadvantage that dissolved radionuclides continuously build up in solution. Thus, radiation fields around the decontamination equipment and hoses tend to be much higher during LOMI than during a regenerative organic acid process.

When deposit dissolution is complete, a two-stage cleanup is required – cationic resin to break the chelate complex and capture the metal ions, followed by anionic resin to capture the picolinate and formate ions. The chemical reactions involved are shown below.

Removal of Metal Ions on Cationic Ion Exchange Resin

$V(Pic)_3$	$+ Ni(Pic)_3^-$	$+ Fe(Pic)_3^-$	$+ 7H{:}R$	$\rightarrow V{:}R_3$	$+ Ni{:}R_2$	$+ Fe{:}R_2$	$+ 7HPic$	$+ 2Pic^-$
metal picolinate complexes			resin	metals on resin			picolinic acid	

Removal of Picolinic Acid on Anionic Ion Exchange Resin

HPic	+ R:OH	→ R:Pic	+ H_2O
picolinic acid	resin	picolinic on resin	water

The anion columns will contain very little activity compared to the cation columns. To obtain maximum shielding benefit and minimum radiation fields in the work area, the anion columns are placed in front and the cation columns behind them.

Typical process conditions for a LOMI decontamination are summarized in Table 7-4.

Table 7-4
Typical Process Conditions for LOMI Decontaminations

Parameter	**Concentration or Value**		
	(milliMolar)	**(wt %)**	**(ppm)**
Vanadium (II) formate	8	0.08	800
Formic acid	16	0.07	700
Picolinic acid	36	0.44	4,400
Sodium hydroxide	12	0.05	500
Total - all chemicals	72	0.64	6,400
pH	4-5		
Temperature	180-200 (°F)		
Time	Up to 6 hours		

LOMI-2

The traditional advantages of the LOMI process are its low corrosivity and its effectiveness on certain oxide types, specifically, the nickel ferrite films that occur in BWRs operating under HWC (see Chapter 10). Its chief disadvantages are that it is non-regenerative, which leads to more waste volume than other DCD processes, and LOMI is effectively limited to a concentration of 10 mM vanadium because of solubility restrictions. Thus, there is a limit as to how much oxide deposit can be dissolved in a given volume of decontamination solution. For many subsystem decontaminations this is not a problem. However, there has recently been interest in applying LOMI to the bottom of a BWR reactor vessel where the amount of corrosion product present might be in excess of the amount that can be dissolved in a standard LOMI application. LOMI is not usually chosen for decontamination applications where there is a high deposit loading, or a high surface area to volume ratio. See the following section.

To circumvent this limitation, EPRI commissioned work at Bradtec to see if the picolinic acid could be recycled during the decontamination by using cation exchange resin (94, 95) Vanadium (III) and dissolved metals would be continuously removed and the lost vanadium would be replaced by injection of fresh vanadous formate. Additional sodium hydroxide may also be required for pH control. Operation of the process in this way would remove the restriction of oxide dissolution capacity thus making LOMI effectively regenerative.

The researchers at Bradtec demonstrated that when cation resin is used continuously during the LOMI process, it initially becomes saturated with picolinic acid (in the form H_2Pic^+)[1] but as the decontamination proceeds, the picolinic acid is displaced by metal ions, principally V^{3+} and Fe^{2+}. This process is shown in the following series of reactions where R symbolizes cation resin. Up to 90% of the picolinic acid can be recovered before significant metal leaks into the effluent.

Regeneration of Picolinic Acid During LOMI-2

$HPic + H{:}R \rightarrow H_2Pic{:}R$
picolinic cation captured
acid resin picolinic

$3H_2Pic{:}R + V(Pic)_3 \bullet V{:}R_3 + 6Hpic$
captured vanadic captured picolinic
picolinic picolinate vanadium acid

$2H_2Pic{:}R + Fe(Pic)_2 \bullet Fe{:}R_2 + 4Hpic$
captured ferrous captured picolinic
picolinic picolinate iron acid

The LOMI-2 process is different from the basic LOMI process in the following ways:

- sodium picolinate is injected initially and allowed to circulate;
- vanadous formate is injected slowly and continuously throughout the decontamination as opposed to a single addition at the start of the decontamination;
- cation exchange resin is placed on line when injection of vanadous formate commences;
- spent vanadium (V(III)) and other metal cations (Fe^{2+}, Co^{2+}, etc.) are continuously removed during the decontamination;
- picolinic acid is initially retained by the resin but then is released as metal ions take its place on the IX resin exchange sites;

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[1] In the Brønsted-Lowry theory of acids and bases, picolinic acid is a conjugate base since it can accept a proton due to the presence of the nitrogen atom in its structure. The nitrogen atom is capable of donating a pair of electrons to form a bond with a second H^+ ion.

- additional sodium hydroxide may have to be periodically injected for pH control;
- it is also possible to use anion exchange columns in an advantageous way to preferentially remove formate (which tends to build up in solution due to continuous injection of vanadous formate), but a detailed description of this procedure is beyond the scope of this report.

For the most part, these differences are procedural and require no significant changes in equipment or application conditions.

The advantages of LOMI-2 can be summarized as follows:

- removal of the reagent capacity restriction of LOMI;
- ability to decontaminate systems with a high deposit loading, or a high surface area to volume rations, systems that were previously not amenable to the LOMI process;
- reduction in the amount of picolinic acid required, hence a corresponding reduction in the volume of radioactive waste ion exchange resin;
- reduction in the proportion of chelant in the waste (but does not eliminate chelant);
- continuous removal of radioactive species such as Co-60 results in lower general area radiation fields around the equipment and lower radiation exposure to personnel;
- longer time that V(II) is present in the system, thereby providing additional corrosion protect of carbon steels and low alloy steels.

There are also some disadvantages of LOMI-2:

- formate builds up in the system due to the continuous injection of vanadous formate, but this can be minimized through judicious use of anion columns, as referred to above;
- additional sodium hydroxide is required to maintain the proper pH;
- control of the process is not straightforward because the cation resin first binds then releases picolinic acid. The recycling scheme requires an initial injection into the system of a very dilute LOMI formulation followed by operation of a cluster of small cation exchange columns during the decontamination. Although stability of process conditions is best achieved by a large number of small columns, the technique can be applied with just two or three columns. For the most part, these differences are procedural and require no significant changes in equipment or application conditions.

Based on laboratory scale work, procedures have been developed for plant implementation. A U.S. patent has been obtained. LOMI-2 is now available for plant applications to decontamination vendors who are LOMI licensees.

LOMI Compared to Regenerative Organic Acid Processes

LOMI is a non-regenerative process so the amount of deposit that can be dissolved is directly proportional to the amount of solvent. For systems that have a relatively small surface area to volume ratio (e.g., large diameter piping, steam generator channel heads), the total amount of chemicals required to dissolve the deposit can be added to the system in one step without exceeding the recommended upper limit of concentration (i.e., 10 milliMolar V^{2+}). The LOMI process is very well suited for these types of systems. For systems that have a larger surface area to volume ratio (e.g., heat exchangers in an RWCU or letdown system, long lengths of small diameter piping, etc.), it may not be possible to add the required amount of reagent for the LOMI process without exceeding the recommended concentration limit. In addition, catalytic decomposition of the LOMI reagent (see reaction below) in these types of systems may be severe (due to the large surface area) and additional reagent equivalent to 100%, or more, of the theoretical amount may be required. The use of a regenerative organic acid process such as CAN-DEREM or CITROX that employs a fixed reagent concentration may be the best choice for these types of applications. The amount of deposit that these processes can remove is limited only by the amount of cation exchange resin available. It is usually not a problem to supply as much IX resin as necessary to complete the job.

The LOMI-2 process described above is designed to get around this limitation by recycling the picolinic acid. Once this process has been demonstrated in a plant application, it should put LOMI on an equal footing with the traditional regenerative organic acid processes.

Decomposition of Vanadous Picolinate
(Note: this reaction is catalyzed by metal surfaces)

$$\underset{\text{vanadous picolinate}}{2V(Pic)_3} + \underset{\text{proton}}{2H^+} \rightarrow \underset{\text{vanadic picolinate}}{2V(Pic)_3} + \underset{\text{hydrogen}}{H_2}$$

NITROX

The NITROX process has been recently introduced by PN Services, principally for decontamination of pump impellers (74). Impellers are made of cast material and tend to have small pores into which radionuclides migrate, making effective decontamination difficult. A more aggressive process that can remove a small amount of base metal is required. Such a process is NITROX. The decontamination processes designed for retired plants prior to decommissioning work (described in Chapter 13) would likely also be effective, but to date have not been used for these small applications.

NITROX is a dilute version of CONAP that has been applied by the Westinghouse European Service Center for a number of years with much success. However, CONAP is a concentrated process and is not amenable to cleanup by ion exchange resin. Although it has been applied in the USA, treatment and disposal of the waste involved evaporation and solidification (74). This proved to be difficult, does intensive, and expensive.

NITROX is a modified, dilute version of CONAP in which all wastes can be cleaned up on IX resin in an identical manner to other DCD processes employed in the USA. It is a two-step process consisting of:

1. Nitric permanganate (NP) for oxidation of chromium. This process is described in the following section.

2. Oxalic acid for removal of the chromium-depleted oxide film. It is applied in a regenerative manner similar to CAN-DEREM and CITROX. This technology has been described in the previous sections and will not be repeated here. Oxalic acid is employed in the 1,000-4,000 ppm range (the exact concentration remains proprietary to PN Services) until activity removal drops to very low values. Such process conditions mean that a small amount of base metal is removed. However, since impellers are thick, cast material, loss of a few microns is inconsequential. Potential IGA/IGSCC is also not a concern with cast material.

Several cycles (3-4) are usually applied. DFs in the range 30-60 are typical (74). Although the concentration of oxalic acid is higher than traditional DCD processes, the relative small volume (RCPs are decontaminated in tanks) means that the actual volume of IX resin required for cleanup is not excessive. Typically 10-30 ft^3 is generated per impeller.

Oxidation Processes

CAN-DEREM, CITROX and LOMI work very efficiently with oxide deposits that contain predominantly iron and nickel. If the deposit contains a large amount of chromium (i.e., >10%, approximately) in the form chromium oxide, Cr_2O_3, or a mixed spinel such as iron chromite, $FeCr_2O_4$, it will not dissolve in any of these processes. Chromium (III) oxides will not dissolve by simple acid dissolution in the mild acids employed in CAN-DEREM and CITROX, nor by reductive dissolution in the LOMI process. At concentrations greater than about 10% (there are some reports that LOMI will tolerate up to 20% chromium) (96), it stabilizes the oxide films to dissolution by these processes. Chromium (III) oxides are, however, readily oxidized to the highly soluble chromate, CrO_4^{2-}, or bichromate, $HCrO_4^-$, ions. Chromium-rich deposits dominate the contaminated oxide films found in PWRs and are often found in BWR films, especially those that have operated under hydrogen water chemistry for several cycles. To remove them a chemical oxidation step is required. Although many chemical oxidizing agents will work, those most commonly used in nuclear power plants are based on the permanganate ion, MnO_4^-. Three methods have evolved, alkaline permanganate, nitric permanganate and permanganic acid. Each is discussed separately below.

Alkaline Permanganate (AP)

AP consists of a dilute solution of potassium permanganate (1,000 ppm) and sodium hydroxide (100 ppm). It operates at a pH of 10-11. It is applied at a temperature of 200°F for 6-12 hours. The high pH minimizes production of MnO_2 and also minimizes corrosion. It is the slowest acting of the three oxidation processes but it is also the most benign.

Oxidation of Chromium Oxide in Alkaline Permanganate

Cr_2O_3	$+ 2MnO_4^-$	$+ 2OH^-$	$\rightarrow$ $2CrO_4^{2}$	$+ 2MnO_2$	$+ H_2O$
chromium oxide	perman-ganate	hydroxyl	chromate	manganese dioxide	water

Nitric Permanganate (NP)

NP consists of a dilute solution of potassium permanganate (1,000 ppm) and nitric acid (200 ppm). It operates at a pH of 3-4. It is applied at a temperature of 200°F for 4-6 hours. The low pH results in more efficient oxidation, since permanganate is a much stronger oxidizing agent at pH 3-4 than it is at pH 10-11. However, the low pH and the presence of nitric acid result in it being somewhat more corrosive than AP. General Electric has recommended that it not be used for FSD applications but it may be suitable for subsystem decontaminations, subject to a case-by-case materials review (97). The low pH also promotes decomposition of the permanganate as shown in the reaction below. Thus, more MnO_2 is generated with NP than with AP.

Oxidation of Chromium Oxide in Nitric Permanganate

Cr_2O_3	$+ 2MnO_4^-$	$+ H_2O$	$\rightarrow 2HCrO_4$	$+ 2MnO_2$
chromium oxide	permanganate		bichromate	manganese dioxide

Decomposition of Permanganate in Acid Solution

$4H^+$	$+ 4MnO_4^-$	$\rightarrow 4MnO_2$	$+ 3O_2$	$+ 2H_2O$
acid	permanganate	manganese dioxide	oxygen	water

Recent work has extended the experience base with NP significantly, particularly when it is applied in conjunction with the LOMI process (98). Results from five artifact test programs and three plant applications have been complied into a single corrosion database. The quality and quantity of NP-LOMI corrosion data is now equivalent to any other decontamination process in use. The data provides strong support that the process can be used with minimal risk. This position is especially justified in plants where IGSCC concerns are mitigated with HWC. Despite the positive experience with NP-LOMI for subsystem decontaminations since 1995, a plant specific materials review and an artifact test program are still recommend prior to its use.

There are still some concerns with low alloy steels such as A-106 Gr. B and Inconel 182 welds. These concerns preclude the use of NP-LOMI for BWR FSD applications at this time (at least those which include the RPV), but the possibility exists that it could be qualified in the future for such applications. The extent of additional corrosion testing would need to be addressed on a plant specific basis.

Permanganic Acid (HP)

HP consists solely of a dilute solution (50-300 ppm) of permanganic acid, $HMnO_4$. There are no other additives. It is employed at a temperature of 190-200°F and a concentration of about 300 ppm, although there are reports of it being effective at as low a concentration as 50 ppm (70). At a concentration of 300 ppm the pH is about 2.8-3.0. This low pH results in HP being an even stronger oxidizing agent than NP thus allowing equivalent results with a lower concentration in a shorter time. The process is complete in 2-3 hours. The lower concentration and the absence of extraneous ions such as K^+, Na^+ and NO_3^- results in significantly lower waste quantities than for either AP or NP.

The oxidation reaction in HP is identical to that shown above for NP. Surprisingly, both decomposition and corrosion are much lower than with NP. This is attributed, in part, to the absence of nitrate ions, NO_3^-, which appear to promote corrosion. HP is an integral part of the CORD process previously described, and is widely used by Siemens/KWU in Europe and Asia. It has seen limited commercial use in North America.

Cleanup Following Oxidation Step

Following the application of either AP or NP (HP is discussed separately below), cleanup of the residual permanganate and dissolution/removal of any deposited MnO_2 is required before the actual decontamination step (CAN-DEREM, CITROX or LOMI) can be applied. This can be accomplished in one of two ways:

1. Direct ion exchange to remove all dissolved solids followed by a dilute oxalic acid "wash" or "rinse" to dissolve any residual MnO_2, as shown in the following reaction. A final cleanup on IX resin is then required. This method is the faster of the two and generates the least spent IX resin. The major disadvantage is that permanganate is a strong oxidizing agent and may react with the IX resin. These resin degradation products, which may contain sulfur, may be released from the IX resin and introduced to the plant system.

<u>Dissolution of Deposited Manganese Dioxide With Oxalic Acid</u>

$$\underset{\substack{\text{manganese}\\ \text{dioxide}}}{MnO_2} + \underset{\substack{\text{oxalic}\\ \text{acid}}}{H_2C_2O_4} + 2H^+ \rightarrow \underset{\substack{\text{manganous}\\ \text{ion (soluble)}}}{Mn^{2+}} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2CO_2} + \underset{\text{water}}{2H_2O}$$

2. Conversion of all residual MnO_4^- to Mn^{2+} with oxalic acid, as shown by the following reaction, followed by cleanup on ion exchange resin. Any deposited MnO_2 is dissolved at the same time. The chief advantage of this method is that it avoids contact of the IX resin with the strong oxidizer, $KMnO_4$, and the possible introduction of resin degradation products into the reactor system. The disadvantages are several: it takes longer; it is more difficult to operate the decontamination equipment since much more gas (CO_2) is generated and almost continuous venting is required; more oxalic acid is required; more spent IX resin is generated.

<u>Dissolution of Deposited Manganese Dioxide With Oxalic Acid</u>

$$\underset{\substack{\text{manganese}\\ \text{dioxide}}}{MnO_2} + \underset{\substack{\text{oxalic}\\ \text{acid}}}{H_2C_2O_4} + 2H^+ \rightarrow \underset{\substack{\text{manganous}\\ \text{ion (soluble)}}}{Mn^{2+}} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2CO_2} + \underset{\text{water}}{2H_2O}$$

HP has only been used commercially as part of the CORD process. Conversion of the residual MnO_4^- to Mn^{2+} is an integral part of that process and a separate cleanup step is not required. Should HP ever be used prior to a CAN-DEREM, CITROX or LOMI application, then cleanup by one of the two methods described above would be necessary.

Initial Step in a Multi-Step Process

When applying a multi-step process involving both oxidizing steps and reducing steps, the question is often asked – Which type of step should the application begin with, oxidizing or reducing? This problem has been addressed (99, 100, 101) but there is not a clear-cut answer. Which ever step is applied first, it is going to be less than 100% effective. If a reducing step is applied initially, the presence of some chromium will render it less effective than it otherwise could be. Similarly, if an oxidizing step is applied first, the presence of magnetite, nickel ferrite, etc. serves to mask the chromium and render its oxidation less effective than it could be. A rule-of-thumb sometimes employed by decontamination vendors is that if at least 30% of the activity can be removed by an initial reducing step (i.e., a DF of 1.4), it should be applied first. Less than 30%, an oxidizing step should be applied first. This can only be determined through an artifact testing program prior to the decontamination.

As a general rule, the more steps that are applied, the higher the DF. A four-step process that begins with an oxidizing step will give a higher DF than a three-step process that begins with a reducing step.[2] A five-step process will give still higher DF. Thus, it becomes a cost-benefit issue. How much is the extra step (or steps) going to cost and how much additional dose is it going to save? This question can only be answered on a case-by-case basis using plant-specific parameters.

If the LOMI process is being used there is an additional consideration. Vanadous formate is by far the most expensive of the chemicals employed in DCD applications. If a step is going to be less than 100% effective, it is best not to make this a LOMI step. Thus, for AP/LOMI or NP/LOMI applications, it is usually most cost effective to start with the oxidizing step (AP or NP) and remove as much chromium as possible so that the subsequent LOMI step will be as effective as possible.

Generally, the issue of a 4-step versus a 5-step process only arises for BWRs on HWC and PWRs. For BWRs on NWC, it is almost always best to apply a reducing step first and then evaluate whether an oxidizing step, followed by a second reducing step, is required.

LWR Decontamination Application Techniques

The mechanical techniques associated with applying DCD process to BWR RRS and PWR SG channel heads have been described in the previous edition of this manual (1). The basic

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[2] It is assumed that all applications end with a reducing step. There is little point in "conditioning" the film with an oxidizing step and then not removing the now-soluble oxide that contains the radioactivity. Thus, applications with an even number of steps begin with an oxidizing step, while those with an odd number of steps begin with a reducing step.

techniques for these types of decontaminations have not changed significantly since that time so only a brief overview of them will be presented here. For a more complete description the reader is direct to the aforementioned reference.

BWR Reactor Recirculation System

The majority of BWRs in the U.S. have a RRS consisting of two piping loops, each containing a high flow centrifugal pump complete with suction and discharge isolation valves and interconnecting piping. Most also have decontamination flanges (2"–4" diameter) on the suction and discharge side of each pump. These were originally designed to facilitate decontamination of the pump internals, but have been adapted by the decontamination vendors for complete RRS decontaminations.

The piping on the suction side leaves the vessel through the N-1 nozzles located at the bottom of the annulus. There is a short horizontal section followed by a long vertical run to the suction of the pump. This pipe is typically 24"–28" diameter.

On the discharge side, the large diameter piping connects to a horizontal ring header from which five discharge risers extend vertically upward to where they penetrate the reactor vessel and rise approximately another 10 feet. Once inside the vessel their designation changes and they are called jet pump risers and are considered part of the jet pump assembly rather than the RRS piping. Despite the designation change, each riser is a continuous pipe that is used to contain decontamination fluid during the application. On some plants the two discharge headers are interconnected with a cross-tie line. This line generally contains two isolation valves that are closed during normal reactor operations. However, they can be opened during decontaminations to create a continuous flow path from one loop to the other. This can simplify decontamination of the discharge piping, as will be shown below.

Discharge Side Decontamination (No Cross-Tie)

- Vendor’s decon equipment connected to decon connections at main pumps using flexible hoses (See Figure 7-1)
- Close main pump suction valves; open discharge valves
- Establish flow from Loop A to Loop B using vendor’s pump (main RCPs are not operated)
- When level reaches 2-3 ft up jet pump risers inside vessel, reverse flow at the vendor’s equipment
    - This level ensures that the discharge risers and the horizontal penetration through the vessel will be effectively decontaminated
- High level pump trips to avoid overfilling
- Reverse flow at vendor’s equipment, (typically hourly)
- Transfer system fluid from Loop B (which is now full) to Loop A (which is now empty)
    - Fluid inventory critical – when one loop is full, level should be as low as possible in the other – just sufficient to prevent vendor’s pump from cavitating

- This method of transferring fluid from one loop to another is called “sloshing”
- System heatup with sloshing
- Perform decon with sloshing
- Typical system volume 5,000-6,000 gallons

Discharge Side Decontamination (Plants with Cross-Tie)

- Establish flow path from Loop A to Loop B through ring header and cross-tie valves
- Only necessary to lower level to approximate mid point of ring header (typically a 22” diameter pipe)
- Adjust cross-tie valve so that ΔP is sufficient to force fluid up one set of risers as before
- Reverse flow to drain this set of risers & remix solvent in the ring header
- “Force” solvent up other set of risers
- Reverse flow hourly
- Perform heatup and decontamination as above

Suction Side Decontamination Using Annulus

- Vendor’s equipment connected to decon connections at main pumps (See Figure 7-2)
- Close main pump discharge valves; open suction valves
- Establish flow from Loop A to Loop B via annulus
    - This method requires that the vessel be defueled and drained below the level of the slip-joint
    - Nozzle plugs are discussed below. Their use permits the decontamination to be performed with the vessel full and also avoids passing solvent through the annulus
    - Level critical – nozzle full but below jet pump slip joint
- System heatup with DI water
- Perform decon
- Flow reversal usually performed hourly in each process step
- Typical system volume 8,000-9,000 gallons

Sloshing can also be applied to suction side to avoid flow through annulus (usually requires N-1 nozzle plugs or dams – see below):

- Advantages:
    - less waste volume (lower system volume without annulus)

  - avoids contact of decontamination fluids with potentially sensitive welds in the annulus
  - positive isolation between decon system & RPV requires use of N-1 nozzle dams or plugs
  - isolation of RPV permits other work (e.g., defueling) to proceed in parallel
- Disadvantages:
  - nozzle portion of suction pipe not decontaminated
  - require nozzle dams to isolate suction piping from RPV
  - sloshing rate dependant upon size of vents in suction nozzle dams

Decontamination Behind Nozzle Dams or Plugs

- Nozzle dams can be employed for both discharge and suction side decontaminations
- Plugs or dams must be installed in both the jet pumps and suction N-1 nozzles in the annulus to be of benefit
- Advantages:
  - Decontamination can be performed without defueling and with the vessel full
  - May save critical path time
  - However, cost:benefit analysis must include:
    - Cost of plugs
    - Cost of installation/removal
    - Time for installation/removal (critical path?)
    - Dose received during installation/removal
- Disadvantages:
  - Transfer rates are limited to capacity of vents in various installed plugs
  - Difficulty may be encountered maintaining process temperatures in RRS piping inside vessel
  - Care must be taken during setup to ensure that accurate level monitoring can be maintained throughout decon

Discharge Side Decontamination Using Jet Pump Plugs

- Sloshing performed as before
- Vent size of typical plug (1/4") is too small - limited air flow restricts rate of sloshing
- Upper end of jet pump risers cool due to large gaps of time (~2 hours) between exposures to hot decon fluid, and heat loss to vessel water on OD
- DFs in upper parts of the discharge RRS may be lower for this reason

Suction Side Decontamination Using N-1 Nozzle Plugs

- Sloshing must now be employed
- No continuous flow path available unless spray wands are employed (see below)
- Level usually restricted to below horizontal portion of nozzle
  - May be possible to completely fill nozzle if it can be shown that the nozzle plug can withstand pressure from the back side.
- Nozzle and upper portion of the suction pipe not decontaminated
  - DRF in drywell may be affected, especially at upper levels
- Vent size of typical dam (1/4") is often too small
  - limited air flow restricts rate of sloshing
  - increasing the vent size may not be possible

RRS Decontamination Using Spray Wands

- Can be employed in discharge and/or suction side
  - Establishes a continuous circuit so sloshing avoided
- Only applicable to plants that are going to replace piping since it requires drilling into the main piping
- Improved DFs on higher elevation piping since there is continuous flow and a continuous supply of fresh reagent at system operating temperature
  - Also longer contact time since the system is full at all times
  - Using the sloshing method, the upper regions of the RRS are empty up to 75% of the time
- Discharge Side:
  - A wand is installed in each riser in the horizontal portion where it converts from a discharge riser to a jet pump riser
  - Many holes in wand to spray and wash all regions of horizontal portion of riser
  - Liquid level about 1 foot below elbow in each riser
  - Continuous flow path:
    - Vendor’s equipment to spray wands (header required to distribute flow)
    - Suction taken at decon connections on plant pumps
    - No flow reversal
  - Loops can be decontaminated independently or flow paths can become common at vendor’s equipment (recommended method)
- Suction Side:

  - Main purpose is to avoid flow through the annulus
  - A plug or dam is required in each nozzle to isolate annulus
  - A wand is installed in each nozzle in the horizontal portion
  - Many holes in wand to spray and wash all regions of horizontal portion of nozzle
  - Liquid level about 1 foot below elbow in each nozzle
  - Continuous flow path:
    - Vendor's equipment to spray wands
    - Suction taken at decon connections on plant pumps
    - No flow reversal
  - Loops can be decontaminated independently or flow paths can become common at vendor's equipment (recommended method)
- Single Phase Application
  - By flowing from the vendor's equipment to both discharge side and suction side spray wands simultaneously, it is possible to decontaminate the entire RRS in a single application with obvious savings in time

Discharge Side Decontamination Employing Low Pressure Coolant Injection Connections

- Another method of establishing a continuous flow path is to use the LPCI connections on the discharge risers (See Figure 7-3)
  - They are located part way up the external part of each discharge riser
  - Can establish continuous flow path:
    - From vendor's equipment to one set of 5 LPCI connections
    - Down this set of risers and main discharge piping
    - Cross over to other loop through hose connected at decon connections on pumps
    - Up the discharge piping and risers on second loop
    - Out the LPCI connections and return to vendor's equipment
    - Liquid level can be "forced" up the set of risers on discharge of vendors pump to the appropriate level (usually 1-2' above horizontal portion)
    - Hourly flow reversal as before
  - Advantage is that all of the risers below the elevation of the LPCI connection are exposed to a continuous flow of solvent; only that portion above the LPCI is subject to sloshing

System Fluid Cleanup After Decontamination – Two Phase Application

- Perform “rough” cleanup on both sides
    - Usually means separate cation and anion beds employed for the decon
- When these beds are saturated, switch to mixed bed polishing column
- “Polish” suction side by flowing through annulus; discharge side by sloshing
- Usually have to switch back and forth several times because of small leaks through the main isolation valves; they seldom seal 100%
- Option: Drain system fluid through mixed bed IX to radwaste system to speed up cleanup once acceptable water quality achieved in RRS
    - Advantage:
        - Save time
    - Disadvantage:
        - Some small amounts of residual chemicals may be left on RRS surfaces

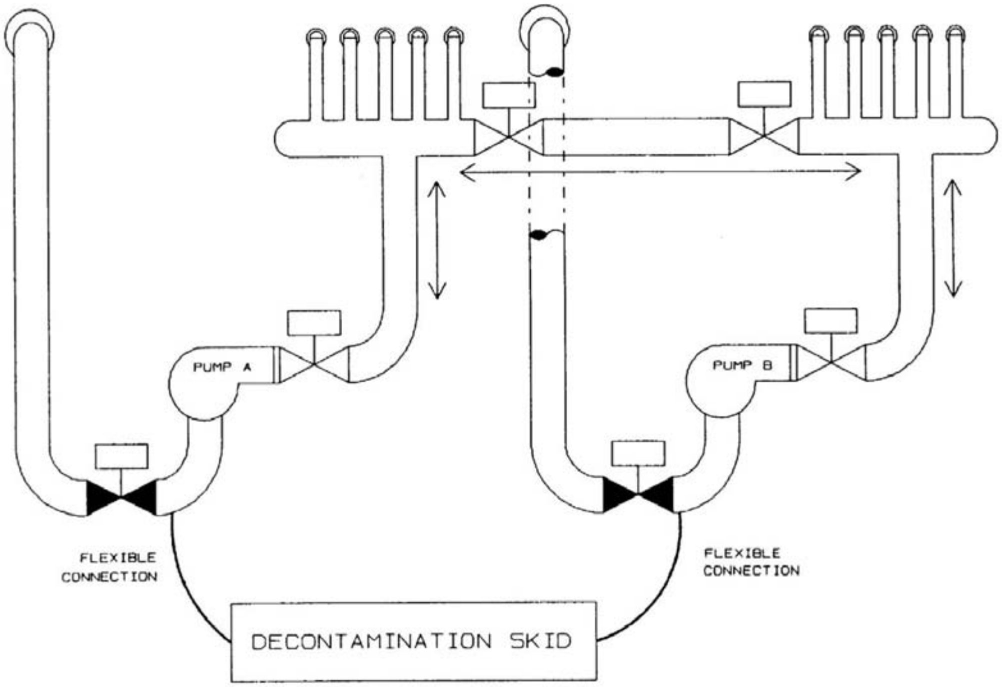

Figure 7-1
Schematic of BWR RRS Discharge Side Decontamination Flow path

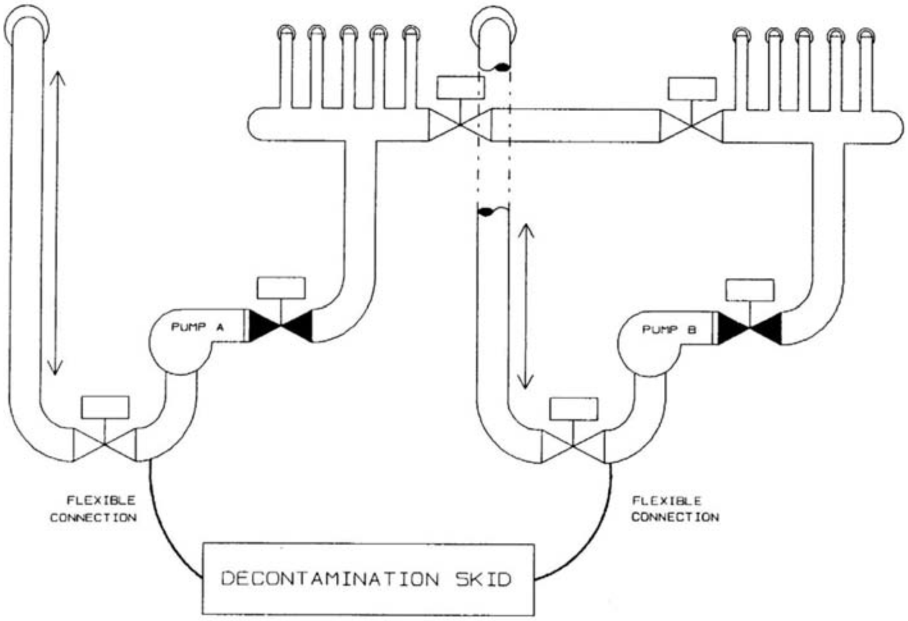

Figure 7-2
Schematic of BWR RRS Suction Side Decontamination Flow Path

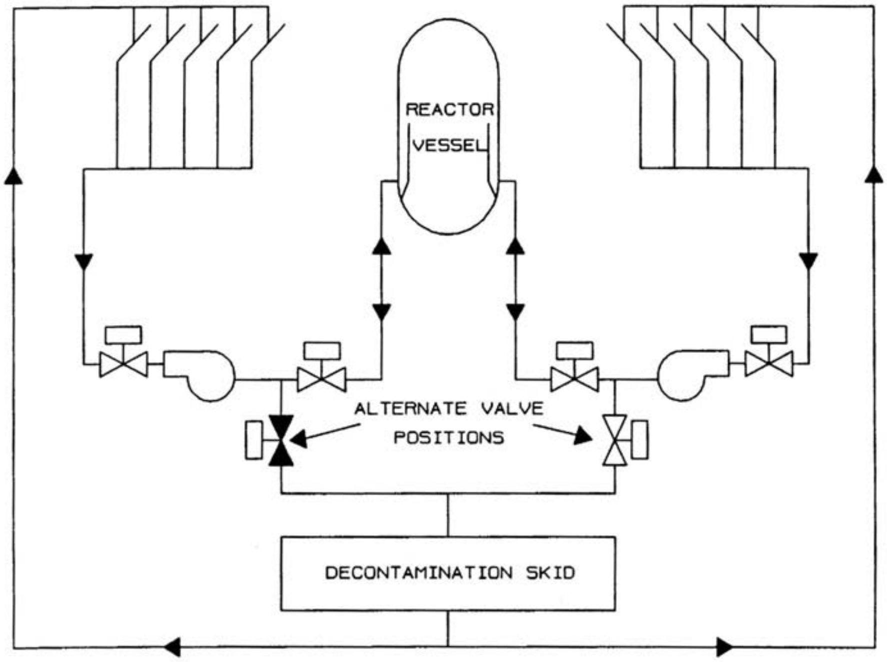

Figure 7-3
Schematic of Discharge Side Decontamination Using LPCI Connections

PWR Steam Generator Channel Heads

Decontaminations are performed in the channel heads of PWR steam generators to reduce the amount of radiation exposure necessary to complete major maintenance activities at the tubesheet on the primary side (e.g., sleeving, plugging, etc.). To maximize the benefit, 2-3' of the SG tubes above the bottom of the tubesheet need to be exposed to the decontamination reagents. This achieves maximum dose reduction while minimizing the amount of radwaste generated. To isolate the SG channel heads from the remainder of the RCS, dam assemblies must be installed in each nozzle (hot leg and cold leg). These are large diameter sealing devices capable of withstanding the maximum differential pressures involved and are compatible with the reagents used.

Access to the channel heads is through the manway openings on each of the hot and cold legs. Temporary manway covers are used to enable the decontamination equipment to be connected to the SG via connections on the covers. Connections are also provided for level instrumentation, venting, and pressurizing. High-pressure, flexible hoses are used to connect the vendor’s equipment to the manway connections. The major components of the vendor’s equipment are a pump, heater, cooler, chemical injection facilities, sampling facility, and ion exchange columns.

Typically, both channel heads of one SG are decontaminated simultaneously. Two approaches are possible – a series flowpath and a parallel flowpath. These are described below. It is possible to decontaminate two SGs simultaneously, resulting in a significant reduction in application time. If a second SG is added to the flowpath, it is usually placed in parallel with the first.

Channel Heads in Series

In this flowpath, system flow is from the vendor’s equipment into one leg of the channel head, out of that leg and into the other, and finally out of the second leg and back to the vendor’s equipment. See Figure 7-4. The pressure drop in the line interconnecting the two channel heads results in a slightly higher level in the upstream channel head. With the correct flow, pressure drop and system volume, a level of 2-3' up the SG tubes can be established on the upstream channel head while the level is just below the bottom of the tubesheet on the downstream channel head. When the flow is reversed, the levels are reversed. With periodic flow reversal, the lower 2-3' of the tubes in each channel head can be decontaminated.

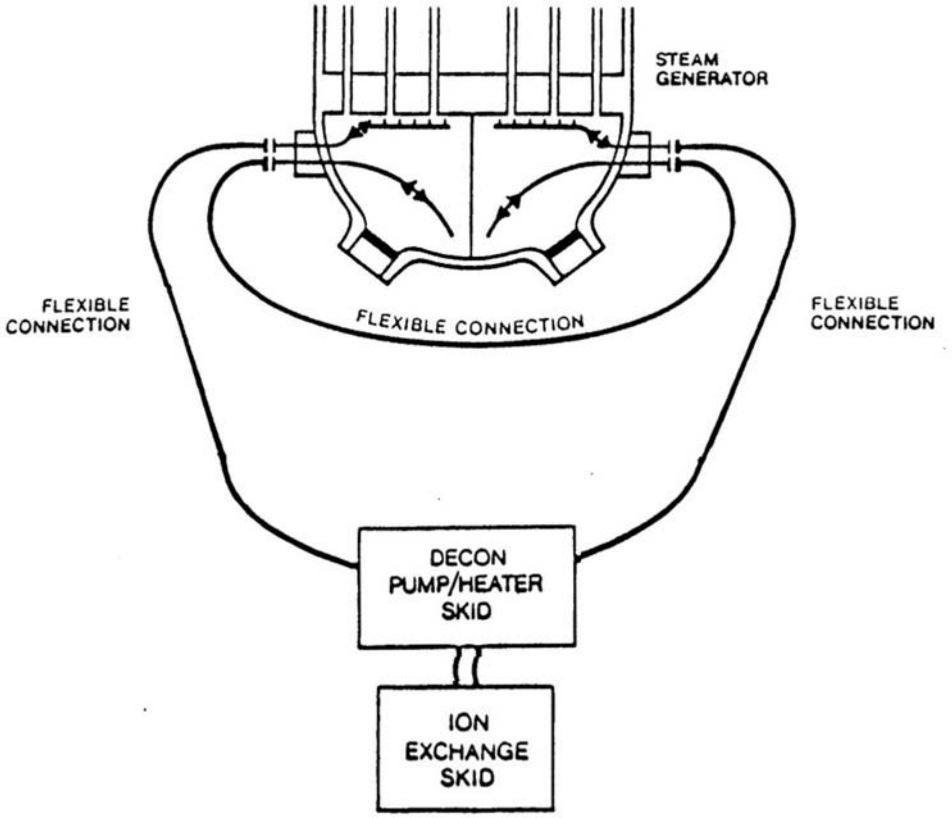

Figure 7-4
Schematic of PWR SG Channel Head Series Decontamination Flow Path

Channel Heads in Parallel

In this flowpath, system flow is from the vendor’s equipment to a header that feeds both of the channel heads. After circulation inside each one, the flow returns to a second header and back to the vendor’s equipment. Level adjustment is achieved by adding and removing system fluid at regular intervals from a supplementary tank that rides on the system.

The advantage of this approach is that it is easier to control the level than with the series method. The disadvantage is that more equipment and flexible hoses are required.

Loop Stop Decontamination

This is a subsystem decontamination option for the 14 Westinghouse PWRs that are equipped with loop stop isolation valves (102, 103, 104). By closing these valves, the RCS loop containing the SG and RCP can be isolated from the RPV. It involves connecting a 500-gpm external

8

DECONTAMINATION CORROSION ISSUES

Corrosion issues and test programs relating to the three major decontamination processes employed in North America, CAN-DEREM, CITROX and LOMI, were reviewed in the Decontamination Sourcebook (1) and in the three editions of EPRI's Radiation Control Manual (3, 4, 5). In addition, a large amount of published data exists for these processes. Therefore, information obtained prior to 1991 will only be discussed briefly as required for continuity. The emphasis of this section will be on tests performed in the period 1991 to 1999. The CORD and NITROX processes have not been previously reviewed, so a brief summary of all published corrosion information will be presented.

CAN-DEREM

CAN-DEREM was developed by AECL from the CAN-DECON process after some tests showed that under certain conditions CAN-DECON could cause IGA of highly sensitized material. The cause was established to be oxalic acid and removal of it from the formulation eliminated all concerns regarding IGA (77-81). The modified process was renamed CAN-DEREM.

The AP/CAN-DEREM process was one of two evaluated by Westinghouse for the full system decontamination at Indian Point 2 (56). More than 50 different reactor coolant system materials were exposed to one five-step cycle and two four step cycles of AP/CAN-DEREM (equivalent to three FSDs) to obtain data on general corrosion, localized corrosion, stress corrosion cracking, and the influence of exposure on other material properties. A separate set of coupons was exposed to one five-step cycle of off-normal (i.e. "fault") conditions (62). The types of evaluations performed included weighing, dimensional measurements, visual examinations, sensitization etching, hardness measurements, surface roughening measurements, and destructive examinations. Key observations from these tests include the following:

- maximum general corrosion metal loss of 50 mils (after three multi-step applications) on A-533 low alloy carbon steel (e.g., reactor pressure vessel and pressurizer);
- less than 1.1 mils general corrosion loss on all other metals, alloys and ceramics;
- slight etching of graphitar;
- color and weight change of Crane packing;
- less than 1 mil of surface roughening on 400 series stainless steels;
- deepest penetrations less than 1 mil on stressed specimens;
- no surface penetration on stressed Alloy X-750 springs;

- chromium plating microcracks opened and interfacial attack under the chromium plate on the Type 410 stainless steel;
- no stress corrosion cracking;
- no acceleration of stress corrosion cracking initiation kinetics on Alloy 600.

These evaluations demonstrated that full RCS chemical decontamination using the AP/CAN-DEREM process can be performed with a high degree of confidence, and that significant impacts on plant equipment will not occur.

Based on these positive findings, a full system decontamination was performed at Indian Point 2 in March, 1995. The application is described later in this report. Examination of corrosion specimens and coupons that were exposed to FSD solvents at Indian Point 2 did not reveal any material compatibility issues that would have an impact on operation of the plant following the decontamination. Detailed assessments are available (106, 107). Key observations were:

- General corrosion of 304 SS, 316 SS, mill annealed Alloy 600, and Stellite™ 6B was at least a factor of two lower than that observed in the qualification program. The first three materials had penetrations of <0.01 mils while Stellite 6B had approximately 0.02 mils.
- Corrosion of 410 SS was higher than expected from the qualification program (0.016 mils expected versus 0.04 mils observed). However the actual penetration was still very low and Westinghouse engineers had previously established that a metal loss of 0.15 mils would still be insignificant (56).
- There were no indications of crack initiation in the 410 SS bent beam, sensitized 304 SS U-bend, Alloy 600 mill annealed reverse U-bend, Alloy 600 thermally treated reverse U-bend, or Alloy 690 reverse U-bend specimens.
- The corrosion penetration of the cobalt-free hard facing alloy, Norem 02, was low (0.01 mils) and there were no indications of intergranular attack or surface roughening.
- The only materials that exhibited any significant corrosion during the decontamination were the Deloro 50 and Colmonoy 4 hardfacing alloys, which suffered corrosion losses of 0.14 and 0.20 mils, respectively. These losses were attributed, in part, to the welding procedure used to fabricate the test specimens.

CITROX

The only published references dealing with corrosion in dilute CITROX date back to the 1980s (108-111). IGA up to 75 µm (3 mils) was reported on stressed specimens and IGSCC was observed on CERT specimens that were subsequently exposed under BWR conditions. The vendor attributed these results to a combination of high ferric iron concentration and high sensitization. Based on work performed at AECL during development of the CAN-DEREM process, it seems more likely that these results were due to exposure to oxalic acid (77).

Ferric ion corrosion can be a problem with CITROX since there is not a strong chelant in the solvent to complex the ferric ions as there is with CAN-DEREM. This concern is minimized in field applications by ensuring that the total dissolved iron concentration is maintained at <20 ppm (<10 ppm preferred) through adequate online cleanup with ion exchange resin.

For these reasons CITROX is generally not employed for primary system decontaminations. It was not one of the processes selected by Westinghouse and EPRI for evaluation for full system applications. However, it is regularly employed for subsystem decontaminations, such as the RWCU, RHR and fuel pool cooling systems, because of its high degree of effectiveness and simplicity of application. Components in these subsystems can more easily be inspected and replaced if required, but in practice replacement has never been necessary. Results from a multitude of field applications have not confirmed the IGA observed in the laboratory testing. This is most likely because in field applications the base metal is protected from direct contact with the solvent for most of the decontamination. It is only for the last hour or two that the base metal is actually exposed. During laboratory testing there is no protective oxide and the base metal is exposed for the entire period of the test. Exposure time is certainly a relevant factor. In the lab testing, specimens exposed to a three-step process (CITROX/AP/CITROX) invariably showed much more IGA than those exposed to a single CITROX step. The difference cannot be attributed to the AP step, which is benign compared to CITROX. See the discussion on oxidation steps earlier in Chapter 7.

CORD

Siemens/KWU personnel have given papers about the CORD process at essentially every conference dealing with water chemistry and decontamination since the third BNES conference at Bournemouth in 1983. They have provided great detail about individual decontamination applications, but very little specific corrosion, materials compatibility, and post-decontamination IGSCC crack growth rate data has been published. A summary of the available information is presented in Table 8-1. This information was extracted from three references (86, 112, 113).

Attack of chromium-plated materials by CORD has been reported (114). This is similar to that reported for the AP step (56, 61) and is undoubtedly due to the HP oxidation step.

Rather than providing specifics about corrosion, Siemens/KWU personnel tend to give more generic statements such as "*All materials in contact with the decontamination chemicals have been tested. No detrimental effects such as material loss or local corrosion have been observed.*" (87), and "*The material compatibility test data for CORD are sufficient to prove that no adverse effects are expected due to decontamination.*" (70). Their current philosophy regarding process qualification can be summarized as follows: "*Due to the number of decontaminations performed, the material qualification tests are increasingly less important. Decontamination processes have been applied in many nuclear power plants for years with good results and without any problems. This practical field experience is better proof of material compatibility than would be possible on a laboratory scale with small coupons*" (115).

Table 8-1
Summary of Materials Compatibility Data for the CORD Process

Material	Corrosion in Typical Application		Visual Observations
	(mils)	(µm)	
SS 304	0.004-0.04	0.1-1.0	Surface roughening of <1 mil
SS 304 welds (bent beam specimen)	.		After decontamination, specimens exposed to BWR conditions. No IGA or IGSCC
SS 308L	0.03	0.8	Surface roughening of <1 mil
SS 321	0.008	0.2	
SS 347	0.02	0.5	
SS 410	0.22	5.6	Slight attack with grain boundaries accentuated
SA 508 Cl. 2 (clad crack specimen)			Pitting 2 mils deep
SA 533 Cl 1 (clad crack specimen)			Pitting 2 mils deep
Alloy 600	0.01-0.03	0.3-0.8	No localized corrosion
Alloy 800	0.015	0.4	
Zircaloy 4	0.0006	0.015	Unaffected. No attack.
DIN 1.4122	0.08	2	
DIN 1.4313	0.08	2	

LOMI

Extensive corrosion testing of the LOMI, AP/LOMI and NP/LOMI processes for subsystem applications was performed in the 1980s (91, 108, 116-119). In the 1990s, evaluations were performed for a full system application of the LOMI process in BWRs (54, 55, 97) and of the AP/LOMI process in PWRs (57-61). The latter program was performed by Westinghouse and was very similar to that described above for the AP/CAN-DEREM qualification program. Results of all these programs can be summarized as follows:

- Corrosion of all 300 series stainless steels and nickel alloys such as Alloys 600 and X-750 showed very low corrosion rates (<0.1 µm/hr) during typical LOMI applications.
- Corrosion of the 400 series stainless steels was slightly higher at 0.5-1.0 µm/hr.
- Carbon steels and low alloys steels exhibit corrosion rates in the range 1-2 µm/hr.
- The above corrosion rates may increase by a factor of between 5 and 10 during exposure to spent and faulted LOMI conditions.
- LOMI does not cause IGA or IGSCC, nor does it exacerbate existing IGA or IGSCC. This conclusion applies to all materials found in BWRs and PWRs, including sensitized stainless steels and nickel alloys, and low alloy steels.
- IGA up to 15 µm (0.6 mils) was observed on furnace sensitized specimens of SS 304 and Alloy X-750 following exposure to six cycles of AP/LOMI under PWR conditions.
- The NP/LOMI process was shown to cause:
    - propagation of IGSCC and TGSCC from fatigue cracks in SA-302;
    - IGA of up to 10 µm in sensitized specimens of Alloy 600, SS 304 and SS 321;
    - enhanced crack growth rate (by a factor of 29) in WOL specimens of A-508;
    - enhanced general corrosion of low alloy steels relative to LOMI and AP/LOMI.

The final result of this testing was that the LOMI process was considered fully qualified for all BWR applications and the AP/LOMI process for all PWR applications. The AP/LOMI and NP/LOMI processes may be acceptable for some BWR applications subject to a case-by-case review and possible additional testing. The same conclusion applies to the NP/LOMI process for PWR applications.

In 1996, additional testing of the AP/LOMI process was performed to qualify it for a “loop-stop to loop-stop” decontamination at the Zion plant (103). Previous qualification testing results were reviewed and compared to the ZION RCS materials for applicability. Those materials that could not be reconciled were tested as part of this program. In addition, extensive testing on mill-annealed Alloy 600 was performed to determine the influence of decontamination solutions on samples with pre-existing flaws. Key observations from this program were:

- Based on measurements obtained on roll transition specimens, C-rings and reverse U-bends of Alloy 600, no appreciable differences in subsequent primary water SCC rates were observed.
- Coupons of SA-182, Grades F11 and F22, showed corrosion losses of 2.9 and 1.7 mils, respectively. There was no enhancement of these rates in crevice environments. Metallographic sections of the coupons showed some roughening of the surfaces on F11 and shallow pitting to a depth of approximately 2 mils on F22. Limited corrosion to this extent is not significant for valve stems and seats.
- Stressed bent beams of SA-182, Grades F11 and F22, above their yield strength gave no indication of stress corrosion cracking or localized attack.

- Low temperature (<200°F) crack extension was observed in both AP/LOMI and pure water reverse U-bend specimens of mill annealed Alloy 600. This result was unexpected. It was attributed to the prior precracking operation in high temperature steam plus hydrogen.
- Apart from the previous observation, the data generated in this program supports the conclusion that application of the AP/LOMI process will not contribute to steam generator tube degradation.

The assertion that the crack propagation observed in the reverse U-bend specimens of Alloy 600 was due to the precracking operation in high temperature steam plus hydrogen could not be definitively proven. Since any risk of increasing the susceptibility of the Zion steam generators to additional PWSCC was unacceptable, the decontamination process for Unit 1 in the 1995 fall outage was canceled. Since the reasons for performing a loop-stop to loop-stop chemical decontamination are still valid, additional testing is warranted to determine the cause of the unexpected crack extension and to verify that the risk of affecting steam generator tube integrity is small enough to be inconsequential.

In the period 1995-1998 additional corrosion testing was performed with the NP/LOMI process (98). This testing was necessary since it had been found empirically that the oxide films formed in BWRs after prolonged exposure to HWC could only be effectively dissolved with this process. See Chapter 10 for additional details. In summary, it was found that:

- The corrosion database for NP/LOMI has been significantly expanded and is now equivalent in both quantity and quality to any other decontamination process in use.
- Several materials qualification programs and in-plant applications provide strong support that the process can be used with minimal risk for RRS and subsystem decontaminations.
- There are still some unresolved issues with respect to FSDs which include the RPV:
    - general corrosion of carbon steels and low alloy steels under faulted LOMI conditions
    - crack propagation in stainless steel-clad low alloy steels
    - dendrite attack in Inconel 182

It remains for the plant owners to work with the NSSS and the decontamination vendors to determine, on a plant-specific basis, if the database is sufficient to support use of the NP/LOMI process. For RRS and subsystem decontaminations, the evidence appears overwhelmingly positive. For FSD applications, the extent of additional corrosion testing would need to be evaluated on a plant-specific basis.

NITROX

General corrosion data for the NITROX process has recently been reported (74). That information is reproduced in Table 8-2. Although no deleterious effects have been observed, more sophisticated localized corrosion tests designed to detect IGA, IGSCC, enhanced crack growth, etc., have not been performed. Some IGA may occur (oxalic acid is well-known to case IGA under certain conditions – see the CAN-DEREM and CITROX sections earlier in this Chapter), but IGSCC is most unlikely to occur in cast SS. The database is sufficient for decontamination of pump impellers, but would likely be considered inadequate for an in-plant application.

The statement is made that *"non-metallic materials in the system should be carefully chosen to ensure durability and long-term solvent compatibility"* (74). This seems to imply that some non-metallics are not compatible with NITROX.

Table 8-2
Summary of Materials Compatibility Data for the NITROX Process

Material	Corrosion in Typical Application	
	(mils)	(µm)
SS 304	<0.01	<0.25
SS 308 welds	<0.01	<0.25
SS 316	<0.01	<0.25
SS 347	<0.01	<0.25
17-4 PH	<0.01	<0.25
CF8 Cast SS	<0.01	<0.25
A-487	0.01	0.25
Alloy 600	0.03	0.76
Stellite 6B	0.03	0.76
1182 W	0.04	1.01
1182 W (sensitized)[1]	0.02	0.51
A-106 Gr. B	2.8	71.1

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[1] These results appear anomalous. Sensitized material general exhibits a higher general corrosion rate than non-sensitized material in acidic decontamination solutions since some of the corrosion protection afforded by chromium is lost at the grain boundaries. However, details of the applications were not available and it is possible that the non-sensitized material was exposed for a shorter time than the sensitized material. Also, there is considerable experimental scatter inherent in corrosion measurements of this type and these values may, in fact, fall within the same range.

9

DECONTAMINATION WASTES

Current Situation

The waste resulting from DCD applications consists almost entirely of spent ion exchange resin. All waste water is usually processed by the decontamination IX system to purity levels such that the plant will retain the water for internal use, or transfer it to the plant's rad waste system for additional treatment and eventual release. If filters were employed during the application, the cartridges or bags are usually placed in the waste container along with the IX resin. More recently, backwashable filters have been selectively employed to eliminate handling of highly radioactive cartridges or bags and thus minimize radiation exposure of the DCD crew. These filters can be backwashed to either the plant's rad waste system or the DCD IX system.

In the 1980s, the preferred method of disposal of spent IX resins was solidification in cement followed by burial at one of the three licensed waste disposal sites - Barnwell, Richland or Beatty (120, 121). However, during some LOMI resin solidifications, the mixture did not solidify adequately. The problem was attributed to the use of lime for pH adjustment (122). Although waste processing vendors adjusted their formulations to alleviate the problem, they eventually adopted dewatering of resins and disposal in a high-integrity container (HIC) as a more cost-effective and trouble-free processing method. From the late 1980s through the early 1990s, this was the preferred method of disposal of resin wastes from LOMI applications, (i.e. dewatering in HICs followed by direct burial of the HIC).

In the late 1980s, tests with stabilized cement monoliths of CITROX, CAN-DEREM and CAN-DECON IX resin wastes demonstrated that they could potentially crumble once buried (123). This indicated that the existing test program to demonstrate 300 year stability was faulty and that the current cement formulations did not guarantee long term stability. New requirements were placed on waste processors, which forced them into lower waste ratios in the cement mix to increase the compressive strength of the product (124). This increased the waste volume and hence the cost of disposal. Thus, dewatered resin in HICs also became the preferred option for organic acid resin wastes.

In the mid-1990s the use of concrete overpacks for HICs was instituted by the State of South Carolina as part of more stringent licensing requirements for continued operation of the Barnwell site beyond 1995, not because of any technical problems with HICs. However, this requirement was rescinded in the late 1990s and as of this writing, dewatered resin in HICs is the preferred and accepted method of disposal at Barnwell. If the resin contains between 0.1% and 8% chelants, it is designated a "chelant waste" and the resin must be segregated from other wastes at the burial site. A surcharge is applied for chelant wastes. Barnwell has an upper limit of 8% chelants in the waste. Wastes that contain >8% chelants are not accepted at Barnwell.

At Richland there is no upper limit on the chelate content of the waste. However, the site does require that chelated wastes (>0.1 wt%) be stabilized and segregated from other wastes. In practice, this means the resin is dewatered in a HIC. If a high density polyethylene (HDPE) HIC is used, it is placed in an engineered barrier. This site only accepts waste from the northwest states and those belonging to the Rocky Mountain Compact.

The Envirocare site in Utah has been in operation since the 1970s, accepting very low level (<10^{-3} µCi/g) waste from naturally occurring radioactivity. Recently it has received a license amendment to allow Class A waste to be accepted. This may permit the anion and polishing resins from DCDs to be buried there, but it is unlikely that the cation resins, which contain most of the radioactivity, would meet the Class A requirements. Mildly radioactive scrap from decommissioning applications, for which it is not cost effective to continue decontamination to free release limits, would likely meet the Class A requirements and be acceptable for burial. The advantage of this approach is cost. Burial charges at Envirocare are approximately a factor of 10 less than at fully licensed burial sites that can accept up to Class C wastes.

Another option for nuclear power plants is long term storage of the IX wastes on the plant site pending opening of the WIPP site which is being designed to accept greater than Class C wastes. However, this is certainly not the preferred option and would only be used as a last resort.

Mixed Waste Issues

Mixed wastes are defined as those that are both hazardous and radioactive. Such wastes cannot be buried at any of the licensed radioactive waste disposal sites. The one component of decontamination wastes that has the potential to create a mixed waste is chromium. The EPA defines a waste as toxic (or hazardous) if a representative sample of the leachate from the waste contains >5 ppm chromium (125). Preparation of the leachate is defined by the toxic characteristic leach procedure, TCLP (126). It involves leaching the sample with a solution of acetic acid adjusted to a pH of 4.5. Provided the chromium content of the leachate does not exceed 5 ppm, the waste can be classified as nonhazardous. To date, all decontamination resin wastes have easily passed the TCLP requirement.

Recently the EPA has proposed a revised rule that would dramatically lower the allowable chromium concentration in the leachate. Should this rule be passed into law, some of the decontamination resins might not pass. If this happens, a nuclear utility would have to store the resin on site pending opening of a disposal site which will accept mixed waste, or find a treatment technology that would allow the waste to meet the new requirements.

Waste Classification Issues

The NRC has defined three classifications for radioactive wastes for near surface burial – Class A, Class B or Class C – based on their radionuclide content (127). Those which exceed the values for Class C (generally referred to as “greater than Class C”) are not acceptable for shallow land burial. Generally, the most restrictive criterion for decontamination wastes is that applied to *“alpha emitting transuranic nuclides with half-life greater than 5 years”*. Their concentration must not exceed 100 nCi/g to avoid being greater than Class C. For plants that have had a history of fuel failures, it may be necessary to replace ion exchange columns during the decontamination based on TRU concentration rather than allowing the resin to become fully saturated chemically. Depending upon the level of TRU in the plant, this may result in several times more waste being generated than would be necessary if the resin could be 100% utilized. To date, there have been no instances where the TRU level was so high that the solution described above was impractical.

Future Developments

Over the last 15 years, many techniques have been proposed for volume reduction of waste resins and for alternative solidification methods (120, 121, 128-134). These techniques include:

- bituminization
- resin oxidation
- vitrification
- biological digestion
- acid digestion
- incineration
- drying (vacuum, hot air, microwave)
- compaction/super compaction
- ELOMIX waste treatment process

Some of these are no longer viable for technical reasons (e.g., bituminization) while others continue to show promise but are being funded at a very low level, if at all (e.g., resin oxidation and ELOMIX). New technologies that have recently been, or are still being studied include:

- Scientific Ecology Group (SEG), in conjunction with Molten Metals, has developed a Catalytic Extraction Process (CEP) for ion exchange resin (135). This results in a significant volume reduction factor of the resin. However, there are strict limits on the dose rate of the waste and at present it does not appear that decontamination resin wastes will be acceptable.
- Chem Nuclear has partnered with GTS Duratek to form DuraChem. DuraChem is planning to install a vitrification system at Barnwell to process IX resins but the facility has yet to go into the construction phase. Here again there are likely to be limits on the radionuclide content and/or dose rate of the waste, potentially making it unsuitable for decontamination resin wastes.
- Studsvik has announced a pyrolysis technology for IX resin that is to be installed at a former nuclear fuel fabrication site in Tennessee (136). This technology was developed in Sweden and has been fully tested in that country. The USA facility is now operational with non-radioactive IX resins. It should be fully operational with radioactive resins in late 1999 or early 2000.
- Vectra developed the Enviroglass™ vitrification process (133), which is suitable for decontamination resins, but has not pursued the technology.

All of the above methods have the potential for significantly reducing the volume of IX resin by factors of at least 30. All operate at sufficiently high temperatures to destroy any chelant on the resin, thus eliminating the concern about the 8% chelant limit. However, the concentration of radionuclides in the residue from such processes will increase by the same ratio as the volume reduction factor. For example, a waste that was only at 10% of the Class C limit for TRU (10 nCi/g), would see the concentration in the residue rise to at least 300 nCi/g thus making it greater than Class C and unacceptable for shallow land burial. One solution being studied is to blend such waste with other waste that has a negligible TRU loading. Another option is to store the residue pending opening of the national repository for waste that is greater than Class C.

As of this writing several resin treatment processes on the horizon may supplant the existing technology of dewatering in a HIC followed by shallow land burial. However, none is yet in commercial operation and it is likely that the existing technology of dewatering in HICs will be the principal method of disposal of decontamination resin wastes for the next several years.

10

EFFECT OF HYDROGEN WATER CHEMISTRY (HWC) ON DECONTAMINATION

Background

HWC was proposed by General Electric in 1977 to reduce oxygen levels in BWR primary coolant, which would in turn reduce the susceptibility of the primary system piping to stress corrosion cracking. It was first employed at Dresden-2 in June, 1983. Additional plants adopted the technology and by November 1995, 14 BWRs in the USA were operating under HWC (137). By November 1998, the number had increased to 24 (98), 55% of the 44 operational BWRs. In addition, 11 off-shore BWRs have also implemented HWC.

It was recognized early in the program that the change in redox potential from oxidizing conditions (+0.3 V vs SHE) to less oxidizing (~0 V vs SHE), and eventually to reducing (–0.23 V vs SHE), would have some effect on the composition of the oxide film on system surfaces and might affect the effectiveness of decontamination processes. However, over the next 10 years very little effect was observed. Decontamination factors of 5-10 were routinely obtained with a single step application be it CAN-DEREM, CITROX or LOMI. Addition of an oxidizing step, generally AP, increased the DFs to >10. But commencing with the decontamination at Monticello in February, 1993, some difficulties began to be encountered. A DF of only 2 was obtained in an RRS decontamination even though three steps (LOMI/AP/LOMI) were applied. Monticello had been on HWC for four years at this time. During earlier decontaminations in 1989 and 1991, DFs in the range 10-30 were obtained (138).

Recent Experience

An experience similar to that at Monticello occurred at Brunswick (139). HWC was initiated in Unit 2 in 1989 and in Unit 1 in 1990. Three RRS decontaminations were performed in the period 1990 to 1993 with DFs in the range 5-10 being obtained. However, in 1994 a DF of only 1.5 was obtained following a decontamination of the Unit 2 RRS even though a three-step process was used (CITROX/AP/CITROX). Artifact testing prior to a similar decontamination of Unit 1 in 1995 showed a DF of only 2 with both a three-step AP/LOMI and a three-step AP/CITROX decontamination. Addition of two more steps increased the DF to about 4 in both cases. This was still well below the utility's goal of a DF >10. Substitution of NP for AP resulted in a DF of >100. Based on this result a two-step process (NP/LOMI) was applied in the plant. The initial LOMI step was eliminated based on the artifact testing which indicated negligible activity removal. The application was highly successful with a DFs of 11 and 54 being obtained on the RRS discharge and suction sides, respectively

The reason for the failure of AP and the success of NP at Brunswick is due to changes in the oxide composition brought about by prolonged exposure to HWC at hydrogen concentrations of 1-2 ppm in the feedwater. When HWC was first initiated at Brunswick, the concentration of H_2 in the feedwater was <1 ppm. Over the next few years it was slowly increased to 1-2 ppm on the advice of General Electric when new data indicated that <1 ppm H_2 did not provide adequate protection against IGSCC to all vessel internals. Analysis of the oxide film in 1995 indicated a high proportion of chromium (39%) and some nickel (15%) (98). The oxide film appears to become more tenacious and protective after prolonged exposure to HWC. "Low" HWC (i.e., <1 ppm H_2 in the feedwater) does not appear to have a significant effect on the film composition. This is the reason for the apparent lack of effect of HWC observed during the first 10 years of operation with HWC, as discussed above. "High" HWC (i.e., 1-2 ppm H_2 in the feedwater) appears to have a much more rapid effect on the formation of high chromium and high nickel films. Recent research has concluded that a film containing substituted chromites and nickel ferrite is most effectively removed through the use of the NP/LOMI process (98). AP does not result in adequate oxidation of the chromites formed under HWC. The poor result obtained with AP at Brunswick was not due to zinc. Monticello uses GEZIP while Brunswick does not and both experienced the same result.

Numerous scientific papers describe the reasons for the change in composition of the oxide film in BWRs under HWC and the effect HWC has had on radiation fields. A cross-section of these papers can be found in the following references (137, 139-149).

A recent decontamination at Plant Hatch (150) also required use of the NP oxidation step for effective decontamination. This plant had been on HWC since 1987 and on GEZIP since 1991. As at Brunswick, it appears that a tenacious and recalcitrant deposit had formed. NP was used as the oxidation step during decontamination of the reactor recirculation and reactor water cleanup systems, while AP was used during decontamination of the fuel pool cooling system. The latter was not exposed to HWC and so had not developed the more intractable film. Good decontamination factors in the range 4 to 37 were obtained on the various systems.

The HP/CORD UV process also appears to be effective in dissolving the oxide film formed under HWC. A recent decontamination of the RRS at Santa Maria de Garoña achieved an average DF of 40.7 with two cycles of HP/CORD (151). Three cycles had been planned, but the third was cancelled because of the satisfactory DF after two cycles. The plant had been on HWC for 13 years at the time of the decontamination.

11

EFFECT OF ZINC INJECTION ON DECONTAMINATION

BWRs

A mid-1980s review of BWR radiation field buildup found that so-called "natural zinc plants" had significantly lower radiation fields than those without zinc (152). It was determined from theoretical considerations and laboratory testing that the presence of zinc results in a much thinner and "tighter" oxide film that significantly reduces the rate of incorporation of Co-60 (153). Zinc ions preferentially displaced cobalt in the oxide lattice. These observations eventually led to the GEZIP™ process in which approximately 10 ppb zinc (in the form of zinc oxide, ZnO) is injected into the feedwater of BWRs to reduce the rate of radiation field buildup (154). An overall evaluation of zinc injection and recommendations with respect to decontamination for plants implementing zinc injection is available (155, 156).

When this technology was implemented in 1986, there was concern that it might affect the effectiveness of the currently available decontamination processes. Would this "tighter", zinc-rich oxide be more difficult to dissolve? However, decontamination experience at several BWRs employing GEZIP has allayed these concerns. For example, DCDs at Millstone-1 in 1987 (157), three plants in the period October 1991 to February 1993 (158), and four plants in the period June 1993 to November 1995 (138), all of which were on GEZIP (some were also on HWC), generally resulted in DFs typically associated with DCDs, i.e. 5-15. Some of these DCDs employed an oxidizing step while others did not. The requirement for an oxidizing step was based on the amount of chromium in the oxide film to be removed and the DF required. It did not appear to be directly related to zinc injection. Although some of the laboratory studies suggested that the thinner, tighter film formed in the presence of zinc would promote a chromium-rich inner layer (159), field experience has shown that this does not necessarily occur to a great enough extent to automatically warrant an oxidizing step. Some BWRs on zinc injection require an oxidizing step to obtain satisfactory DFs while others do not. The identical situation exists with plants not on zinc injection. Plants operating on "high" HWC all require an NP oxidizing step regardless of whether zinc injection is employed or not. In summarizing the effect of zinc injection on decontamination effectiveness, various authors have made statements such as:

- *"results equal to or better than 1984 decon"* (157),
- *"zinc had no impact"*(157),
- *"no apparent effect on decons"*(138).
- *"for NWC plants which have operated with zinc injection, the modified oxide film is not more difficult to dissolve than the oxides at other NWC plants"* (98)

- *"for HWC plants that have operated with zinc injection, the modified oxide film is not more difficult to dissolve than the oxides at other HWC plants"* (98)
- *"the decontamination effectiveness using either AP or NP appears to be unaffected by zinc injection"* (98)
- *"the decontamination results are independent of whether DZO or NZO is used"* (98)

No additional information is available as of this writing to dispute these statements. The addition of zinc to BWR feedwater appears to have negligible effect on DCD processes currently used on a commercial basis.

The most notable effect of zinc injection is the amount of Zn-65 removed by a DCD. Traditionally Co-60 accounts for 60-80% of the activity removed during a BWR decon with Zn-65 being a very minor contributor, i.e., typically <5%. However, for those plants on zinc injection, Zn-65 typically accounts for 30-50% of the activity removed. In one case Zn-65 accounted for 173 out of the 229 total curies removed (75%) (157). Such large inventories of Zn-65 partially or totally offset the benefit of a reduced Co-60 inventory. This problem is being addressed through the introduction of DZO – depleted zinc oxide (156, 160). Natural zinc contains 48% Zn-64 which can be activated to Zn-65. Depleted zinc contains <1% Zn-64 (the other isotopes of zinc undergo negligible activation). The use of DZO will have no additional effect on the ability of current decontamination processes to dissolve LWR oxide films. To date this effect has been negligible, as discussed above.

PWRs

Because of the success of zinc injection in BWR plants for exposure reduction, programs were initiated to evaluate zinc injection for PWRs, with the potential benefits expected to be:

- thinner, denser and more protective oxide films (161);
- lower rate of incorporation of Co-60 into the oxide films hence lower radiation exposure (162, 163);
- mitigation or inhibition of primary water stress corrosion cracking (PWSCC) on Alloy 600 steam generator tubes due to the presence of a more protective oxide (162, 164)

To date there has been no experience with decontamination of a PWR using zinc injection. There have been no decontaminations at the lead plant currently employing the technology, Farley Unit 2 (162, 163, 165). One of the reasons there has not been a decontamination at Farley is that radiation fields have generally remained low, thus reducing the need for decontamination. There has also been very little laboratory work with zinc-rich films formed under PWR conditions. Zinc injection has recently been started at Diablo Canyon 2 and Palisades, but as of this writing there is no data relevant to decontamination.

Based on experience from BWR plants, it seems that zinc injection will have little effect on the ability of current decontamination processes to perform effectively. However, prudence dictates that an artifact testing program be performed the first time such a decontamination is to be undertaken. If, for example, a zinc-rich outer layer has been formed (zinc ferrite?), it may be imperative to remove it by an initial reducing step, rather than applying an oxidizing step that would be totally ineffective. A cost-benefit assessment may have dictated that a four-step process be performed (i.e. start with an oxidizing step) (99, 101), but technical considerations could override it. At this time such a scenario is purely hypothetical but it serves to illustrate the type of situation that could arise with zinc injection. Until there is a significant database of experience with decontaminations of PWRs on zinc injection, an artifact testing program prior to a decontamination should be considered almost mandatory.

In addition to the references cited above, several papers on zinc addition to reactor circuits, principally PWRs, were presented in 1996 (166). The reader is referred to these papers for a more complete discussion of zinc addition to PWR primary circuits.

Noble Metal Chemical Addition

General Electric has determined that the ECP of vessel internals must be controlled to –0.23 V (vs SHE), or lower, to assure that no IGSCC initiation occurs (137). This is done by maintaining 1-2 ppm H_2 in the feedwater, as discussed above. Recently, GE has discovered that addition of small amounts of noble metals (Pt and Rh) at low concentrations (~60 ppb each) via the RHR, coats internal plant surfaces and provides a catalytic effect that makes the available hydrogen more effective in reducing the ECP (167-169). The net result is that the hydrogen concentration in the feedwater can be reduced to about 0.2 ppm while achieving even lower ECPs than with 1-2 ppm hydrogen (–0.5 mV vs SHE). GE has patented this technology under the trade name NobleChem™. It is also known in the industry as NMCA, noble metal chemical addition.

Duane Arnold was the first plant to use NMCA technology. The process was applied there in October, 1996 and will be reapplied in the fall of 1999 at the end of two 18-month fuel cycles after the initial application (167). There are several EPRI reports that describe this project (170-175). Preliminary indications are that radiation fields are lower than expected, thus reducing the need for decontamination. This may be an additional benefit of NMCA. Peach Bottom Unit 2 was the second plant to employ the technology in October, 1998. As of this writing, 14 BWRs worldwide are committed to applying NobleChem™.

There are several implications for decontamination of plants using NMCA:

1. The much lower hydrogen concentration may slow down conversion of hematite to a spinel-type structure, making decontamination “easier”. The situation may revert to that of the first 10 years of HWC, i.e., no noticeable effect on decontamination. Once again, it may be possible to decontaminate BWRs with a single step process, or, if an oxidizing step is required, the less corrosive AP may suffice instead of resorting to NP.

2. On the other hand, the long-term effect of the very much lower ECP (–0.5 V vs SHE) on oxide film structure, composition and morphology is unknown. The technology is designed to lower the ECP of the coated stainless steel component and the theory behind this is well-documented (167). However, there has been no discussion in the literature of possible effects on the overlying oxide film composition.

3. If the entire system behaves more like a PWR, which traditionally have lower radiation fields than BWRs, then NMCA may lower the rate of radiation field buildup, thus reducing the need for decontamination. Indeed, there is some preliminary evidence from Duane Arnold that this is the case.

4. The presence of small amounts of Pt and Rh in the oxide film is not expected to have any direct effect on the ability of DCD processes to dissolve the film. General Electric has determined their concentrations to be in the range 2-5 atomic %, or ~0.2 μg/cm^2 (168). Using Cr as an analogy, it has no noticeable effect on decontamination until its concentration becomes >10%.

12

EXPERIENCE WITH FULL SYSTEM DECONTAMINATION

Introduction

Full system decontamination (FSD) refers to chemical decontamination of the entire primary system of the reactor, including the core. FSDs may be performed with or without the fuel in place. There are many benefits of FSD when compared to smaller subsystem decontaminations (176), the principal ones being:

- general reduction in radiation fields all around the plant, with consequent saving in radiation exposure of all the workforce and not just those involved with maintenance on a particular system;
- reduced rate of recontamination since the major source of radionuclides (i.e. in-core deposits) will have been removed, assuming the decontamination was performed with the fuel in place;
- longer interval between subsequent decontaminations because of the lower rate of recontamination.

The earliest reports of FSD are at the plutonium recycle test reactor (1962 and 1965), a pressure tube reactor, and at Shippingport (1964), a prototype PWR (177). These FSDs employed concentrated (i.e., 5 to 10%) chemical solutions. As of 1979 the Hanford N-reactor, a pressure tube PWR, had been decontaminated 10 times with the fuel in place using 8% phosphoric acid (178). There are also reports of regular FSDs at Rheinsberg (70 MWe PWR - Germany) and Novo Voronezh-1 (265 MWe PWR - Russia) (179).

Commencing in 1969, the Winfrith SGHWR, a unique pressure tube BWR, was decontaminated annually with the fuel in place. Up to 1985, 21 FSD applications had been performed (there are two primary circuits and each is decontaminated separately) (180). Prior to reactor shutdown in 1990. the total had been extended to 31 (180). Between 1985 and 1990 these FSDs at Winfrith employed the LOMI process and so are directly relevant to the FSD program in the USA, thus they are discussed separately below.

Since 1975 there have been 13 FSD applications at various CANDU plants in Canada using the CAN-DECON process (182). All have been with the fuel in place. Since these applications represent a significant database of FSD experience with a DCD process, they are discussed in more detail below.

In 1984 the entire primary system of the retired Dresden-1 plant was decontaminated using full-strength NS-1 solvent (concentration of active ingredients is ~7%) (40). This solvent is no longer used commercially so no additional description of this FSD will be given.

Commencing in 1991, KWU has performed eight FSDs employing the CORD process (69-71, 87-90, 113-115, 183). Since this is one of the processes described in detail in this report and is being used on a regular basis in Europe and Asia, this experience is described in more detail below.

In the USA, work on qualification of the LOMI process for BWRs (54) and the AP/LOMI and AP/CAN-DEREM processes for PWRs (56, 57, 60–62) commenced in 1987. All qualification work is now complete (55, 59) but to date there has been only one application – the Indian Point 2 FSD using the AP/CAN-DEREM process in March 1995 (63). The qualification work and the actual application are summarized in the sections below.

Experience at the Winfrith Steam Generating Heavy Water Reactor

A total of 31 decontaminations were performed in the Winfrith SGHWR in the period 1969 to 1990 – 16 on the south circuit and 15 on the north circuit.[1] Ten (five in each circuit) were performed with TURCO 4521, a proprietary mixture of ammonium citrate and oxalic acid similar to concentrated CITROX. The rest have used LOMI. The plant changed to LOMI in 1980 for two main reasons (184):

1. corrosion of the stainless steel rolled joints, critical components, had reached a total of 12 mils (310 µm) and further corrosion at the rates experienced with the TURCO reagent was unacceptable; LOMI would give much less corrosion;

2. the DF was being limited by the slow buildup of a chromium-rich film and it was thought that LOMI would dissolve chromium better than the TURCO reagent.

Although LOMI did result in much less corrosion, chromium continued to build up and limit the DF. Eventually the NP oxidizing process had to be employed. It was applied three times in the south circuit and twice in the north circuit. Thus, all major components were exposed to at least 15 decontaminations and two NP steps. Some common parts of the system (e.g., the blowdown lines and chemical injection system) were exposed to all 31 applications. Through all these decontaminations no significant problems were encountered that could in any way be attributed to the decontaminations. There was no evidence of any long term effects on any of the reactor internals or any other close tolerance components. There was no evidence to suggest premature wearing of valve stems or packings, or of pump seals or bearings. None of these components required increased maintenance or more frequent replacement because of the decontaminations. The TURCO product did cause some minor corrosion of the 410 stainless steel rolled joints as mentioned above, but the amount was still well below the allowance that had been assigned for decontamination. When the change was made to the LOMI process in 1980, corrosion of these

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[1] This prototype plant was shutdown in 1990 for economic not technical reasons.

components essentially ceased. LOMI decontamination of the reactor with the fuel in place became routine at Winfrith and was performed annually in both circuits from 1980 until the plant was shutdown in 1990.

Each of the 31 decontaminations included the nuclear fuel. Some fuel assemblies were decontaminated up to five times. When removed from the reactor, the fuel came out deposit-free. There was no evidence of any problems. On the contrary, only beneficial effects were observed. These included:

- fuel life was prolonged;
- surface temperatures were kept lower;
- heat transfer was improved;
- the potential for failure due to overheating was reduced;
- a major source of radionuclides for recontamination was removed.

Prior to beginning plant applications with TURCO in 1969 and with LOMI in 1980, Winfrith staff performed a complete validation exercise. This included a wide variety of corrosion tests with all materials found in the plant, and decontamination of an irradiated fuel assembly in a shielded test loop. A comprehensive post-irradiation examination was then performed. No unacceptable corrosion was observed on any materials or components so permission was granted to apply the processes in the plant.

Experience with CANDU Pressurized Heavy Water Reactors

A total of 13 full system decontaminations have been performed in Ontario Hydro CANDU reactors since 1975 (182). Seven different CANDU reactors have been decontaminated. Two of the reactors have had three decontaminations, two have had two and the rest have had one. There have been no instances of excessive corrosion, premature wear or failure of any components that could in any way be attributed to decontamination. Virtually every material and component in the reactor was tested prior to the first application. This testing included coupon-size corrosion tests, full size components in a large test loop, fuel bundles with gross defects, end fittings, full scale pumps, and all type of valves, flanges, sealing mechanisms (Graylok couplings and Cono Seal fittings) representative of those found in the reactor. Following this successful testing, the CAN-DECON technology was further tested in a small prototype reactor (NPD) before being used in a large plant. No unacceptable corrosion was observed so permission was given to use the process in a full scale plant. There has been at least one comprehensive examination of all critical components following a decontamination. Nothing unusual was observed. All components appeared normal.

There is an initial crud burst immediately following chemical injection. Crud concentrations may be as high as 100 ppm initially but then steadily fall over the course of the decontamination due to a combination of dissolution, removal by filters and a steadily decreasing release rate. Eventually 10 to 20% of the activity is removed as insoluble particles on the filters. This is remarkably similar to experience at Winfrith except there the particles were allowed to continue circulating and partially dissolve during the decontamination. They were eventually removed during the cleanup phase.

The staff of Ontario Hydro consider the use of filters mandatory during a full system decontamination. In 1990 they upgraded the filtering capability to provide a filtration half life of 15 minutes. This is in direct contrast to Winfrith experience where filters were not used. The reasons for the different philosophies seem to lie in reactor design. The Winfrith plant did not have areas that were susceptible to deposit settling, so the particles could be allowed to circulate until removed in the cleanup phase. Winfrith had vertical pressure tubes with single ended (top) refueling while CANDUs have horizontal pressure tubes with double ended refueling. CANDU reactors have a crud trap at each endfitting on the reactor faces. Since this is the area where maximum field reduction is required, it is important to minimize crud settling by removing as much of it as possible as quickly as possible.

One other important aspect is the way in which particulate material is released. Experience at both Winfrith and the CANDUs indicates that there is a crud burst immediately after chemical injection. The concentration of particles slowly drops off with time as the particles are either removed, dissolve, or settle out. In order to maximize the effectiveness of the filters, the filtration half-life must be kept as short as possible right from the beginning of the decontamination.

Decontamination of the reactor with the fuel in place is routine in Ontario Hydro reactors. All 13 full system decontaminations have been performed in this manner. There is little direct benefit in decontaminating the fuel, since the deposits are very thin and removal of them does not result in the same benefits as observed at Winfrith. However, not having to remove the fuel before a decontamination avoids expending a large amount of critical path time.

No special precautions are taken because of the presence of failed fuel. It is not removed prior to decontamination. There is no evidence of fuel breakup or increased fission product release or exacerbation of the failure because of decontamination. In fact, laboratory tests have shown that fission product release during CAN-DECON is less than during normal operation. If any reagent is trapped in the defected fuel assembly, it is expended when the fuel temperature increases at reactor start-up and has not caused increased fission product release.

Experience with the CORD Process

Since 1991 the CORD process has been applied nine times (five BWRs, three PWRs, and one PHWR) in Europe, Asia and the USA for FSD applications. Table 12-1 summarizes these applications. Three of the applications were to small (<60 MWE), prototype reactors that were shutdown for decommissioning, two were to large power reactors that were also shut down for decommissioning, but four were to large (>400 MWe) power reactors that went back into service following the decontamination. All had several common characteristics:

- the fuel was removed prior to each FSD;
- maximum use was made of existing nuclear power plant systems;

- specific components of the Siemens AMDA (automated mobile decontamination appliance) were used such as ion exchange columns, UV decomposition module, chemical injection equipment and pump modules where the reactor pumps could not be employed.

Brief descriptions of most of these applications are given below. Decontaminations employing the “D” option of CORD (see Chapter 13) are more correctly called decommissioning applications, since each was applied to a plant that was permanently shutdown. However, it was considered easier for the reader to include them in this chapter. Haddem Neck is a special case since it was the first FSD application in the USA employing the CORD process. It is described in Chapter 13.

Table 12-1
Summary of CORD FSD Applications by Siemens

Plant	Country	Supplier	Type	Process	Year
MOL/BR3	Belgium	Westinghouse	PWR	HP/CORD	1992
VAK	Germany	Siemens/GE	BWR	HP/CORD D UV	1993
Oskarshamn 1	Sweden	ABB	BWR	HP/CORD UV	1994
Loviisa 2	Finland	AEE	PWR	HP/CORD UV	1994
MZFR	Germany	Siemens	PHWR	HP/CORD D UV	1995
1-Fukushima 3	Japan	Toshiba	BWR	HP/CORD UV	1997
Wηrgassen	Germany	AEG/GE	BWR	HP/CORD D UV	1998
Haddem Neck	USA	Westinghouse	PWR	HP/CORD UV	1998
1-Fukushima 2	Japan	Toshiba	BWR	HP/CORD UV	1998

BR3

The CORD process was first applied for FSD in the BR3 plant located in Mol, Belgium in 1991 (69, 114, 183). This was a 10.5 Mw(e) PWR that operated from 1962 to 1986. It has been decommissioned and is to be dismantled so it was an ideal choice to demonstrate CORD FSD technology. Primary system volume is about 4,000 gallons. Three cycles of CORD were applied (equivalent to three oxidizing steps and three reducing steps) at a temperature of 90-95°C over a nine day period in April, 1990. The reactor coolant pumps were used as the heat source. Each CORD cycle lasted for 10 to 16 hours. The decontamination process removed 55 Ci of radioactivity (99% Co-60) and 52 lbs (23.6 kg) of corrosion products (69% Fe; 22% Cr; 9% Ni). Contact DFs on piping and pumps averaged 9.1, while general area fields dropped by a factor of 3.6. DFs on the steam generators were about 30. Dose savings due to the decontamination in the decommissioning work following the decontamination were estimated at 450 rem. Total waste generated was 48 ft^3 of ion exchange resin. This could have been reduced to about 20 ft^3 had the UV destruction option been available at that time

Kahl VAK

This is a small (15 MWe), natural circulation BWR that operated from 1961 to 1986. It is located in Kahl, Germany. Late in 1992 it was decontaminated with five cycles of the CORD D UV process (69, 70). DFs ranged from 20 to 120. Approximately 168 Ci of radioactivity and 302 lbs (137 kg) of corrosion products were removed from a system volume of 15,800 gallons. Following the decontamination, the pressure vessel head was sufficiently clean (<5 nCi/g) that it could be melted for reuse. Dose savings due to the decontamination in the decommissioning work following the decontamination were estimated at 220 rem

Oskarshamn 1

This is an ASEA-ATOM BWR (440 MWe) that went into commercial operation in 1972. By 1994, extensive inspection and repair work was required and an FSD became necessary to minimize radiation exposure to maintenance staff (87, 113, 185). The fuel was removed but most other pressure vessel internals were left in place. The control rod drives were removed and each housing was connected to the decon loop. Four CORD UV cycles were applied over a seven-day period to all major reactor systems and components. Approximately 62 Ci of radioactivity and 66 lbs (30 kg) of corrosion products were removed from a system volume of 42,300 gallons. It is estimated that 99.5% of the radionuclide inventory was removed. DFs ranged from 30 on the recirculation piping to 1,200 in the bottom of the pressure vessel. About 90 ft^3 of spent IX resin was generated. The bulk of this (90%) was cation resin for removal of Mn^{2+} (from the permanganic acid) and radionuclides and corrosion products. Only a small amount of mixed bed resin was required after the fourth cycle for final cleanup to obtain high quality water. The decontamination chemicals (i.e., oxalic acid) were decomposed by hydrogen peroxide and UV light to CO_2 and water. The reactor returned to operation following the maintenance outage. Personnel dose savings as a result of the decon were estimated at 300 rem based on 300 hours of work in the reactor pressure vessel (RPV). In actual fact, about 6,000 hours of additional work was done because of the much lower dose rates.

Loviisa 2

This is a 445 MWe PWR of the Russian VVER 440 type located near the town of Loviisa in Finland. It went into commercial operation in 1981. In 1994 extensive steam generator work was required and the plant operators decided that the best method to keep radiation exposure ALARA was through an FSD (71, 113). The reactor was defueled and the control rod drives removed, but all other pressure vessel internals remained in place. Four CORD UV cycles were performed over an eight day period. Approximately 1,120 Ci of radioactivity and 640 lbs (291 kg) of corrosion products were removed from a system volume of 80,000 gallons. DFs ranged from 14 to 153 and it is estimated that 98.5% of the radionuclide inventory was removed by the decontamination. Personnel dose savings in the 1994 outage as a result of the decontamination were estimated at 800 rem. Low recontamination after one year of operation meant that additional benefit was realized in subsequent outages.

About 1,100 ft^3 of spent IX resin were generated. This is much higher than expected based on Oskarshamn experience. Due to a tight schedule and low flow rates to the UV module, only a partial decomposition of the oxalic acid was performed. Thus, a considerable amount of anion resin was required for reagent removal. Had there been sufficient time and flow to permit efficient operation of the UV module, it was estimated that the waste volume would have been reduced to 370 ft^3. The reactor returned to normal operation following the maintenance outage.

MZFR

This is a 55 MWe heavy water moderated PWR located in Karlsruhe, Germany. It operated from 1965 to 1984. It was decontaminated in 1995 using the CORD D UV process. Approximately 50 Ci of radioactivity and 161 lbs (73 kg) of corrosion products were removed from a system volume of 12,400 gallons. Waste generated included 102 ft^3 of spent IX resin and 16,400 gallons of clean water. The average DF was 16. Some components were sufficiently free of radioactivity that they could be melted for reuse.

Fukushima Dalichi 3

This is a 760 MWe BWR of GE design built by Toshiba. It went into commercial operation in 1976. After 21 years of continuous operation, extensive repair and maintenance work (e.g., core shroud replacement) had to be performed. Without a decontamination, such repair work would have resulted in extremely high personnel exposure rates.

All reactor internals were removed for the decontamination. In order to avoid filling the RPV. and to reduce the decon solvent inventory, a spray ring was installed in the upper part of the RPV. This spray ring constantly “washed” the RPV walls during the decontamination. Flow to the spray ring (~2,000 gpm) was provided by the AMDA equipment.

The RPV was filled to a sufficient height such that the reactors recirculation pumps could be operated, alternately, one at a time, during the decontamination. This provided the main recirculation flow of ~20,000 gpm. Total system volume was ~85,000 gallons. Total surface area was estimated 12,300 ft^2. The decontamination solution was continuously cleaned up with a by-pass flow of 400-500 gpm through temporary IX columns on the AMDA equipment.

Three cycles of CORD UV were applied over 167 hours (7 days). A total of 278 Ci of activity and 220 lbs of corrosion products were removed. The average dose rate at the bottom of the RPV was reduced from 410 to 11 mR/hr. Mechanical decontamination further reduced it to 2-3 mR/hr. This represents an overall DF of 160. The average DRF in the vicinity of the recirculation pumps was 46. The DF on the recirculation pipe walls was >300. Approximately 200 ft^3 of spent IX resin waste was generated (186).

Würgassen

This was a 640 MWe BWR of GE design that was permanently shutdown in 1994 after 22 years of operation. A multi-phase decommissioning effort over 12 years was instituted in 1995. Two priority targets were established for the decommissioning:

- recycling of as much material as possible for unrestricted release (target: >90% as non-radioactive scrap);
- minimization of both individual and total collective radiation exposure.

To meet these targets, extensive decontamination was required. A paper describing these efforts is available (89), so only a brief summary will be given here. The following decontamination techniques were used:

- blasting with steel shot of large diameter carbon steel piping with low contamination levels, and brass tubing from the turbine condensers;
- use of the CORD CS UV process for carbon steel components and piping with high contamination levels;
- use of the CORD D UV process for stainless steel pipes and components
- a variety of other techniques such as steel shot blasting of concrete, high pressure water spraying, ultrasonic cleaning, acid cleaning, electrochemical processes, and melting (without decontamination) of some small, highly contaminated components, are being used.

In general, the decontamination and decommissioning are proceeding as planned. Several tons a day of steel and concrete are being prepared for unrestricted release. Chemical decontamination is providing DFs as high as 1,200.

USA BWR Experience

Shortly after BWR subsystem operational decontaminations became an established technology for reducing radiation exposure, it was realized that full system decontaminations offered even greater benefits (187). EPRI became involved and funded three projects directed towards BWR FSD:

- engineering feasibility and cost benefit analysis using Quad Cities as the reference plant (176);
- the effects of LOMI and CAN-DECON on BWR fuel and core materials (188–190);
- qualification program for the LOMI process for application to the complete reactor coolant system of BWRs, including the reactor vessel with the fuel in place (54).

These studies were extended to the LaSalle (191) and Brunswick stations (192). The conclusions from all these studies can be summarized as follows:

- The LOMI process is qualified for application to the full primary system of a BWR, including the core with the fuel in place (55). This conclusion is based on the more than 700 entries in the LOMI corrosion database. All indicate very low or negligible corrosion in LOMI, as do the 21 FSD applications at Winfrith, all of which were performed routinely without incident. More than 80 materials were evaluated in 30 test configurations (93). No intergranular attack (IGA) or intergranular stress corrosion cracking (IGSCC) was observed as a result of applying LOMI. Constant extension rate tests (CERT), crack growth tests and large-scale welded pipe tests indicated no acceleration in crack growth rate of existing cracks, or predisposition towards accelerated crack initiation as a result of exposure to

LOMI. Tests with highly irradiated 304 stainless steel which is susceptible to irradiation assisted stress corrosion cracking (IASCC), showed no adverse effects of exposure to LOMI (1). The fuel and other core components were essentially unaffected.

- A thorough evaluation of corrosion effects and an engineering assessment of materials interactions have not identified any unresolved safety issues associated with application of the LOMI process for FSD in BWRs.
- A plant-specific materials review of all LOMI-wetted surfaces is required to verify the existing database, i.e. there are no materials present that have not been evaluated.
- The AP/LOMI process for FSD of BWRs appears promising, but the corrosion database is not as large as for LOMI and additional testing is required before it can be approved (193).
- The NP/LOMI process for FSD of BWRs is unacceptable because of the possibility of accelerated crack growth in SA-508 and SA-302, Gr. B (193). Although the database for NP/LOMI has been significantly expanded since this conclusion was drawn, NP/LOMI is still not considered qualified for BWR FSD applications without a plant-specific evaluation (98).
- Decontamination of a BWR with the fuel in place, while technically qualified and beneficial from a recontamination point of view, was considered very unlikely in 1990 given the large quantity of radionuclides estimated to reside on the fuel surfaces (i.e. 210,500 Ci consisting of 128,500 Ci of gamma–emitters and 82,000 Ci of Fe-55 which decays by electron capture and emission of a weak X-ray) (188). Handling, transportation and disposal of ion exchange resin containing this quantity of radionuclides would be very difficult and costly. However, as pointed out in Chapter 3, more recent estimates place the total amount of activity that would be removed during a BWR FSD with the fuel in place at about 17,000 curies, a much more manageable figure.
- An engineering assessment concluded that the following systems should be included in the decontamination:
  - the reactor pressure vessel (RPV) with the fuel removed
  - the reactor water recirculation system (RRW or RRS)
  - the reactor water cleanup system (RWCU)
  - the control rod drive system (CRD)
  - optional – residual heat removal system (RHR)
- The engineering assessment also described the preferred method for performing the decontamination. The major steps are summarized below:
  - remove the RPV head and all RPV internals necessary to remove the fuel
  - remove the fuel
  - reinstall the RPV head but not the steam separators and dryers
  - fill the RPV with sufficient water such that when the decontamination chemicals are added the fluid level will be just below the feedwater nozzles
  - displace air above the fluid with nitrogen

  - final system preparations including valve alignment, system modifications, isolation of RPV nozzle connections to prevent decontamination chemicals from moving beyond identified boundaries, installation of supplementary equipment, etc.
  - perform decontamination
  - reagent removal, final cleanup and system restoration.

- It is estimated that between 1,000 and 2,000 Ci of radionuclides would be removed by decontamination of a typical BWR with the fuel removed. Total waste IX resin generated would be between 1,000 and 2,000 ft^3.
- A BWR FSD is only cost beneficial if performed in conjunction with a major maintenance outage involving a large project such as replacement of the recirculation piping. For routine outages there is not enough radiation exposure to save to offset the cost of the FSD. Only if the value of a person-rem increases from the currently accepted industry value of $10,000 to >$15,000 does it become cost effective.

In summary, FSD of BWRs with the LOMI process has been thoroughly qualified but to date there have been no applications and none are planned as of this writing. The principal reason for this is the economics associated with radiation exposure. When BWR FSDs were first contemplated in the early 1980s, potential savings in radiation exposure were estimated at 2,000 rem per year (176, 187). At $10,000 per rem, the savings could be as much as $20M. However with the average BWR now expending <200 Rem per year, this large potential saving no longer exists. Only if a large scale maintenance or inspection activity was planned, such as that at Oskarshamn (87) or Fukushima (186), would a BWR FSD become attractive.

USA PWR Experience – Fuel Out

In the late 1980s, EPRI, Westinghouse and a group of 10 PWR utilities embarked on a program to qualify two DCD processes, AP/CAN-DEREM and AP/LOMI, for FSD applications in PWRs with the fuel removed. The program was divided into three phases, each of which is now complete and is briefly described below.

Phase 1 - Parametric Studies

In this preliminary phase the major issues relating to a full RCS decontamination were evaluated. These issues included:

- estimated activity removal with both fuel in and fuel out;
- radiation exposure savings in the five fuel cycles following the FSD;
- cost benefit analysis for a FSD;
- fluid systems evaluation, i.e., which systems should be included in the FSD;
- identification of system modifications and new equipment required for implementation of an FSD

- chemical calculations (i.e., quantities of chemicals required and waste generated) for each of the two selected processes.

This work determined that a PWR FSD was both feasible and cost beneficial (194). An effective decontamination factor of about five was anticipated. Radiation fields were predicted to return to pre-FSD levels within 3-5 years if the FSD was performed with the fuel removed, and within 6-10 years if performed with the fuel in place. Collective dose savings in the 10-year period following the FSD were estimated at 3,500-4,500 rem. Between 3,000 and 6,000 curies of activity would be removed if the decontamination was performed with the fuel out, and between 5,000 and 10,000 curies if the fuel was left in place. New equipment required would be a decontamination processing system for chemical removal and addition, and interconnecting piping to the residual heat removal system where the equipment would tie in to the plant. Modifications to the plant would be relatively minor. The most significant change would be to install a nitrogen blanket system for the pressurizer for pressure control.

Phase 2 - Qualification Program

The purpose of this phase was to define and complete a systematic evaluation of the major issues that needed to be addressed for the successful decontamination of the entire primary system of a Westinghouse PWR with the fuel removed. The workscope was large and encompassed a broad spectrum of engineering evaluations, materials and chemistry evaluations, radiological assessments, and equipment designs (58). The work was divided into seven tasks, each of which is briefly described below along with the major conclusions. This work culminated in a Topical Report (59) that was approved by the NRC and formed the basis for the actual FSD at Indian Point 2 in 1995.

Task 1 - Process Qualification Test Program

A comprehensive test program to evaluate corrosion, friction and wear effects of two decontamination processes, AP/LOMI and AP/CAN-DEREM, was performed under expected plant application conditions. The program clearly indicated that there were no significant detrimental effects on primary system materials and components. For most materials of construction, the corrosion was very low (much less than 1 mil) and there was no evidence of stress corrosion cracking. Some material effects were noted on chromium-plated surfaces, 410 stainless steel, SA-533 low alloy steel and Stellite materials. However, these issues were not considered significant, especially for one cycle of chemical decontamination solvent application. Based on these observations, an inspection of critical components was recommended before and after a full RCS decontamination.

Task 2 - Fluid Systems Evaluation of Decontamination Process Integration with RCS and Auxiliary Systems

This task concluded that the residual heat removal system (RHR) was the optimum interface location with the decontamination processing equipment for efficient addition and removal of decontamination chemicals. Existing plant systems and equipment could be utilized to maintain the RCS within process requirements without the fuel installed. New features would include a nitrogen blanket for the pressurizer for system pressure control, a 1,500 gpm decontamination processing system for chemical addition and removal, and interconnecting piping to the RHR system.

Task 3 - Engineering Evaluation of RCS Components and Systems

The objective of this task was to assess generically the impact of an FSD on the physical condition and operability of the equipment, components and mechanical systems that comprise the RCS, the CVCS and the RHR of a four-loop Westinghouse pressurized water reactor nuclear steam supply system (NSSS). It was determined that the full RCS decontamination, using either the AP/LOMI or AP/CAN-DEREM process, could be performed with a high degree of confidence that significant impacts on plant equipment will not occur provided certain reasonable and prudent actions are implemented by the candidate plant (195). The results of the equipment evaluations indicated no significant impacts on the structural integrity of any pressure boundary materials for either process. The possibility for limited impact on operability, reliability, or life expectancy was identified for several components. These potential impacts could be avoided through a combination of inspections, routine maintenance, temporary modifications and administrative controls during the decontamination process.

Task 4 - Waste Management Methodology and Waste Characteristics

In this task the two candidate processes were studied to estimate chemical and waste quantities. Approximately 650 pounds of corrosion products containing 6,700 curies of radioactivity would be removed for an FSD of a 10-year old plant with the fuel removed. For a five-step AP/CAN-DEREM process applied to a four-loop Westinghouse PWR, it was estimated that 3,279 ft^3 of waste IX resin would be generated. For a four-step AP/LOMI process the volume would be 3,988 ft^3. Two burial options were identified - stabilization in a high integrity container or stabilized cement. The option selected would depend on the burial requirements at the selected disposal site. No unresolved safety issues were identified. Mixed wastes would not be generated. The waste was not expected to be classified as hazardous or toxic, but onsite testing would be required prior to disposal.

Task 5 - Evaluation of Long-Term Benefit of Full RCS Decontamination Including Decontamination and Passivation Issues

Estimates of exposure savings ranged from 900 rem for a low exposure rate, low maintenance plant performing only one FSD with the fuel out, to 16,000 rem for a high exposure rate, high maintenance plant performing six FSDs with the fuel in place over the remaining lifetime of the plant. A typical plant performing a single FSD with the fuel removed, the most realistic case, would save about 1,200 rem in the five fuel cycles following the FSD. After that, radiation fields would have returned to their pre-FSD levels. Actions such as eliminating sources of cobalt and maintaining proper primary water chemistry could increase the benefits.

Task 6 - Preparation of a Report Addressing Industrial and Nuclear Safety Issues

The safety evaluation generically addressed the nuclear safety implications on the existing systems and mechanical equipment of a typical four-loop Westinghouse PWR, of as many as three FSDs of the RCS with the fuel removed from the core. It was generically determined that the integrity and ability to function-as-designed of existing systems and mechanical equipment would not be adversely affected. As many as three FSDs would not adversely affect safe plant operation, would not involve a change to the plant's Technical Specifications, and would not involve an unreviewed safety question per the criteria of 10 CFR 50:59, provided that certain required actions are addressed on a plant-specific basis prior to, during, and after the FSD, and prior to a return to power (196).

Task 7 - Full RCS Decontamination Project Conceptual Design

A conceptual design of the decontamination processing system (DPS) was developed in this task (197). It consisted of three modules or subsystems:

- a cleanup subsystem that would be connected to the plant's RHR system and provide the necessary flow to the ion exchange columns employed for reagent regeneration (CAN-DEREM only) and removal;
- a resin processing subsystem that provides the capability for filling and emptying the ion exchange columns;
- a chemical injection subsystem consisting of a chemical mixing tank, recirculation pump, heater and chemical injection pumps.

Phase 3 - Detailed Design and Implementation

In January 1992, after a competitive bidding process, Con Edison awarded a contract to VECTRA Technologies (now known as PN Services) to proceed with detailed design of a DPS for a FSD at Indian Point 2, with implementation to follow in February 1995 (198). The process selected for the FSD was a five-step AP/CAN-DEREM, partly because Con Edison personnel were familiar and "comfortable" with this process since it had been used for several subsystem decontaminations at IP-2. In addition to DPS design and procurement, many other issues had to be addressed including:

- NRC review and approval (which was given in January 1993) of the Topical Report (199);
- procedures for plant operation during the FSD (200, 201);
- field implementation details such as design and construction of plant interfaces, DPS operating procedures, DPS installation, waste handling and processing, plant restoration, etc. (202, 203).

All preparations were completed by February 1995 and the FSD was successfully performed over 8½ days in the period March 1-9. Results of the application have been reported (2, 63, 204). Some highlights are given below.

- fuel and control rod drive shafts removed

- reactor head reinstalled with 1/3 of the studs torqued
- three of four main pumps operating to provide flow and heat
- systems decontaminated were:
    1. reactor coolant system including the vessel and steam generators
    2. residual heat removal system
    3. most of the chemical and volume control system
    4. portions of the primary sampling system
- the process employed consisted of the following steps
    1. initial CAN-DEREM step to remove outer iron-rich layer
    2. AP step to oxidize exposed chromium
    3. oxalic acid rinse to remove residual MnO_2
    4. second CAN-DEREM step
    5. second AP step
    6. second oxalic acid rinse
    7. third CAN-DEREM step
    8. final cleanup of water to specifications for refueling operations (i.e., pH 5-8, conductivity <10 μS/cm and total organic carbon <5 ppm)
- each CAN-DEREM step lasted about 20 hours, each AP step about 14 hours and each oxalic acid rinse about 10 hours
- total gamma-emitting activity removed was 3,906 curies consisting of 46% Co-60, 36% Co-58, 8% Sb-124, 7% Cr-51 and 3% others (predicted 5,100 curies consisting of 56% Co-60, 20% Co-58 and 24% others)
- 275 pounds of metals removed by FSD consisting of 37% Ni, 33% Cr and 30% Fe (predicted 630 pounds consisting of 26% Ni, 33% Cr and 40% Fe)
- average contact DF was 7.8 based on radiation measurements at 55 locations throughout the plant (goal >5)
- waste resin volume was 1,770 ft^3 (goal <2,400 ft^3)
- outage dose avoided 650 rem (goal >560 rem)
- estimated dose avoided over next five operating cycles (approximately 10 years) is 3,500 rem (goal >3,000 rem)

- corrosion of all 300 series stainless steels and Inconel 600 <0.01 mils (predicted 0.003 to 0.03 mils)
- corrosion of 410 stainless steel 0.04 mils (predicted 0.016 mils)

In general, most parameters were in reasonable agreement with the goals or predicted values as can be seen from the data presented above. The most notable exception is the amount of deposit removed. It had been estimated that 630 lb. of deposit (metals only) would be removed whereas only 275 lb. was actually removed. The estimate was based on 15 different plant samplings of both SG tubes and stainless steel surfaces. Obviously, these samplings were not representative of the deposits found in IP-2.

Corrosion of 410 stainless steel was about 2.5 times that expected, but the actual penetration of 0.04 mils was still very low. Westinghouse engineers had determined that a metal loss of 0.15 mils was still considered insignificant and would have no effect on the ability of the affected components to function as intended (56).

All waste IX resin was placed in high integrity containers (HIC), dewatered and shipped to Barnwell, SC for disposal. Prior to burial each HIC was placed inside a concrete overpack in accordance with the site licensing requirements in effect at the time.

USA PWR Experience – Fuel In

Commencing in about 1989, the feasibility of performing a PWR FSD with the fuel remaining in the core was examined (64–68). The advantages of such a decontamination compared to a fuel-out FSD are:

- No need to remove the fuel from the core thus greatly simplifying the project;
- More cost effective;
- Removal of a large source of activated corrosion products which would redistribute around the system when the fuel was reinstalled, and contribute to recontamination;
- Lower recontamination rates;
- Improved heat transfer from the fuel to the coolant and lower fuel surface temperatures. In theory, this should improve fuel performance and lower the rate of cladding failures, but experience with LWR fuel in this regard has generally been excellent so any such benefits would be very slight.

New and irradiated PWR fuel assemblies have been decontaminated with the AP/LOMI and AP/CAN-DEREM solvents (64). No deleterious effects were found after application of the solvents and after two of the assemblies were reirradiated for an additional fuel cycle (66).

In a recent study, the benefits of a fuel-in PWR FSD have been reexamined and remaining challenges identified (68). This study, the first phase of a study to qualify the fuel-in option for FSD applications in PWRs, confirmed the advantages of leaving the fuel in and in addition reached the following conclusions:

- No new equipment concerns were identified during the fuel-related equipment evaluations. The fuel-out case recommendations are still applicable.
- The best option for the control rod driveline material concern is to replace the 410 stainless steel couplings during the outage following the fuel-in FSD application.
- To maintain safe shutdown margin during fuel-in FSD, a minimum of 350 ppm boron is required. This analysis is prudently conservative.
- Required boron control and monitoring mandate further testing and evaluation of laboratory techniques.
- Decomposition of decon process chemicals due to fuel-in gamma fluence has the following effects:
  - Additional decomposition of AP, but no new material qualification concerns
  - There are no obvious adverse effects of radiolysis on LOMI (indeed they may be beneficial), but further evaluation of the effect of high radiation fluence on LOMI may be warranted.
  - Decomposition of EDTA in CAN-DEREM will occur rapidly and maintaining its concentration will be impractical. However, the radiolysis products of EDTA may perform the same function of EDTA, but this approach requires further evaluation.
- Dissolution of fuel pellets through breaches in the fuel cladding is not a concern.
- Completion of safety evaluations and associated checklists and the submittal and defense of evaluation results to the NRC will be accomplished in Phase 2.

One of the major differences identified between a fuel-in and a fuel-out FSD is the need to monitor and control boron in the former. Boron is a strong neutron absorber that is added as boric acid to the primary coolant for criticality control to ensure that safe shutdown conditions are maintained. A minimum boron concentration must be strictly maintained to ensure safe application of the FSD. In the past there have been difficulties in measuring boron concentrations using standard plant techniques[2] in the presence of decontamination solvents. A study was commissioned by EPRI to evaluate boron control and monitoring during decontaminations (205). This study determined that either Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Spectrometry (ICP) were practical for field boron analyses. Both gave accurate and reproducible results under a variety of decontamination conditions.

As of this writing, PWR FSD with the fuel in place is not deemed to be officially qualified. A topical report has not yet been issued and approved by the NRC. Phase 2 of the study has yet to be completed. Some questions regarding decontamination reagent stability in high radiation fields remain. Nevertheless, work is proceeding, albeit at a relatively slow pace, and it remains the industry's goal to fully qualify PWR FSD applications with the fuel in place. No insurmountable challenges have been identified. Given the large database of worldwide

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[2] These are based on AST Method 3082 B – Mannitol Potentiometric Titration.

experience with FSD with the fuel in place described earlier in this chapter, the continuing efforts of EPRI, Westinghouse, and the Westinghouse Owners Group, such qualification is entirely feasible within the next year or two.

13
DECONTAMINATION OF RETIRED FACILITIES

Background

Decontamination processes used at operating plants are designed to avoid any damage to the plant's materials exposed to the processes since the components or systems decontaminated must be returned to service. Such damage could occur either as a result of corrosion during the application of the process, or as a result of exposure of the plant items to the operating conditions of the nuclear plant after the decontamination. The restriction of avoiding damage has resulted in processes which do not attack the base metal but which operate by dissolving the overlying layer of corrosion product metal oxides. Because of this, the effectiveness of such processes is limited since some radioactive ions become incorporated into the base metal during plant operation. Nevertheless, sufficient activity removal is achieved for reducing radiation dose to workers, typically 80-95% (i.e., DF of 5-20).

The effectiveness of such processes is not, however, sufficient for the purposes of removing essentially all of the radioactivity from the surfaces thereby allowing the plant items to be treated as non-radioactive waste. Activity removal of >99.9% (i.e., DF >1,000) is generally required. In order to achieve this, it is necessary to remove a thin layer of the underlying base metal so as to release radioactivity trapped in fissures in the metal. When decontaminating retired plants prior to decommissioning, the restriction concerning plant damage is not so severe because the plant items are not required for further operational duty. The only requirements with regard to damage are that the items must maintain their structural integrity against leakage during the operation of the process and they must remain structurally sound. The removal of a thin layer of base metal is consistent with these requirements, although if too much metal is removed there may be a problem concerning the amount of radioactive waste generated.

Attempts have been made to improve the effectiveness of some DCD processes either by increasing the number and length of the cycles (e.g., CORD (71)) or by increasing the concentration of the reagents (e.g., CAN-DEREM Plus (206)). Although one mildly contaminated reactor component, the vessel head, was decontaminated to free release levels by such techniques, in general, operational DCD processes are inherently non-corrosive and are not appropriate for decontamination of retired facilities prior to decommissioning work. More aggressive processes that have been developed especially for such applications are described in the following sections.

Concentrated Fluoroboric Acid

One reagent developed specifically for aggressive decontamination of reactor materials is fluoroboric acid, (HBF_4). It was developed by Jozef Hanulik in Switzerland in the 1980s under the name DECOHA and originally patented in that country in 1985 (207, 208). A USA patent was granted in 1989 (209). It has been applied commercially by the Alaron Corporation for decontamination of radioactive scrap material to free releasable limits (210). A plant for decontaminating high-grade steel from Chernobyl was constructed in 1991 but technical, political, and financial considerations have prevented it from becoming operational (211).

Fluoroboric acid is prepared from a solution of boric acid by reaction with HF as shown below. Contaminated boric acid, which would otherwise be considered waste, can be used, but to date there are no reports of this option being employed. The resulting solution of HBF_4 can be distilled to increase its concentration, or to separate it from undesirable contaminants if contaminated boric acid was used to produce it.

Production of Fluoroboric Acid

H_3BO_3	$+ 3HF \rightarrow$	HBF_4	$+ 3H_2O$
boric acid	hydrofluoric acid	hydrofluoric acid	water

HBF_4 is employed at a concentration of 5-50% and a temperature of 80-100°C. It will readily dissolve BWR oxides (i.e., those oxides free of chromium) and corrodes most base metals at a sufficient rate to achieve dissolution of the top few mils of metal, where the radioactivity is trapped, in 1-4 hours. The reactions involved in deposit dissolution and base metal corrosion are shown below.

Dissolution of Magnetite in Fluoroboric Acid

$Fe_3O_4 + HBF_4$	$\rightarrow 2Fe(BF_4)_3$	$+ Fe(BF_4)_2$	$+ H_2O$
magnetite	fluoroboric acid	iron fluoroborates	water

Corrosion of Base Metal by Fluoroboric Acid

$Fe + 2HBF_4$	$\rightarrow Fe(BF_4)_2$	$+ H_2$
iron fluroboric acid	ferrous fluoroborate	hydrogen

HBF_4 is ineffective on deposits that are high in chromium such as most PWR deposits. For these deposits an oxidation step is required before application of HBF_4. For most other deposits, including those found on aluminum and lead, DFs of >1,000 are possible. In most cases the metals can be decontaminated to below free release limits.

Dilute Fluoroboric Acid – The EPRI DFD Process

A dilute version of the fluoroboric acid process has recently been developed under an EPRI-sponsored project (212–216). The process consists of a dilute solution of fluoroboric acid, 10 millimolar or 0.088%, plus sequential additions of an oxidizing agent (potassium permanganate) and a reducing agent (oxalic acid). It is applied at about 200°F for periods up to 200 hours using a continuous process "step". The pH and redox potential must be controlled within specified ranges. During application the solution is circulated through the system to be decontaminated and is cleaned up by cation exchange resin. It is a more aggressive process than operational-type decontamination processes such as LOMI, CAN-DEREM and CITROX with decontamination factors (DFs) of >1,000 being reported (213). It achieves these very high DFs through a combination of oxide film dissolution and removal (corrosion) of the top few microns of base metal. The process is described in detail below.

As mentioned in the previous section, the use of fluoroboric acid for decontamination of reactor materials was developed by Jozef Hanulik in Switzerland in the 1980s under the name DECOHA and originally patented in that country in 1985 (207, 208). A USA patent was granted in 1989 (209), and a second one dealing with the addition of oxidizing agents for enhanced decontamination of lead, in 1994 (217). These patents cover the use of fluoroboric acid in the concentration range 0.5-50%. In EPRI DFD it is employed at a much lower concentration of ~0.1% which makes the process amenable to cleanup by ion exchange resin, a technology with which decontamination vendors are very familiar.

Early in the development program of the EPRI DFD process, it was found that high DFs could not be achieved on some materials, particularly 300-series stainless steel (SS). This was attributed to a combination of a high concentration of chromium in the oxide layer, which impeded its dissolution (particularly SS from PWRs), and the presence of a thin, highly protective, chromium-rich film on the stainless steel itself. For operational-type decontaminations, only the chromium in the oxide film is removed; that in the thin, inner protective film is left in place to minimize base metal corrosion. It was determined that exposing the SS surface to a low concentration of potassium permanganate (100-300 ppm) in the presence of dilute fluoroboric acid would oxidize the chromium in both the deposited oxide and the in-situ film, thus allowing both oxide dissolution and base metal corrosion to take place. The chemical reaction involved in oxidation of chromium oxide to the soluble bichromate form is shown below.

Oxidation of Chromium Oxide in Potassium Permanganate

Cr_2O_3	$+ 2KMnO_4$	$+ H_2O \rightarrow$	$2HCrO_4$	$2MnO_2$	$+ 2K^+$
chromium oxide	permanganate		bichromate	manganese dioxide	potassium

The permanganate that does not react with the chromium oxide eventually decomposes to manganese dioxide as shown in the following reaction.

Decomposition of Permanganate in Acid Solution

$4H^+$	$4MnO_4^-$	$\rightarrow 4MnO_2$	$+ 3O_2$	$+ 2H_2O$
acid	permanganate	manganese dioxide	oxygen	water

Once all permanganate has been consumed, either through oxidation of chromium or by decomposition to MnO_2, the manganese dioxide is dissolved by the addition of a stoichiometric amount of oxalic acid as shown in the following reaction. An excess of oxalic acid may be added to assist in oxide film dissolution and removal of a small amount of base metal.

Dissolution of Deposited Manganese Dioxide With Oxalic Acid

MnO_2	$+ H_2C_2O_4$	$+ 2H^+$	$\rightarrow Mn^{2+}$	$+ 2CO_2$	$+ 2H_2O$
manganese dioxide	oxalic acid		Manganous ion (soluble)	carbon dioxide	water

The oxalic acid also converts the bichromate, $HCrO_4^-$, to Cr^{3+} as shown in the following reaction.

Reduction of Bichromate With Oxalic Acid

$8H^+$	$+ 3H_2C_2O_4$	$+ 2HCrO_4^-$	$\rightarrow 2Cr^{3+}$	$+ 6CO_2$	$+ 8H_2O$
	oxalic acid	bichromate	chromium	carbon dioxide	water

A complicating factor with Cr^{3+} is that it tends to form chromium oxalate, $Cr(C_2O_4)_3^{3-}$, from the excess oxalic acid.[1] This compound is not broken down by cation exchange resin and thus chromium tends to build up in solution during the course of an EPRI DFD application. Only a small fraction is removed by the cation resin. It is removed very efficiently at the end of the application when anion exchange and mixed bed resins are placed on line.

Following addition of the oxalic acid, the solution is then passed through a cation exchange column to remove all cations (e.g., K^+, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, etc.) leaving only fluoroboric acid in solution.[2] The reaction involved in removal of cations on ion exchange is shown below.

Removal of Cations by Ion Exchange Resin

Fe^{2+}	$+ 2H:R$	$\rightarrow Fe:R_2$	$+ 2H^+$
iron	cation resin	captured metal	hydrogen ions

If excess oxalic acid was added, a stoichiometric amount of $KMnO_4$ is added to convert it to CO_2 and water. The removal of cations, particularly Mn^{2+}, must be completed before the start of the next cycle. This is called the “transition phase” of the cycle.

Once all cations have been removed, the ion exchange columns are valved out and additional potassium permanganate is then added to start the second cycle. As many cycles as necessary

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[1] This compound also exists in the mono $\{Cr(C_2O_4)^+\}$ and bis $\{Cr(C_2O_4)_2^-\}$ forms, depending upon the relative amounts of Cr and oxalate, as well as the solution pH.

[2] In theory, this is what should happen. In practice, chromium builds up in solution and is only removed during the final cleanup phase when anion exchange resin is placed on line.

are then performed, depending upon the thickness of the film and the final DF required. Typically, between 6 and 12 cycles are applied.

In summary, the EPRI DFD process consists of the cyclic application of three chemical phases that are summarized below. The solvent base is 10 millimolar (0.088%) fluoroboric acid that results in a pH of ~2, a value that is maintained throughout the process. It is added initially once the operating temperature is reached. For 300 series stainless steel and Inconel systems, 200ºF is the temperature typically used. A crud burst and some metal dissolution may occur following its addition. The water in the system is circulated through a filter and cation resin until the dissolved metals are <10 ppm and most particulate material has been removed. The cation exchange columns are then valved out in preparation for phase 1.

i. Oxidation phase. Addition of ~200 ppm $KMnO_4$. It is circulated at 200ºF until it has all been converted to MnO_2 as described above. Ion exchange resin is not used in this phase, which typically takes between 2 and 4 hours.

ii. Reduction phase. Addition of a stoichiometric amount of oxalic acid to dissolve the MnO_2 and assist in oxide film dissolution. It also reduces the $HCrO_4^-$ to Cr^{3+} as explained above. The cation exchange columns are placed online following addition of the oxalic acid. The flow rate should be sufficient to give a purification half-life[3] of <1 hour, with ~30 minutes being preferred. Once manganese dioxide dissolution and cation cleanup are complete, the IX columns are valved out in preparation for phase (iii). Phase (ii) typically takes 4 to 6 hours, but may be as long as 12 hours.

iii Transition phase. The third phase returns the solvent to the fluoroboric acid-only condition.[2] This phase is initiated by taking the IX columns off line and adding a stoichiometric amount of $KMnO_4$ to oxidize any remaining oxalate from phase (ii) to carbon dioxide and water. Cation exchange resin is then employed as in phase (ii) to remove any cations that are generated. Once cation cleanup is complete, the IX columns are valved out in preparation for the second cycle commencing with phase (i). Phase (iii) typically takes 2 to 4 hours.

Completion of the transition phase completes one cycle of EPRI DFD. As many additional cycles are applied as necessary to achieve the desired DF. Typically, between 6 and 12 cycles are required.

After the last cycle, the temperature is lowered to ~160ºF and anion exchange columns are placed online to remove the fluoroboric acid and any other anions that may have accumulated during the application (e.g. SbO_3^-, $Cr(C_2O_4)_3^{3-}$). The reaction of fluoroborate with anion resin is shown below. The anion resin, combined with cation resin to remove the last traces of cations, results in only pure water being left in the system.

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[3] Purification half-life is defined as the time required to reduce the concentration of any species by a factor of 2, assuming it is being removed with 100% efficiency by the ion exchange resin. It is calculated as follows:
$t_{½}$ = System Volume × ln(2) ÷ IX Flow Rate

Removal of Fluoroboric Acid by Anion Resin

H^+	$+ BF_4^-$	$+R:OH$	$\rightarrow R_2:BF_4$	$+ H_2O$
acid	fluoroborate anion	resin	captured fluoroborate	water

The EPRI DFD concept is summarized in Table 13-1. The only three chemicals a vendor brings to the site for a decontamination are fluoroboric acid (typically a 50 wt % aqueous solution), potassium permanganate and oxalic acid dihydrate.

Table 13-1
The EPRI DFD Concept

Feature	Advantages
Uses fluoroboric acid at dilute concentration (10 mM) with redox potential control by potassium permanganate and oxalic acid	Reagent dilute and chemical costs low Suitable for cleanup on IX resin
Three blended steps: i. Permanganate oxidation ii. MnO_2 dissolution and oxide film dissolution with oxalic acid iii. Oxalate destruction	No reagent clean-up between steps Fluoroboric acid continuously recycled
Continuous clean-up by cation exchange resin in step (ii)	System is “rinsed” with progressively cleaner solution, a feature essential for high DFs
Process chemistry progressively dissolves base metal	Essential for high DFs
Process not excessively corrosive to reactor materials	Suitable for use in fuel-out full system decontamination of a permanently shut-down plant
Oxalic acid used in the process is converted to CO_2 and H_2O	No chelants in waste
Fluoroboric acid removed by anion exchange resin	Ion exchange resin waste only
Under ideal conditions, decontamination factors typically range from 1,000 – 500,000, depending on number of cycles	Metal can be cleaned to free release limits

Siemens CORD D UV

The Siemens CORD D UV process is very similar to the basic CORD process already described in Chapter 7. A brief review of CORD is given here along with additional details pertaining to the “D” option. Detailed chemical reactions involved in CORD are not repeated here. The reader is referred to Chapter 7

CORD is an acronym for Chemical Oxidation Reduction Decontamination. It evolved from the OZOX process (from OZone/OXalic acid) in which the original concept was to employ ozone as the oxidizing agent, but because of technical difficulties alkaline permanganate was used for all field applications (86). In the mid-1980s permanganic acid was substituted for alkaline permanganate and the name was changed to CORD. In the early 1990s the UV option was added to decompose the residual oxalic acid and thus reduce the volume of ion exchange resin required (87). In the mid-1990s, the D (for decommissioning) option was added. This involves exposing the decontamination solution to intense UV light (90). This reduces the solution redox potential and makes it much more aggressive to base metal. Removal of some base metal is required for the high DFs associated with decontamination for decommissioning.

The CORD D UV process (D for Decommissioning, UV for exposure to ultraviolet light) is similar to the basic CORD process described in Chapter 7, except in Step (iii), the Decontamination Step. After addition of the oxalic acid, the solution is exposed to an intense UV light source for the duration of step (iii). This results in a reduction of the solution redox potential from ~+100 mV (versus Ag/AgCl) to ~–275 mV (versus Ag/AgCl) and significantly increases the corrosivity of the solution. Base metal attack occurs as a result. Up to 10 µm of base metal dissolution may occur, depending upon the number of cycles applied, resulting in very high DFs, possibly as high as ~1,000 which may make the material suitable for free release. The mechanism by which UV light brings about such a significant reduction in redox potential remains proprietary to Siemens.

In a typical application, two cycles of CORD UV are applied to remove the bulk of the contaminated oxide film, followed by one or two cycles of CORD D UV to remove some base metal thus giving the very high DFs associated with decontamination prior to decommissioning work

The CORD D UV concept is summarized in Table 13-2. Descriptions are also available in the literature (88, 90). The only three chemicals the vendor brings to the site for a decontamination are permanganic acid (2-4 wt% aqueous solution), oxalic acid dihydrate (solid), and hydrogen peroxide (30-50 wt% aqueous solution). For some applications solid potassium permanganate is brought to site from which permanganic acid is produced in a separate IX module prior to addition to the system. As previously mentioned, permanganic acid only exists in solution.

As discussed in Chapter 12, the CORD D UV process has been applied four times to various BWRs and PWRs in a Decontamination for Decommissioning mode. Brief descriptions of the three European applications were give there. A description of the sole North American application (Connecticut Yankee 1998) is given in this chapter.

Table 13-2
The CORD D UV Concept

Feature	Advantages
Four blended steps: Oxidation (of Cr by $HMnO_4$) Reduction (of $HMnO_4$ by oxalic acid) Decontamination (with oxalic acid) Decomposition (of oxalic acid by H_2O_2/UV)	No need to cleanup or drain system between steps Simplifies operation Shorter time Less waste Oxidation step can be omitted in first cycle for BWR application
Oxidation step uses permanganic acid	Faster and more efficient than AP and NP Less waste since lower concentration, no K^+, and no additives such as NaOH or HNO_3
Reduction step performed in-situ with oxalic acid, the same chemical used for the decontamination step	Avoids contact of IX resin with permanganate ion Stoichiometric calculation unnecessary since large excess added so that decontamination step begins as soon as reduction of $HMnO_4$ is complete
Decontamination step is regenerative using continuous flow through cationic IX resin UV light reduces system redox potential and causes base metal corrosion resulting in much higher DFs	Mn^{2+} ions from reduction step are removed Continuous removal of dissolved contaminants so radiation fields remain low around equipment UV light can be left off for first 2 cycles to minimize base metal corrosion and dissolve only the oxide film
For full system application, reactor does not necessarily have to be defueled	Simplifies operation Fuel is decontaminated Reduces rate of recontamination
Decomposition of oxalic acid by H_2O_2 and UV light	Decomposition products are innocuous (CO_2 and H_2O) No anion exchange resin required for reagent removal No chelates in waste
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors Separate pretreatment step not required - it is integral in the process
Each CORD cycle is independent	Number of cycles can be adjusted according to final dose rate or DF required
Decontamination factors range from 10 to >1,000, depending on number of cycles and whether basic CORD UV or CORD D UV is applied	Metal can be cleaned to free release limits, if required.

Experience with Decontamination of Retired Plants

Big Rock Point

The first USA application of EPRI DFD technology was at Big Rock Point in January, 1998 (218). The plant, a 70 MWe BWR, was permanently shutdown in August, 1997 after 35 years of successful operation. Prior to decommissioning activities, a decontamination was required to bring the personnel dose for the project to within NRC guidelines. The EPRI DFD process was selected. The total system volume was 32,000 gallons with an internal surface area of 10,764 ft^2. The system decontaminated comprised:

- the reactor vessel with the internals removed
- the main circulation piping and RCPs
- the steam drum
- the reactor water cleanup system
- the shutdown cooling system

The RCPs provided the main motive force, giving a system turnover time of approximately 1 minute. A mobile treatment plant containing chemical addition equipment and IX resin columns was connected to the system. Flow rate to and from this mobile plant was 600 gpm.

Two separate applications were required. A “hot” application (200°F) was applied to the majority of the system that was stainless steel, and a “cold” application (80°F) to the reactor water cleanup system and the shutdown cooling system that were constructed of carbon steel. The former consisted of 6 cycles of EPRI DFD and took 9 days. The latter was a single cycle applied over 3 days.

Approximately 410 curies of gamma-emitting radionuclides were removed, resulting in an average DF of 27 and a DRF of ~10. All waste was contained on 540 ft^3 of IX resin that was sent to Barnwell for disposal. The resin passed the TCLP for chromium (<5 ppm in the leachate) and thereby avoided being classified as a mixed waste.

Maine Yankee

The Maine Yankee plant, a 825 MWe PWR of C-E design that began operation in 1972, is permanently shutdown and is to be decommissioned. To minimize radiation exposure during the decommissioning, and to meet the Generic Environmental Impact Statement (GEIS) limit of 1,115 Rem for decommissioning, plant management elected to perform a decontamination prior to the start of major decommissioning activities (219–221). The EPRI DFD process was selected.

All major plant systems were included in the decontamination flow path with the exception of the reactor pressure vessel (RPV) and the majority of the steam generator tubes. A flow-through nozzle dam “spider” assembly was installed in the core to interconnect the hot and cold leg nozzles thus completely bypassing the RPV and at the same time providing a flow path from one coolant loop to another. See Figure 13-1. Bypassing the RPV had the advantage of avoiding corrosion of activated material, which could contribute significantly to the amount of radioactivity removed and waste generated, but would have little effect on radiation exposure. Bypassing the SG tubes avoided a large surface area of highly contaminated Inconel, decontamination of which would have contributed very little to exposure reduction since only the outer 10 rows of tubes contribute significantly to external radiation fields. In-situ decontamination of the SG tubes would offer little immediate benefit to the plants.

The plant relied heavily on vendor-supplied equipment for pumps, heaters, and ion exchange columns. A self-sufficient operation was required since availability of plant equipment could not be assured. Essentially no plant equipment was operated during the decontamination. Flow was provided by the vendor's pump. The maximum flow that could be obtained was in the range 300-650 gpm. This turned out to be a major disadvantage. See Chapter 15 – Lessons Learned.

The decontamination was performed in two separate applications, each taking about 8 days. Eleven cycles of EPRI DFD were applied in the first and 13 cycles in the second. An overall average contact DF of 31.5 was obtained. The average initial contact radiation field of 460 mR/hr was reduced to 20 mR/hr. On the most radiologically significant points, i.e., those with an initial field of >500 mR/hr (8 out of 48 points), the average DF was 146. The average general area dose rate reduction factor (DRF) was ~10. Total ion exchange resin waste generated was 625 ft^3 of which ~90 ft^3 was consumed in removing boron leaving a net of ~535 ft^3 attributable to EPRI DFD. A total of 677 lbs. of metal and 103 Curies of gamma-emitting radionuclides were removed during this application. A decontamination of parts of the RCS in 1995 removed about 400 Curies of radioactivity. This contributed to the lower-than-expected activity removal (several hundred Curies had been expected), and also to the lower-than-expected DFs (an average contact DF of >100 had been expected).

Connecticut Yankee

The Connecticut Yankee (CY – also known as Haddem Neck) nuclear power plant is permanently shutdown and is to be decommissioned. To reduce radiation exposure ALARA during decommissioning, management personnel elected to perform a chemical decontamination of all major systems prior to the start of major decommissioning activities. The Siemens CORD D UV process was selected (221).

All major plant systems were included in the decontamination flow path with the exception of the reactor pressure vessel (PRV) and the majority of the steam generator tubes. A flow-through nozzle dam "spider" assembly was installed in the core to interconnect the hot and cold leg nozzles, thus completely bypassing the RPV and at the same time providing a flow path from one coolant loop to another. It was similar to that used at Maine Yankee (Figure 13-1). The advantages of bypassing the RPV and the steam generators have been discussed above under Maine Yankee.

The plant's RHR pump, demineralizers, and pressurizer heaters were used during the decontamination. The RHR pump (only one of two was run) provided a flow rate of ~1,800 gpm compared to 300-650 gpm at Maine Yankee. Minimal vendor-supplied equipment was brought to site. This equipment, which was connected to the system between the core deluge line and the pressurizer, was located on the charging floor. It consisted of:

1. a heater skid containing two 300 kW heaters
2. three UV burners skids each containing two high intensity UV lamps
3. two chemical injection skids
4. a remote monitoring skid assembly for inline measurement of redox potential, pH and conductivity

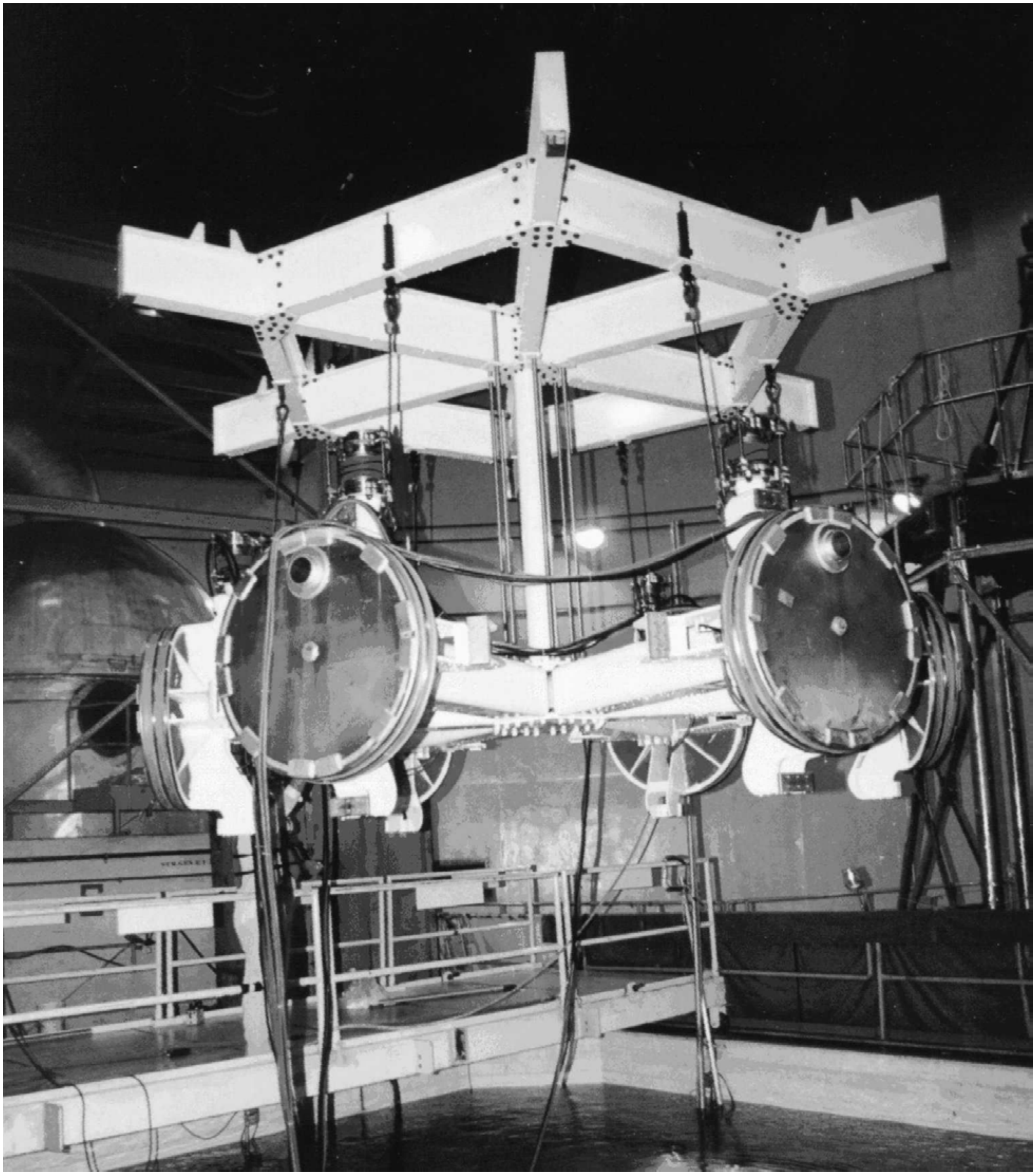

Figure 13-1
Nozzle Dam "Spider" Assembly Employed at Maine Yankee

The decontamination was performed in a single application of two cycles of CORD over a 28-day period. However, only about 9 days were attributable to CORD. The balance was due to delays caused by problems with the plant's letdown system. An average contact DF of 15.9 was obtained. The average initial contact radiation field of 234 mR/hr was reduced to 28 mR/hr. The average general area dose reduction factor (DRF) was ~5. Total waste ion exchange was 465 ft^3 but only 115 ft^3 was directly attributed to CORD. The balance was due to the plant's aim of avoiding a greater than Class C waste as a result of the TRU present in the system from previous fuel failures. A total of 82 kg of metal and 131 Curies of activity were removed. The amount of metals removed was much lower than anticipated, since the "D" option of the CORD D UV process was never implemented during this decontamination. It is this part of the process that removes some base metal. Originally it was planned to apply it in Cycle 3 (and Cycle 4, if necessary), but because of problems with the plant's letdown system (see Chapter 15 – Lessons Learned) and the good decontamination factors obtained after two cycles, the decontamination was terminated after two cycles.

Trojan

Trojan is a 1,130 MWe Westinghouse PWR that was permanently shutdown in 1992. Plant management has opted for immediate dismantlement and decommissioning without a major decontamination since exposure estimates for the entire decommissioning effort are well within the GEIS requirements. Nevertheless, an EPRI DFD application was performed on some tanks and heat exchangers in April/May, 1998 (216). A DF of 66 and a DRF of 33 were obtained with an eight-cycle application.

Decontamination of Components in a Recycling Center

The EPRI DFD process, as well as other chemical and electrochemical processes, has been shown to be effective in decontaminating reactor components such as pumps, heat exchangers, lead, condenser tubes, and spent fuel racks to free release limits. This work was performed in fixed-base centers and the material was free-released and sold as scrap (222–224). In many cases this is much more cost effective than simply burying the contaminated component. As discussed earlier in this report, one possible scenario is removal of the bulk of the radioactivity insitu through either a full loop or full system decontamination, followed by shipment of selected components to a fixed-base facility for dismantlement and additional decontamination to free release limits. If total decontamination is not feasible, the component may be suitable for burial at less expensive disposal sites that accept only Class A waste.

14
RECONTAMINATION

Background

Following removal of the contaminated oxide film by decontamination, the oxide film reforms when the unit is returned to service. Since there is usually a large inventory of activated corrosion products in the parts of the system that were not decontaminated, the new oxide film tends to contain the same concentration of radionuclides as did the old one. Putting it another way, the same equilibrium among pipe deposits, fuel deposits and soluble species is reestablished. Radionuclides tend to “migrate” to cleaned areas where the corrosion rate is higher. The “migration rate” can be minimized by good coolant chemistry. The lowest recontamination rate is achieved by decontamination of the whole reactor, including the fuel.

Following decontamination of PWR steam generator channel heads, the fields typically regrow to about 50% of the pre-decontamination levels within one fuel cycle, and to 70% with two cycles (225). However, as will be shown below, recontamination of the channel heads at Indian Point 2 following the 1995 FSD was much lower than this.

In BWRs the fields tend to redevelop at about the same long term rate that existed prior to the decontamination. For most BWRs this was in the range of 100 to 150 mR/hr/EFPY in the 1980s, but is much lower now. Generally, this means that the fields will have returned to their pre-econtamination levels within about two fuel cycles unless other changes are made (i.e. improved coolant chemistry, HWC, GEZIP, replacement of high-cobalt alloys, etc.) (226, 227).

CANDU piping tends to recontaminate at about the same rate as it contaminated before the decontamination. Decontamination does not result in any fundamental changes to the activity transport processes. These can only be changed as previously discussed under Contamination Mechanism and Activity Transport in Chapter 3. The rate of contamination is low compared to PWRs and BWRs. Typically, fields develop at about 10-20 mR/hr/EFPY, a factor of 10 lower than in BWRs (181).

Recontamination data is available from several plants that have undergone either operational subsystem decontaminations or FSDs. The data available up to 1990 has been previously reviewed (181). Some of the most significant data from that review is reproduced here, and information obtained since 1990 is presented.

Winfrith Steam Generating Heavy Water Reactor

As discussed in Chapter 12, this plant was exposed to the equivalent of 15 FSDs with the fuel in place in the period 1969 to 1989. A standard monitoring program was introduced in 1969, the year of the first decontamination. A summary of the data for the years 1977 to 1989 is shown in Figure 14-1. Prior to 1980, only one-half of the plant was decontaminated each year. This fact, combined with the gradual buildup of a chromium-rich inner layer, contributed to the ever increasing radiation fields to about 3,000 EFPY. At this time two things happened:

1. The decontamination process was changed from CITROX to LOMI. The use of a less aggressive process enabled the entire system to be decontaminated each time, not just one-half.

2. An oxidizing step (NP) was applied for the first time since even LOMI would not dissolve the chromium-rich layer that was slowly building up.

These two changes resulted in a stabilization of the radiation field levels, but the recontamination rate did not change significantly.

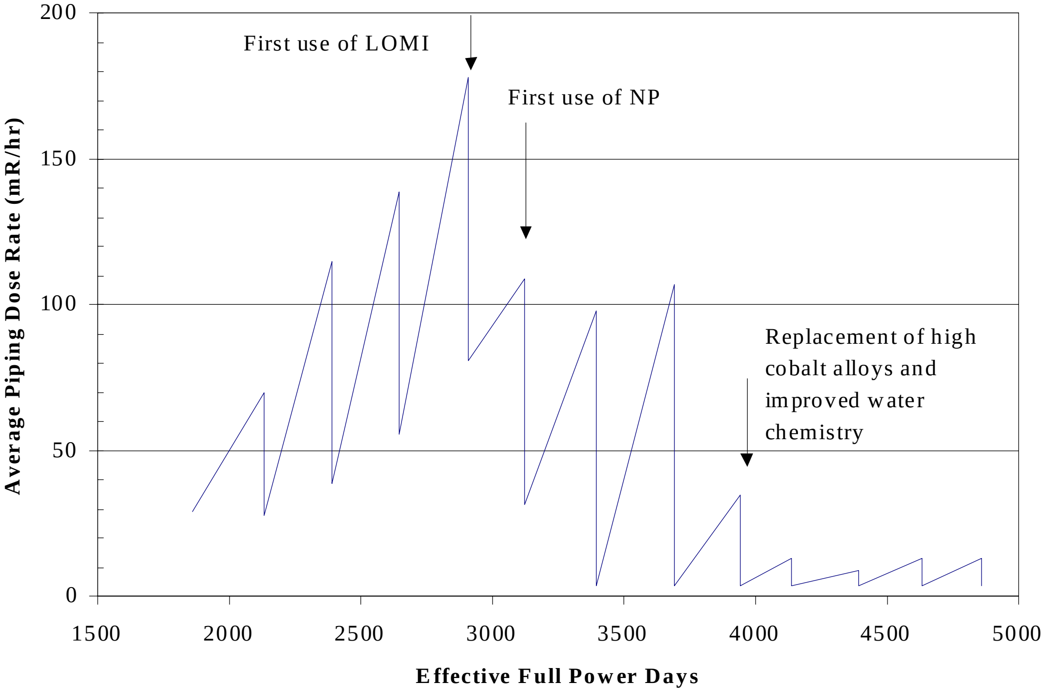

Figure 14-1
Recontamination at Winfrith SGHWR 1977-1989

In the mid-1980s (3,700-3,800 EFPY), three additional changes were instituted:

1. High-cobalt alloys such as Stellite faces on valves, pump wear rings and turbine blade tips were gradually replaced with low cobalt alloys.

2. Improvements in the Powdex ion exchange/filtration system resulted in the average conductivity being reduced to ~0.2 μmho/cm from the previous range of 0.4-1.8 μmho/cm in the 1970s.

3. A new feedwater heater of more corrosion resistant material was installed. This helped to reduce the iron in the feedwater to <1 ppb from 3-5 ppb which reduced the iron addition rate from 14 kg/yr to 4 kg/yr.

These additional changes, coupled with regular FSD, resulted in the much lower radiation fields and rate of recontamination as can be seen in the 4000-5000 EFPY range in Figure 14-1. This example shows that appropriate changes to water chemistry and system materials can signficantly change the rate of recontamination. When combined with regular decontamination, this strategy can result in much reduced radiation fields and dose to plant workers.

Quad Cities Units 1 & 2

Quad Cities Units 1 and 2 were among the first BWR plants to employ DCD in the recirculation system (1984 and 1983, respectively), and are the only plants that have continued to employ it on a regular basis. There have been nine DCDs of the recirculation system at Unit 1 and seven at Unit 2. Average contact radiation fields on the 12″ risers are shown in Figure 14-2 and Figure 14-3. While the absolute values shown in these figures are not representative of the recirculation system as a whole[1], the trends certainly are. Note the increase in recontamination rate with the advent of hydrogen water chemistry in 1990. The first few DCDs consisted of a single step CAN-DEREM or LOMI application, but the last three decontaminations in each unit employed a three-step LOMI/AP/LOMI process. The initial LOMI step only reduced fields to 200-300 mR/hr (from 600-1200 mR/hr) following initiation of HWC, whereas Quad Cities' goal was <100 mR/hr on the risers. Two more steps (AP/LOMI) achieved this goal. Although there has been some effect of HWC, it is not as drastic as at other plants such as Brunswick, Hatch and Monticello. See Chapter 10. In those plants AP was almost totally ineffective; only NP gave good results. Even AP at Quad Cities is starting to have some limitations. The final riser fields have slowly increased to ~125 mR/hr and Quad Cities may have to use NP to achieve <100 mR/hr, but are reluctant to do so because of potential corrosion concerns previously discussed. See Chapter 8.

Quad Cities has recently instituted GEZIP (12/98 in Unit 1 and 3/97 in Unit 2). There have been no decontaminations since GEZIP was started, and while no effects on decontamination are expected (see Chapter 11), it will be interesting to see if the recontamination rate is affected. A complicating factor is that Quad Cities has also recently introduced Noble Metal Chemical Addition (NMCA). This is able to bring about the lower ECPs required to mitigate IGSCC with a much lower hydrogen addition rate. The combination of low HWC, GEZIP and NMCA is

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[1] The risers tend to have the highest dose rates and are the most difficult to decontaminate since they are not directly in the system flow path. Rather they are decontaminated by an up and down "sloshing" process which is less effective than direct flow.

unique. It will be interesting to watch the next round of decontaminations at Quad Cities and the subsequent recontamination rates.

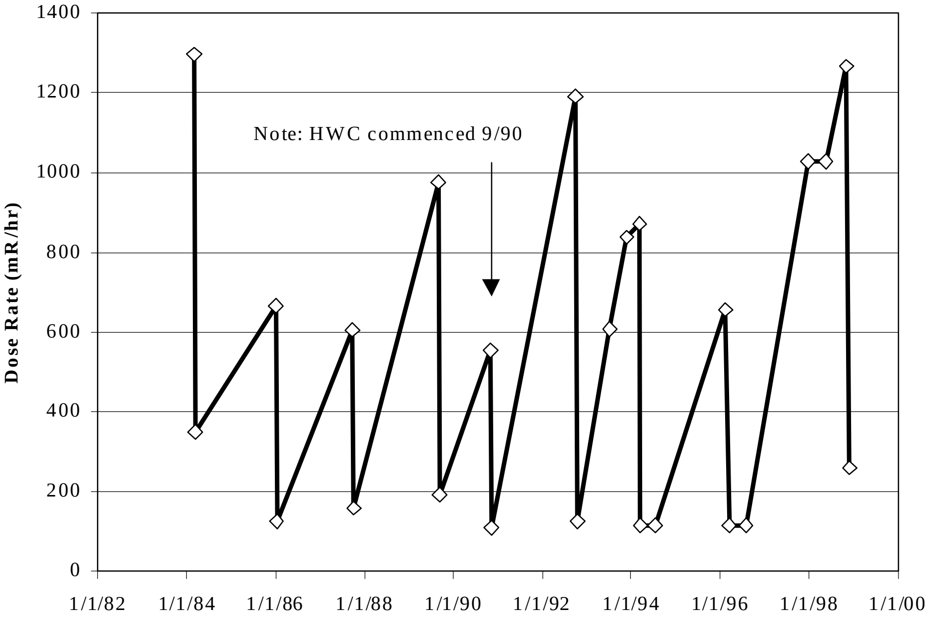

Figure 14-2
Recontamination of 12" Risers at Quad Cities Unit 1 1983-1998

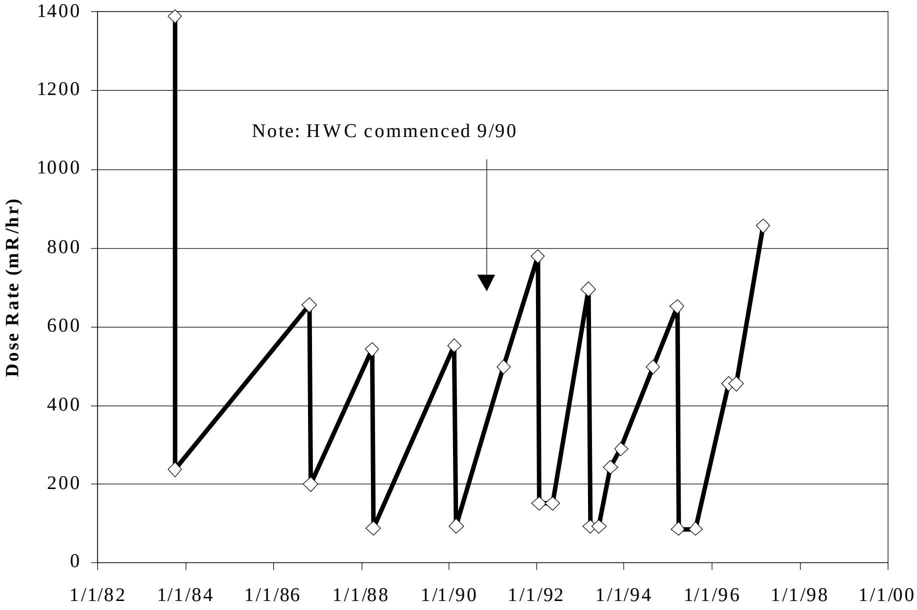

Figure 14-3
Recontamination of 12" Risers at Quad Cities Unit 2 1983-1998

Indian Point 2

As described in Chapter 12, Indian Point 2 underwent a FSD in 1995. A complete set of radiation field measurements was taken just prior to the FSD, immediately afterwards, and again in the 1997 refueling outage. The overall average DF of 7.8 obtained in 1995 had been reduced to 6.4 in 1997 (228). This is much less recontamination than had been predicted. Calculations based on the CORA code had predicted a return to about 50% of the predecontamination levels within the first fuel cycle, i.e., a reduction in the DF to about 2 (229). Clearly, this did not happen, suggesting that the benefits of the decontamination may be much greater and longer lasting than originally predicted.

Results of these surveys for the SG channel heads, the general area around the RCS loops, and the regenerative heat exchangers in the letdown system are shown in Figure 14-4, Figure 14-5, and Figure 14-6, respectively. Figure 14-6 includes radiation field data back to 1989 when the first decontamination of the heat exchangers was performed.

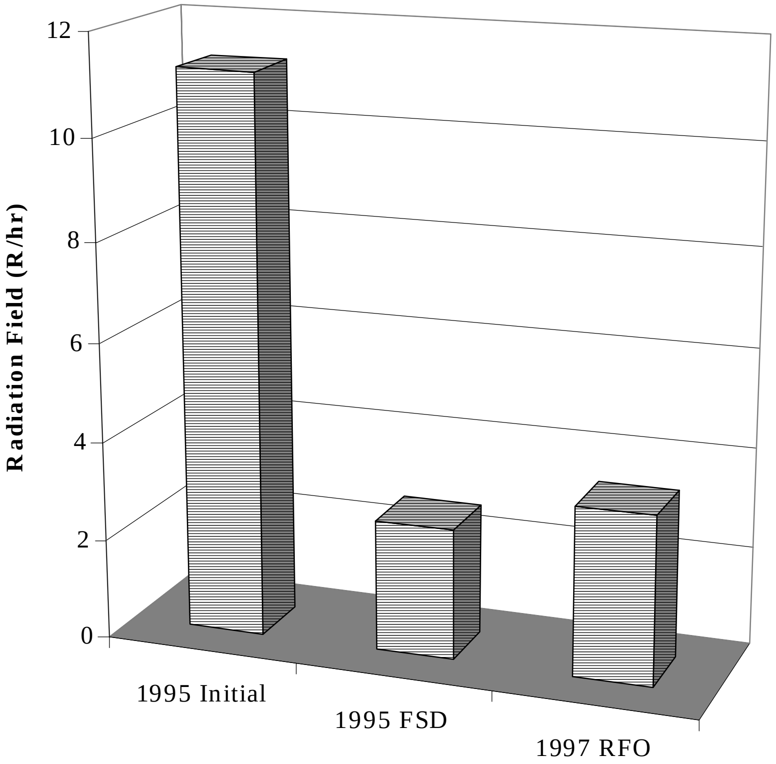

Figure 14-4
Recontamination of Indian Point 2 Channel Heads 1995-1997

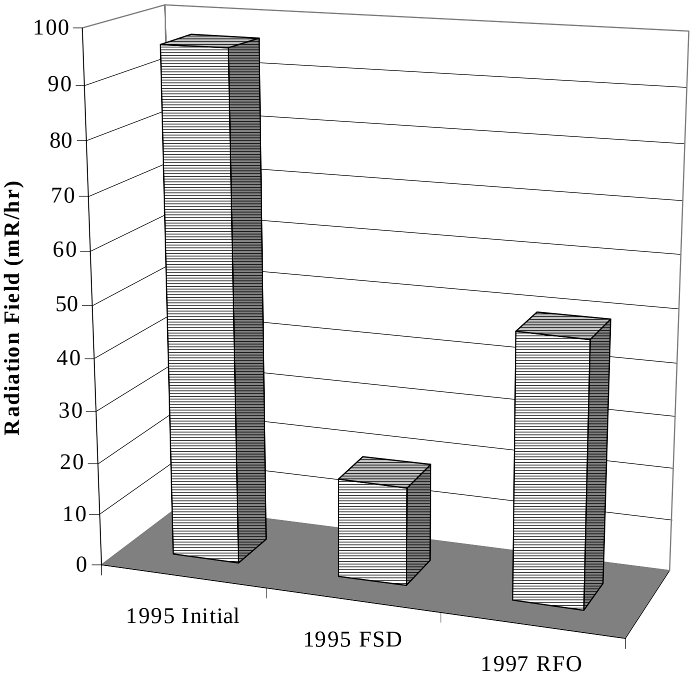

Figure 14-5
Recontamination of Indian Point 2 RCS Loops General Area 1995-1997

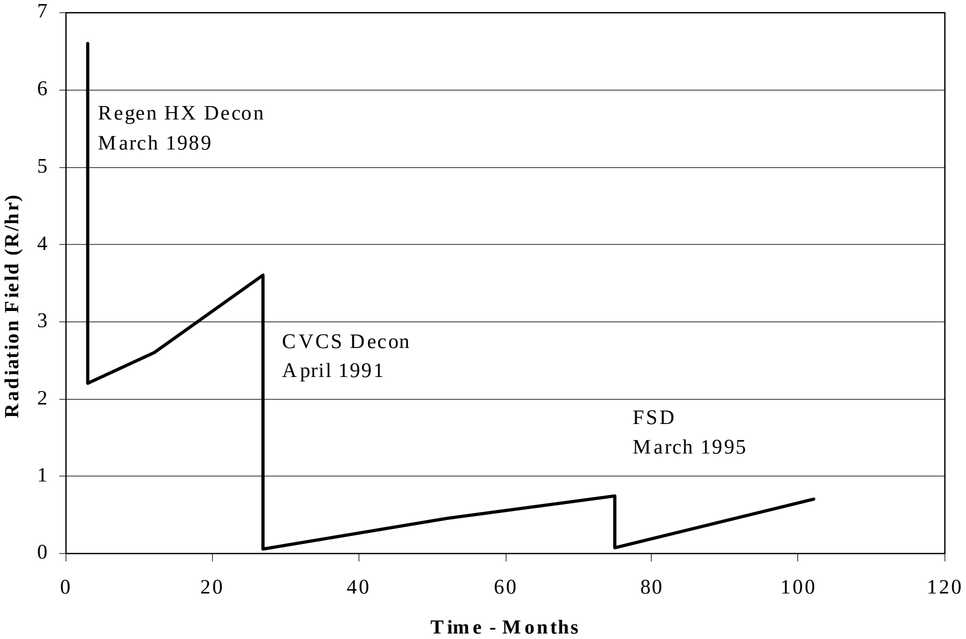

Figure 14-6
Recontamination of Indian Point 2 Regenerative Heat Exchanger 1989-1997

Brunswick Units 1 & 2

Several decontaminations of the RRS have been performed at the Brunswick units, commencing in 1985 in Unit 2, and in 1987 in Unit 1. Average RRS radiation fields from the first decontamination up to 1998 are shown in Figure 14-7 for Unit 1 and in Figure 14-8 for Unit 2. The large increases in the early and mid 1990s are attributed to the effects of HWC. When Brunswick first started HWC, the amounts of hydrogen being added were relatively low. However, the amounts were slowly increased until they reached what is considered “high” HWC, i.e., 1-2 ppm H_2 in the feedwater. At this level, a release of activated corrosion products from the in-core surfaces was observed, as has been seen at several other plants. Decontamination, fuel replacement, and the advent of DZO (5/95 in Unit 1 and 3/96 in Unit 2) eventually overcame the problem and the radiation fields have more or less stabilized over the last couple of years. Additional decontaminations should be able to bring the equilibrium dose rates down to <100 mR/hr.

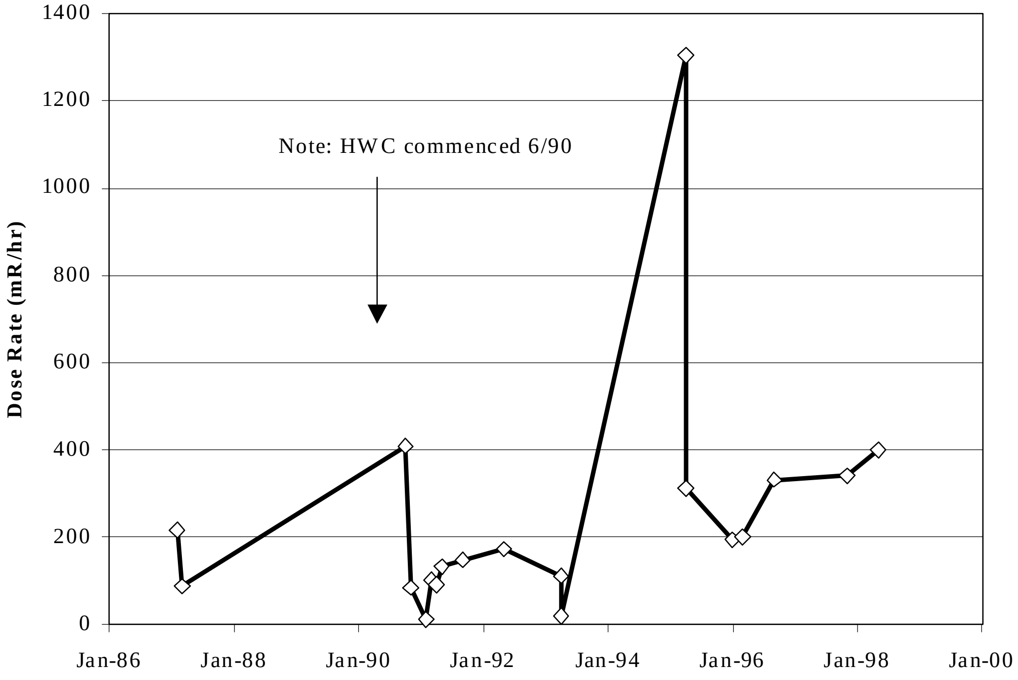

Figure 14-7
Average RRS Radiation Field at Brunswick Unit 1 1987-1998

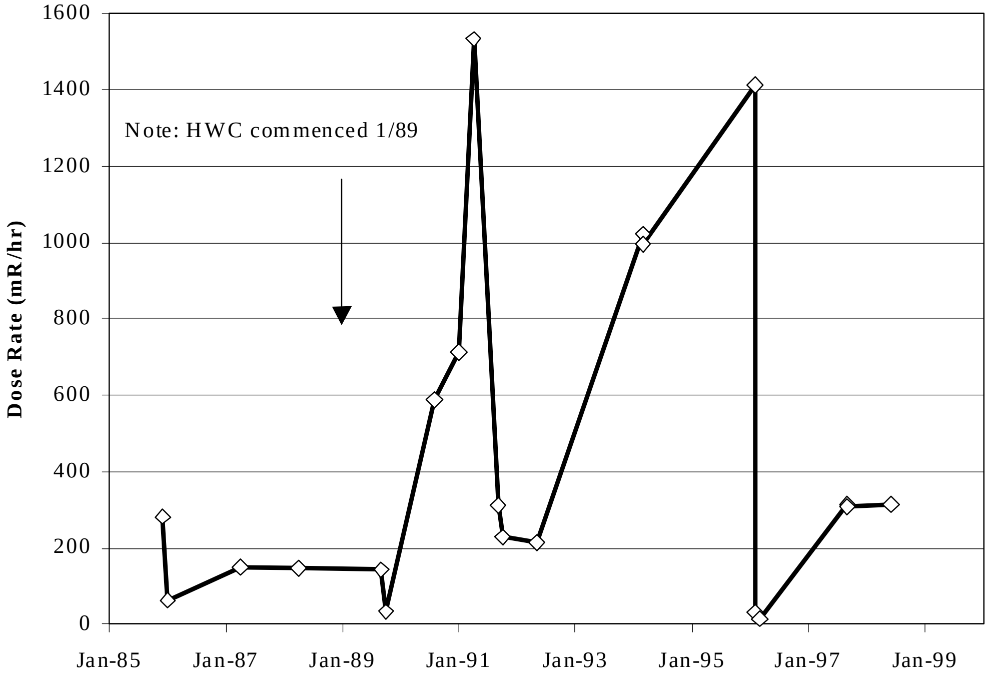

Figure 14-8
Average RRS Radiation Field at Brunswick Unit 2 1986-1998

Passivation

A variety of methods have been tested to reduce the rate of activity buildup on metal surfaces following decontamination, or prior to installation in a plant. These include:

- Electrical and mechanical techniques to polish the surface and thus reduce the effective surface area.
- Exposure to high temperature, clean (i.e., non-radioactive) water under either oxidizing or reducing conditions to promote formation of a protective film before exposure to contaminated water.
- Exposure to high temperature moist air to promote formation of a protective film.
- Corrosion resistant metallic coatings, notably palladium[2], which reduce recontamination by two methods:

    1. reduce corrosion of the substrate thereby suppressing dissolution of the cobalt present as an impurity in the base metal, and,

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[2] Although it showed great promise, this technology never made it to the field.

   2. resist formation of an oxide film under normal reactor operating conditions and thus reduce the propensity for radionuclides to accumulate on piping surfaces.

- Addition of metal ions, notably zinc, to the reactor water to preferentially fill vacancies or defects in the oxide lattice and thus reduce inclusion of radioactive ions such as Co-60 (GEZIP, or DZO).
- Addition of hydrogen to the primary water in BWRs to reduce corrosion by changing the electrochemical potential of the solution (HWC).

These technologies have been previously reviewed (181) and two of them (GEZIP and HWC) are described elsewhere in this report. Other changes that can be made to reduce recontamination are discussed in Chapter 3 under Contamination Mechanism and Activity Transport.

Recontamination can also be minimized by passivation, the formation of a protective layer of magnetite, or other spinel, under controlled, non-radioactive conditions. The conditions must be conducive to the formation of a spinel-type compound such as magnetite (or a substituted magnetite such as nickel ferrite, nickel chromite, etc.) since hematite is not protective. The only process that has been found to give measurable protection is high temperature (300°C) moist air. Application of this process to an installed reactor system is not feasible so it is restricted to new piping before it is installed. Such applications have been beneficial in reducing the rate of activity build up on new, passivated piping compared to unpassivated piping, particularly BWR replacement piping (230, 231).

Formation of a protective oxide film with high temperature oxygenated water on installed piping and other metallic components appears feasible with today's technology. No extraneous chemical additives are required. No additional equipment is required. The necessary temperature can be obtained with pump heat. However, there have been no field applications of this technology.

In CANDUs it is possible to build up a film more easily because of the presence of carbon steel instead of stainless steel. In these plants it is termed hot conditioning. It is routinely performed during the initial startup of each new plant, and after extended outages (232). However, its main purpose is to lay down a protective coating on the carbon steel surfaces to minimize corrosion during operation rather than to reduce the rate of contamination or recontamination. Hot conditioning does not appear to have any effect on the rate of recontamination, which is already very low.

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LESSONS LEARNED

Operational Decontaminations of Subsystems and Components

Lessons learned from operational decontaminations on LWR subsystem and components have been thoroughly documented (104, 227, 233–239). It is not the purpose of this section to reproduce them here, rather the reader is directed to these published references. For the most part, decontamination vendors are well acquainted with these lessons learned and have incorporated them into their procedures. Nevertheless, project managers from those plants performing a decontamination for the first time may wish to review them to ensure that mistakes made in the past are not repeated.

Some of the more common lessons learned that keep coming up time after time are listed below. These represent just a small fraction of all the lessons learned but are among the most important .

- The utility must setup a decontamination support organization that can work within the existing administrative structure of the plant. It must be staffed with competent, knowledgeable utility personnel in order to accomplish a successful decontamination. Augment the project team with subcontractors or consultants if there is inadequate in-house expertise.
- Perform an artifact test. This is especially important for plants that are performing a decontamination for the first time, or after plant chemistry conditions have changed (e.g., start of HWC). It is also important in determining whether the initial step should be oxidizing (e.g., NP) or reducing (e.g., LOMI). It may not be necessary for repetitive decontaminations on the same system if there have been no changes to plant chemistry
- Procedures must be flexible enough to allow the vendor to make changes to chemical and/or physical parameters during the application, while staying within predetermined boundaries. This is essential for maximum decontamination effectiveness. Don’t tie the vendor’s hands by forcing him to perform the decontamination within a very restrictive set of parameters.
- Contingency planning. This includes ensuring that adequate chemicals are either on site or available with short notice (a few hours) should additional steps be required. Similarly, additional IX resin and waste containers should be available on short notice. A reasonable supply of spare parts should be supplied by the vendor (e.g., pump seals).
- Set realistic expectations for a DF. For example, a DF of 10 on a system with initial fields of 1,000 mR/hr would require that the fields be reduced to 100 mR/hr. However, lower pre-decontamination levels may make a high DF unrealistic. The same DF on a system with initial fields of only 200 mR/hr would require that they be reduced to 20 mR/hr, which may be difficult or impossible for the vendor to achieve.

- Pre and post radiation surveys must be taken by the same individual using the same instrument in the same locations with the system in the same condition. For example, if the system was filled with water for the pre-decontamination survey (recommended), it should be filled for the post-decontamination survey. Removal of insulation while the decontamination is in progress may make it impossible to duplicate the survey. This should be avoided.

Full System Decontamination

The sole FSD in the USA was the 1995 application at Indian Point 2 in 1995. This application has been described in Chapter 12 of this report and in numerous presentations and publications (204, 240–246). While these documents describe the decontamination itself, many of them also contain information related to lessons learned. Documents that deal specifically with lessons learned from the IP-2 FSD are also available (246, 247 248). Numerous lessons learned are contained in these documents. For any utility contemplating a FSD, these documents should be considered mandatory reading because of the invaluable knowledge and experience gained during the IP-2 national demonstration. Only a fraction of the most generic and most important lessons learned are listed below.

- Allow adequate planning time for complex projects such as an FSD.
- Integrate plant operations into the FSD planning team.
- Create a “decontamination mode” for operation during the application.
- Ensure that the procedures allow flexibility while maintaining adequate process control within predetermined qualification limits.
- Technical support personnel and a utility decision maker on each shift.
- Use artifact tests to determine solvent effectiveness and the optimum number and sequence of process steps.
- Preoperational trial run of any vendor-supplied equipment.
- Hot functional test of all equipment before addition of any chemicals.
- Remotely operated control and monitoring system worked well and is recommended for future FSDs.
- Avoid threaded fittings in high pressure systems if potentially subjected to vibration or shock loads.
- Backwashable filters plugged during AP step; need to:
    1. avoid use of filters during oxidizing steps (MnO_2 is difficult to filter), or,
    2. increase filter capacity, or,
    3. increase backwashing capability (frequency and volume).
- Realistic estimates of the amount of corrosion products expected to be released are required. In the case of IP-2, 630 lbs. were predicted (430 lbs. min, 830 lbs. max) whereas only 275

lbs. were actually removed. This resulted in the additional equipment being larger and more complex than required.

Decontamination of Retired Facilities

As described in Chapter 13, in the USA there have been four decontamination applications of retired plants prior to decommissioning work – Big Rock Point, Maine Yankee, Connecticut Yankee and Trojan. Many lessons learned have been documented from these decontaminations (218, 219, 221, 249). Here again, it is not the intent of this report to provide a comprehensive list of all lessons learned. Rather the reader is directed to the cited references. However, a few of the more important lessons learned are listed below.

- High flow rates yield better results. Operation of the RCPs is recommended. If they are unavailable, secondary pumps such as RHR pumps should be employed. The last, and least preferred option, is to use vendor-supplied pumps.
- The nozzle dam assembly (the “spider”) employed at MY and CY worked well. It is an ideal way to avoid decontaminating the RPV, which will yield no net benefit to the plant and will only serve to increase waste volumes.
- For PWRs, inclusion of the SGs in the flowpath should be seriously considered. To achieve flow to all the tubes will require operation of the RCPs. While decontamination of the SG tubes will yield little immediate benefit to the plant in terms of dose savings, it will undoubtedly facilitate disposal of the SGs further down the road. In the most optimistic (but unlikely) case, they may be suitable for free release. A more realistic scenario is that the radiation fields are sufficiently low that they can be sent to a recycle center for further decontamination and eventually unrestricted release as scrap. A third scenario is that with the fields significantly reduced, they may be acceptable for shipment and disposal as a Class A Waste at a much reduced cost. The major downside to this option is the additional waste that is generated.
- Start decommissioning and decontamination planning well in advance of the final plant shutdown. Have the maximum number of plant systems and pumps available and online. Ideally, the decontamination should be performed immediately after final plant shutdown while all plant systems are still operational, and while knowledgeable plant operations personnel are still available.
- All decontamination processes tend to leave residual chemicals and undissolved particulates in deadlegs and low flow areas. While high flow rates will alleviate this problem somewhat, some collection in deadlegs should be expected. The plant should identify each of these potential deadlegs in advance and prior to the actual application, develop a plan for flushing them. In some cases the optimum method may be to backflush the lines into the main system during the final cleanup phase of the decontamination. This can only be done if plans and procedures are in place in advance.

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