

Decontamination Chemical & Mechanical

Prepared by

**John F. Remark, PhD
TuDocs Group
Manvel, TX 77578
jremark@gmail.com
434-229-5601.**

TABLE OF CONTENTS

INTRODUCTION	3
RADIOACTIVE CONTAMINATION	4
CORROSION PRODUCT GENERATION, TRANSPORTATION, ACTIVATION AND DEPOSITION.....	4
Corrosion Product Generation	5
Corrosion Product Transportation, Activation, and Deposition	7
DECONTAMINATION FACTORS	8
OXIDE DISSOLUTION.....	9
Reductive Dissolution.....	10
Chromium Dissolution by Oxidation.....	11
Oxalic Acid Rinse.....	12
CHEMICAL DECONTAMINATION PROCESSES: A Historical Prospectus	13
CAN-DECON and CAN-DEREM Processes.....	17
Termination Criteria.....	18
CITROX Process	19
CORD Process	21
LOMI Process.....	23
DFD Process	25
The Four DFD Steps.....	26
Termination Criteria.....	27
NP or AP Steps	27
Oxalic Acid Destruction Step	27
CAN-DEREM, CAN-DECON, CITROX and CORD	28
LOMI	29
Recontamination	29
MECHANICAL DECONTAMINATION TECHNIQUES	31
Decontamination of Exterior Surfaces and Removable Equipment	32
Janitorial-Type Decontamination.....	33
Decontamination Applicability	34
Operational Considerations.....	34
SUMMARY	36

INTRODUCTION

Decontamination is the removal of material from areas in which it is not wanted. This chapter will deal with the removal of radioactive isotopes but the same or similar technology could be utilized for the removal of hazardous material. The technology is similar to the cleaning of dirt, oil, or corrosion products except that radionuclides are associated with the material. Both cleaning and decontamination require similar technologies, methods, equipment, and procedures but the degree of cleaning may be different. The degree of cleaning for nonradioactive work is defined by certain types of cleanliness standards based upon the reason for the cleaning.

Decontamination is based on cleanliness standards that typically revolve around the person dose rate associated with the component or surface being cleaned. For disposal of the cleaning material the chemical composition of the waste must be understood as well as the radionuclide content. The disposal method and packaging will be dependent upon all of these items.

Decontamination is utilized to reduce the dose that workers may receive from a component or surface, to reduce the potential for airborne radionuclides or to reduce the disposal cost associated with the component or material. Some decontamination has been utilized to reuse or recycle the material. An example of reuse of material is the melting of slightly contaminated steels to be manufactured into shield blocks for a particle cyclotron. The shield blocks keep natural radiation sources from interfering with the acceleration of particles. Many tons of materials have been recycled for use in nonradioactive environments. In order to accomplish a use for "free-release" the material must not only be cleaned but then surveyed and found to be below the releasable level of the facility. The facilities that perform "free-release" are licensed by the state in which they operate. The license also identifies the release limits of the facility.

This document is meant as an introduction to decontamination, both chemical and mechanical. References are used throughout to direct the reader to areas where greater detail can be found. The listing of commercial companies should not be construed as a recommendation for the offerings of products or services from any of the commercial companies listed in this report.

There are several good general references on decontamination. These include an old but good general treatise on chemical and mechanical decontamination edited by J.A. Ayres (Ayres, 1970). The proceedings of a conference in 1979 on decontamination and decommissioning of nuclear facilities has valuable information (Osterhout, 1980). The Electric Power Research Institute (EPRI) has published various review articles and proceedings from numerous decontamination conferences (Remark, 1981a), (Remark, 1989b), (Smee, 1999), (Proceedings, 1998), (Proceedings, 1991), (Proceedings, 1993), (Proceedings, 1995).

RADIOACTIVE CONTAMINATION

There are two types of radioactive contamination, smearable and fixed. Smearable contamination is the type that can be easily removed from a material surface. Smearable contamination is typically removed by simply wiping the surface with a cloth rag. There are smearable wipes that health physicists used to wipe the surface (typically 100 cm²) to determine the contamination levels. The smearable contamination typically can be compared to dust that is found in all homes. The dust is removed from the surface by wiping with a cloth that is prepared by spraying a chemical to help “hold” the dust. Smearable contamination can be removed in the same manner. Smearable contamination also can be generated by treating, or attempting to remove, fixed contamination. Some decontamination methods will loosen the fixed contamination rendering it amenable to removal as smearable.

Fixed contamination is held tightly to the surface. Fixed contamination typically is associated with corrosion products on metal surfaces, concrete surfaces in which the contamination has diffused into the material, or other material on which the radionuclides could form some type of electrostatic or chemical bonding with the surface materials. The removal of fixed contamination typically requires harsher removal techniques. Techniques such as chemical dissolution of corrosion films or concrete scabbling are required to remove the fixed contamination. As stated previously the process of removing the fixed contamination from a surface can result in the creation of a smearable contamination. This process of turning fixed contamination to smearable contamination happens routinely during chemical decontamination or in concrete scabbling. Proper contamination and ALARA precautions should be utilized during the application of all decontamination applications.

CORROSION PRODUCT GENERATION, TRANSPORTATION, ACTIVATION AND DEPOSITION

Prior to determining which chemical decontamination process to use as well as the number of steps required for a successful decontamination application the composition and characterization of the corrosion film must be known. The types of corrosion films found in BWRs differ from those found in PWRs. The main difference in the corrosion films is the concentration and oxidation state of chromium.

The normal BWR operating chemistry involves an oxygen concentration of several hundred parts per billion (ppb) while the normal PWR operating chemistry contains several parts per million (ppm) of hydrogen which keeps the oxygen concentration in PWRs in the few ppb range. This difference in oxygen concentration in the two types of reactors results in significantly different concentrations of chromium in the corrosion film.

Corrosion Product Generation

During the operation of a nuclear power plant high temperature water is recirculated through the reactor coolant system. In BWRs the fluid typically is composed of high purity water with a small amount of oxygen (200 ppb). The PWR reactor coolant contains lithium, hydrogen, and boron but contains less than 10 ppb of oxygen due to the high concentration of hydrogen.

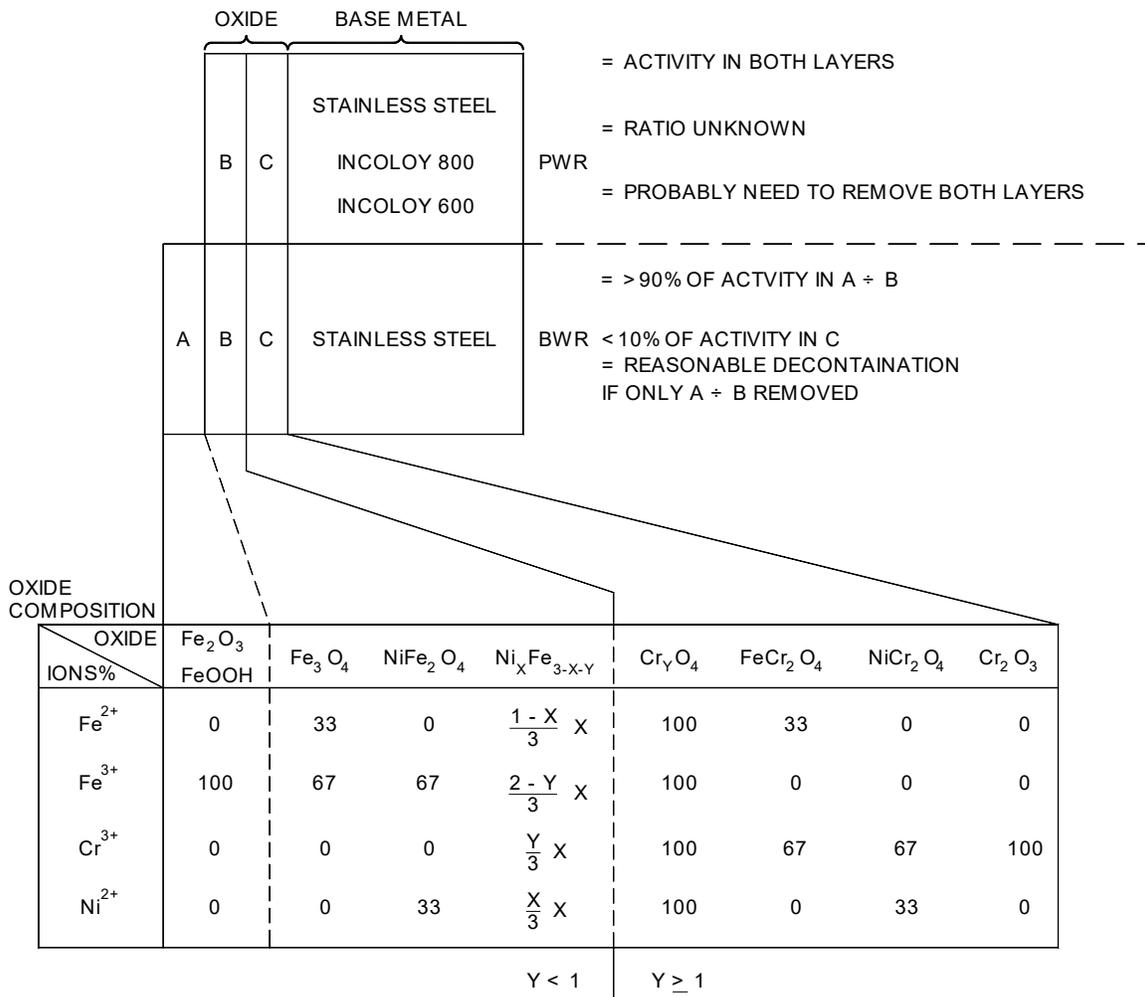


Figure 1. Oxide Types in LWR Systems

The corrosion film on the reactor coolant piping is composed of two discrete layers of corrosion products. The inner corrosion layer, next to the base metal, is formed by the in-situ corrosion of the base metal. The characteristics of the inner layer are based on the chemical composition of

the base metal with some dependence on the recirculating solution chemistry. The inner corrosion layer is developed over the first two to six months of operation at temperature. Any corrosion layer developed at a lower temperature or in different chemical environments will transform as the temperature and solution environment is changed. As the outer layer of the corrosion film develops, the growth of the inner layer is substantially reduced.

The outer corrosion layer is formed from deposition of corrosion products that are in the fluid flow as the coolant is recirculated throughout the coolant system as well as the precipitation of dissolved metals from the coolant flow. The composition of the film is governed by the source of the impurities. In PWRs most of the corrosion product is from the very slow dissolution of stainless steel and Inconel that make up the majority of the coolant surfaces. Cobalt also is a contribution to the corrosion film. The cobalt results from the erosion of stellite hard facing surfaces and is typically found as particulates as opposed to soluble.

The main isotopes causing the high radiation levels in reactor systems are Co-58 and Co-60. The source of the Co-60 is the neutron activation of Co-59. Co-59 presently is incorporated as hard facing materials in various areas of the reactor coolant system. Co-59 also is an impurity (100 to 1000 ppm) in iron-base and nickel-base alloys. Co-58 is produced from the transmutation of Ni-58 by the reaction $\text{Ni-58}(n,p)\text{Co-58}$. The Co-58 activity is more significant in PWRs than BWRs because of the high nickel alloys employed as materials of construction in their primary coolant systems (Remark, 1981).

The concentration of chromium in the corrosion film is a function of the reactor coolant water chemistry. In a PWR chemistry environment, as the surface material corrodes, the chromium is oxidized to the plus-three oxidation (Cr^{+3}) state. Cr^{+3} is insoluble in water and is incorporated into the corrosion layer and helps to protect the stainless steel and Inconel from further attack. In a normal BWR chemical environment the chromium ion is oxidized to the plus-six oxidation state. Cr^{+6} is very soluble in water and thus is solubilized from the corrosion film. In BWRs with hydrogen water chemistry, the chromium will remain as the Cr^{+3} in the corrosion film due to the low concentration of oxygen in this environment.

The chromium concentration in the corrosion film will affect the type of chemical decontamination process that is utilized to remove the corrosion film and the associated radionuclides. In a normal BWR environment, simple chelation chemistry can be utilized to obtain decontamination factors in the range of 6 to 10. This is because there are few if any chromium ions in the corrosion film to help protect the corrosion film from attack by the chelating agents. In a PWR environment or a hydrogen water chemistry BWR environment, the Cr^{+3} in the corrosion film protect the film from attack by chemical chelants. If this chemical environment is encountered, a pretreatment process must be utilized to obtain acceptable

decontamination factors. The pretreatment chemicals typically utilized are alkaline potassium permanganate, nitric acid potassium permanganate, or permanganic acid. All of these treatments will further oxidize the Cr^{+3} in the corrosion film to a water soluble Cr^{+6} . This will then open the film for further attack and dissolution by the chelates utilized in the following step.

Depending upon the thickness of the corrosion film as well as the goal of the chemical decontamination, several steps may be required. Thus, an alternating chemistry of pretreatment followed by a chelation step may be required. If the goal of the chemical decontamination is to have very high decontamination factors in a normal BWR environment, then a multi step process is recommended which will include a pretreatment step involving some type of permanganate ion.

Corrosion Product Transportation, Activation, and Deposition

While the nuclear power plant is in operation or in hot standby, the reactor coolant system is in a continuous recirculation state. This means that the reactor coolant pumps are operating, the chemistry is in the proper concentrations, the temperature is at operational parameters and water is flowing through the pipes at the required rate. Due to the operational parameters, corrosion is taking place on the base metals and erosion of the corrosion film is occurring. The system is in equilibrium so deposition of some of the soluble and insoluble material is occurring, however all this is occurring at a very low rate. None of the corrosion or erosion processes are such that they will impact the safe operation of the plant. This equilibrium of corrosion products does have a significant impact on the radiation levels that occur on out-of-core piping surfaces.

The corrosion products as well as the erosion products can deposit on the piping as well as the reactor vessel and core surfaces due to the equilibrium that is continuously taking place. Once the material deposits in the vessel area, it is exposed to neutrons. These neutrons then activate the material (See "Corrosion Product Generation"). After the material is activated it still participates in the equilibrium that is occurring in the reactor coolant system, and is either dissolved or eroded from the surface such that it is transported by the reactor coolant to a different area of the reactor coolant system. If the surface is an out-of-core surface, the result is a radioactive particle outside of the core. This results in radiation levels on the outside surface of the pipe. As the radioactive material continues to deposit on these areas, the radiation level on the piping surface increases.

The resultant deposits on the reactor coolant system piping become incorporated in the deposits. Some of the radioactive material is dissolved or spalled from the surface and deposited in another area but some of the material is incorporated in the deposit and held in place. Once the particle is held in place it appears to be able to diffuse in the metal surface deposit. Thus, after several years of operation we can find radioactive material throughout the deposit layer. The

radioactive material is not only found in the loose deposits from solid deposition on the surface but also in the tightly held deposits underneath the loose deposits.

Radioactive materials also can diffuse into the pores between the metal grains thus limiting the amount of decontamination that can be achieved with dilute chemical decontamination processes (Smee, 1999). This must be considered when performing a decontamination and when projecting the potential decontamination factor achievable.

Several investigators have performed substantial work on corrosion product generation, activation, and transportation in both boiling water reactors as well as pressurized water reactors. These references can be referred to for further information on this subject (Lister, 1989)(Berry, 1979)(Lister, 1979)(Lister, 1996)(Cunnane, 1978).

DECONTAMINATION FACTORS

The effectiveness of the decontamination is measured by decontamination factors. The decontamination factor is simply the radiation level of material or component prior to the decontamination application divided by the radiation level of the same material or component measured immediately after the decontamination application. A decontamination process that removes radioactive material will result in a decontamination factor greater than 1. There have been decontamination processes that have actually left more contamination behind in certain areas. These unsuccessful processes have resulted in a decontamination factor of less than 1. Some publications have referred to negative decontamination factors but their intent was to identify decontamination factors of less than 1.

In measuring the radiation levels for the determination of the decontamination factor, care should be imposed to maintain all parameters constant so that they do not influence the measurement of the radiation levels. This includes:

1. The person that takes the measurements should be the same. Two different people may hold the meter differently, point it in a slightly different direction, or not measure exactly the same specific area.
2. The exact meter should be utilized for the before and after measurements and it should NOT be calibrated in between measurements. Use a meter whose calibration is good throughout the decontamination application.
3. The exact location should be used for each measurement. Each location should be marked so that, if necessary, a different person can perform a measurement in precisely the same location.

4. Distance from the surface has to be duplicated. It is recommended that all radiation measurements be contact measurements in order to reduce the source term from surrounding and adjacent areas.

Equation 1 below is the formulation that can be utilized to determine the percent of radioisotopes removed from the surface (Remark, 1989). By performing the mathematics it can be determined that a decontamination factor of 10 results in a 90 percent removal of radioisotopes. Likewise a decontamination factor of 100 results in a 99 percent removal efficiency.

$$\text{Percent Activity Removed} = (1-1/DF) \times 100 \qquad \text{Eq 1}$$

A decontamination engineer will determine the cost-effective decontamination factor. In determining this, he will take into account the objective of the decontamination. If the decontamination is being performed to reduce man-rem, the surrounding radiation levels must be taken into consideration along with the work location. It is possible that a decontamination factor of 500 (99.8% removal) will result in a man-rem decontamination effectiveness of only 5 due to higher radiation levels in the surrounding area in which the work will be performed. However, if the work is being performed close to the area that was decontaminated, the man-rem reduction also may be large. The decontamination engineer in conjunction with the health physicist will determine the optimum decontamination factor taking into account the use of valuable resources. There are several types of electronic dosimetry that can be utilized to help measure the man-rem effective decontamination factor. These have been used in several chemical decontaminations so that area radiation level measurements can be made instantaneously and man-rem effective decontamination factors can be calculated. The electronic dosimetry, monitored at a central location, has been very effective in monitoring on-line radiation levels and it has assisted the health physicists in limiting access to high radiation areas of the plant during the chemical decontamination application.

It has been found, during past chemical decontamination applications, that low-dose areas of the plant that have been used for waiting areas have become the higher dose areas after a chemical decontamination application. This has not been because the radiation level has increased in the “low dose” area, but rather the remainder of the plant has become a lower radiation area.

Other reasons for the decontamination may be to ship the material to disposal. In these cases higher decontamination factors may be required in order to meet shipping or disposal requirements.

OXIDE DISSOLUTION

During a chemical decontamination, the corrosion products are dissolved. The corrosion products depend upon the type of environment in which it was generated. In BWR environments

the corrosion film closest to the coolant is typically hematite (Fe₂O₃) while the inner surface of the corrosion film is composed of a nickel-substituted magnetite (Ni_xFe_{3-x}O₄) where x is greater than 0 but less than 1.

In PWRs where the water chemistry contains soluble hydrogen and therefore much less dissolved oxygen, the corrosion film is composed of a chromium and nickel substituted magnetite (Ni_xFe_(3-x-y)Cr_yO₄) where x and y are variable (Segal, 1983). The sum of x and y are typically less than 1 in the outermost portion of the film but will increase as the depth into the film increases.

Due to the two types of oxides on the different reactor surfaces, different chemical solutions are required for optimum removal. A reducing condition is required for removal of a magnetite or nickel-substituted magnetite. However, if the film is composed of a high percentage of chromium, an oxidation environment is required to remove the protective chromium matrix.

Reductive Dissolution

The basis for the dissolution of corrosion films and therefore the mechanism for decontamination is the destabilization of the oxide lattice by attack with protons as in the following reaction.



This is the basis for chemical decontamination methods based on mineral or organic acids. Typically, higher concentrations of these chemicals are needed in order to increase the rate of the dissolution reaction. In order to increase the kinetic rate of the dissolution reaction with low concentration reagents, a reducing agent is employed to help destabilize the film matrix. The chemical reaction listed below is the typical reaction that occurs with the use of a low concentration chemical reagent that has a reducing agent.

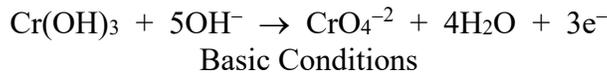
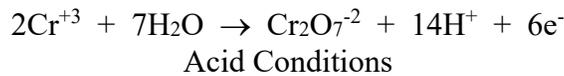


It should be noted that there is no ferric ion (Fe⁺³) on the product side of the reaction. The reducing agent reacts with the ferric ion in the oxide matrix and reduces the ferric ion to the corresponding ferrous ion (Fe⁺²). This reduction destabilizes the oxide film and renders it more susceptible to attack by the chelating agent that is contained in the low concentration chemical decontamination solutions. There are three conditions that a reductive-dissolving reagent must fulfill:

- a) Rapid electron transfer mechanism
- b) Chelation to provide adequate metal-ion solubility
- c) Sufficient proton concentration to give rapid dissolution of oxide anions.

Chromium Dissolution by Oxidation

The chromium that is found in corrosion products is in the plus three-oxidation state. Chromium in this oxidation state is very insoluble and must be either oxidized or reduced to render it water-soluble. It is significantly easier in power plant conditions to oxidize the chromium to the water-soluble chromate (Cr^{+6}) than it is to reduce it. The oxidation of the chromium can be accomplished in either an acid or a basic condition. The reactions are presented below.



The above stated reactions only oxidize the chromium on the surface of the oxide film. They do not appear to leach into the oxide matrix and react with the chromium in the “layers” below the surface. Thus, during the course of a chemical decontamination where the goal is to achieve a maximum decontamination factor, several alternating steps of reductive dissolution followed by chromium dissolution must be performed.

Both acidic oxidation (NP) of the chromium as well as basic oxidation (AP) has been accomplished in nuclear plants. There also was one application that used both acid as well as basic oxidation of the chromium. The acidic dissolution of the chromium works best on stainless steel surfaces but has not been as effective on the removal of chromium on Inconel 600 surfaces. Thus, in one application at Indian Point Unit 3 where the channel heads of the steam generator were being chemically decontaminated the chromium oxidation step was initiated in the basic condition to remove the chromium from the Inconel 600 tube surfaces and then was changed to acidic conditions to effectively oxidize the chromium on the stainless steel surfaces of the channel head. (Remark, 1986)

The composition of the basic solution for the chromium dissolution is approximately 1,000 ppm potassium permanganate with the pH adjusted to 10.5 to 11.5 with sodium hydroxide. This is a relatively stable solution and typically does not have to be replenished during the 6 to 12 hour step. For the acid solution the most common composition is 1,000 ppm potassium permanganate adjusted to a pH of 2.5 with nitric acid. In Europe, Framatome ANP, GmbH (Formerly Siemens KWU) has utilized permanganic acid for the dissolution of chromium (HP). Permanganic acid is potassium permanganate with the potassium replaced by a hydrogen ion (HMnO_4).

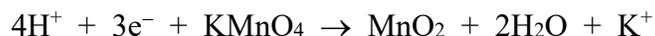
The acid potassium permanganate is not very stable in these conditions and must be monitored carefully during the course of the reaction. Replenishment of the nitric acid as well as the permanganate ion is not uncommon.

The oxidation of the chromium during the AP, HP or the NP process results in the reduction of permanganate anions. This reduction product is manganese dioxide (MnO₂), which is a dark brown precipitate that is very fine in character. It appears to collect on the walls and surfaces of the components in which it was generated and also likes to collect in sludge piles in low flow areas. This material should not be left behind in an operating plant because it will react with any kind of reducing agent that is typically present in the following iron dissolution step. An oxalic acid rinse is utilized to remove the manganese dioxide prior to the iron dissolution step.

Oxalic Acid Rinse

The amount of chemical required must be calculated prior to the oxalic acid rinse step. This calculation is performed by summing the amount of oxalic acid required to reduce the remaining potassium permanganate as well as the manganese dioxide to manganous ion (Mn⁺²). This calculation is performed by knowing the initial concentration of potassium permanganate added

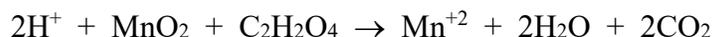
to the system volume as well as the “ending concentration” of potassium permanganate. From the chemical equation below the amount (moles) of MnO₂ generated can be calculated.



The exact amount of oxalic acid can be calculated from the stoichiometric relationships presented in the following two equations in which oxalic acid is reacting with the potassium permanganate as well as the manganese dioxide.



and



Note that the permanganate and the manganese dioxide destruction reactions require an acidic condition. In order for the manganese dioxide to be dissolved by oxalic acid, the pH of the solution must be on the order of 3.5. In order to achieve this pH during the destruction phase after the oxalic acid is added, the solution must be passed through a cation resin column in the hydrogen form. The cation resin column will remove the potassium as well as any manganous (Mn⁺²) that was generated with the addition of the oxalic acid. These ions will be replaced by hydronium ions (H₃O⁺) that will reduce the pH. The pH must be monitored often during this phase of the chemical decontamination process. If the cation resin columns are continuously utilized, it is possible to reduce the pH below 3.0. While these chemical conditions will assist in

the removal of the corrosion film with the associated radionuclides, it also leads to an aggressive condition that has been found to lead to IGSCC on heavily sensitized SS 304. IGA/IGSCC has never been observed in field applications. This is the reason that oxalic acid was eliminated from the CAN-DECON reagent and resulted in the formation of CAN-DEREM. (These solvents will be discussed later in the article).

Bengel and Remark performed research in the early 1990s and determined that formic acid would be a good alternative for oxalic acid in the destruction of permanganate ion and the manganese dioxide (Remark, 1993). The use of formic acid would eliminate any potential for the oxalic acid formation of IGA or IGSCC on heavily sensitized SS 304. The reaction between manganese dioxide and formic acid is listed below:



Notice that no hydronium ions are required for this reaction so, in theory, it could be utilized at a neutral pH.

Carbon dioxide is a major reaction product of all of the destruction reactions. During a chemical decontamination process, the carbon dioxide must be vented off so that the system or component is not over pressurized. There also is concern that the carbon dioxide could react with the water in a pressurized system to generate bicarbonate.



The resultant bicarbonate anion would then result in additional anion resin requirements for the cleanup of the solution. It was found in research as well as in the application of the full system chemical decontamination at Indian Point Unit 2 in 1995, that the carbon dioxide did not result in the formation of bicarbonate anion.

CHEMICAL DECONTAMINATION PROCESSES: A Historical Prospectus

Prior to 1979, all of the chemical decontaminations performed were at government facilities and all utilized concentrated chemicals. Some of the earliest chemical decontaminations were performed at the PRTR at the Hanford Reservation in southeastern Washington State. After an experimental fuel element failure on August 21, 1962, the PRTR was required to be decontaminated (Ayres, 1970a).

The PRTR is of particular interest since it is the first chemical treatment of a complete reactor to reduce radiation levels. The chemical process utilized for the chemical decontamination was APOX (alkaline potassium permanganate and oxalic acid). (Perrigo, 1966) During the decontamination, they found that a ferrous oxalate precipitate formed on the piping and component surfaces. This precipitate was difficult to remove and another application of a

modified solvent had to be performed. The modified solvent was APACE which is alkaline potassium permanganate followed by citric acid with EDTA. This solvent removed the ferrous oxalate precipitate and a decontamination factor of 4 to 16 was ultimately achieved.

The waste from this chemical decontamination was transported to waste tanks at the Hanford reservation where it resided awaiting ultimate disposal.

The N-Reactor at Hanford was another example of concentrated chemicals being used to remove the corrosion products from reactor coolant surfaces. In the case of the N-Reactor, the solvent most often employed was phosphoric acid. This reactor was decontaminated annually from 1967 to 1983 and the decontamination resulted in decontamination factors of 3 to 6 on the carbon steel surfaces. The waste was transported to the waste tanks on the Hanford Reservation.

The first nuclear reactor to decontaminate the primary piping and then put the utilized chemical on resin, was Shippingport PWR which was decontaminated in early 1964 (Abrams, 1966). The process utilized was AP-AC, an alkaline potassium permanganate process, followed by an ammonium citrate process. This decontamination was of great importance in the history of chemical decontamination since it was the first application of very dilute reagents and treatment of all spent solutions by ion exchange resin.

The amount of ion exchange resin was underestimated during this project and the estimated 700 cubic feet of ion exchange resin was expanded to 900 cubic feet. The radiation levels at several areas of the reactor coolant system were reduced by a factor of 50 while other areas resulted in higher radiation levels after the chemical decontamination process. The higher radiation levels were a result of undissolved crud being transported to low or no flow areas. It appears that the diluted ammonium citrate solution was not aggressive enough to dissolve the crud in a timely manner. Thus some of the crud was released to the liquid and “deposited” in areas of the piping system with little or no flow.

The Shippingport chemical decontamination was the first full-scale test of a procedure that essentially was a cyclic or continuous process, requiring no large additional facilities for auxiliary operations such as preparation and storage of solution, and storage and disposal of wastes, The effort merits special commendation in that it showed that the dilute chemical decontamination process is feasible, although much work still needed to be performed (Ayres, 1970a).

The first United States commercial application of low concentration chemical decontamination process occurred at Vermont Yankee in 1979. London Nuclear utilized the CAN-DECON process to decontaminate the Vermont Yankee Reactor Water Cleanup System (RWCU) (Beaman, 1982) (LeSurf, 1982). The average decontamination factor obtained during this first commercial application of dilute chemicals was 5.0 that resulted in the removal of 80 percent of the activity associated with the radiation levels on the piping surfaces. The only waste that resulted from this work was approximately 25 cubic feet of ion exchange resin.

The first North American application of the LOMI process was performed at the Monticello Nuclear Power Station in 1983 (Remark, 1984). The LOMI process was novel in that it utilizes the vanadous (V^{+2}) ion to reduce the ferric ion to ferrous. While this reduction takes place, the vanadous ion is oxidized to vanadic (V^{+3}) ion. The LOMI process is substantially faster than the previously utilized dilute chemical decontamination processes. The entire reactor recirculation system was decontaminated during this process. The decontamination factors achieved during this chemical decontamination were 25. The range of decontamination factors was from 1.6 to 64.3. The process utilized was a LOMI-NP-LOMI.

Bechtel National performed the first major chemical decontamination of a steam generator channel head at Indian Point Unit 3 in 1985 (Nielsen, 1986)(Greenman, 1986). The entire steam generator channel head was decontaminated as well as approximately 6 feet into the steam generator tubes. Due to the fact that this was a PWR and therefore the chromium needed to be removed from both stainless steel and Inconel surfaces, a combination of AP and NP was required. The process was initiated with an AP step and after approximately 12 hours of contact time, the pH was changed to acidic conditions by adding nitric acid.

The decontamination factors achieved for this chemical decontamination were XXX. The only radioactive waste generated was ion exchange resin. Approximately XXX cubic feet of resin was generated.

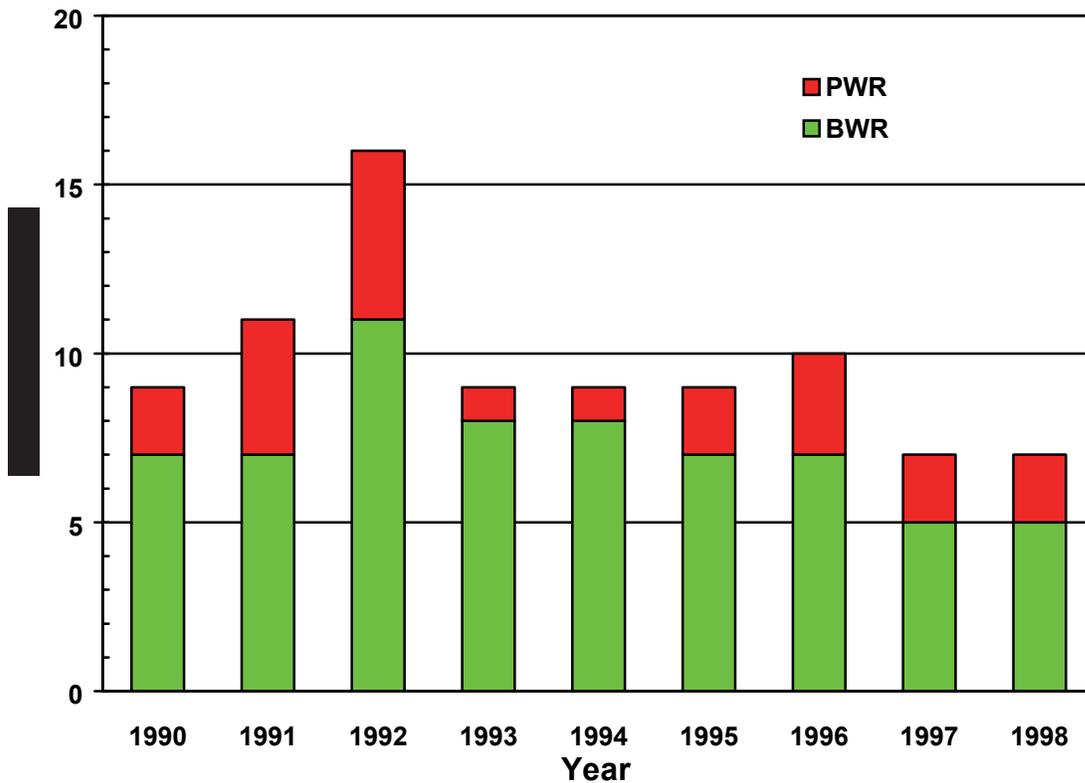


Figure 1. Relationship between BWRs and PWRs Performing a Chemical Decontamination

Figure 1 presents the number of Boiling Water and Pressurized Water Reactors that applied chemical decontaminations from 1990 through 1998. This figure and relationship between BWRs and PWRs performing chemical decontamination is typical of those that were performed prior to 1990. Typically, many more BWRs perform a chemical decontamination than PWRs.

Figure 2 illustrates the type of chemical decontaminations that were performed at the various plants. The LOMI process has been utilized the most at operating commercial nuclear power plants for chemical decontaminations. As will be seen later in this report, the LOMI process generates the most radioactive waste but is favored by most utilities due to its backing by the Electric Power Research Institute (EPRI).

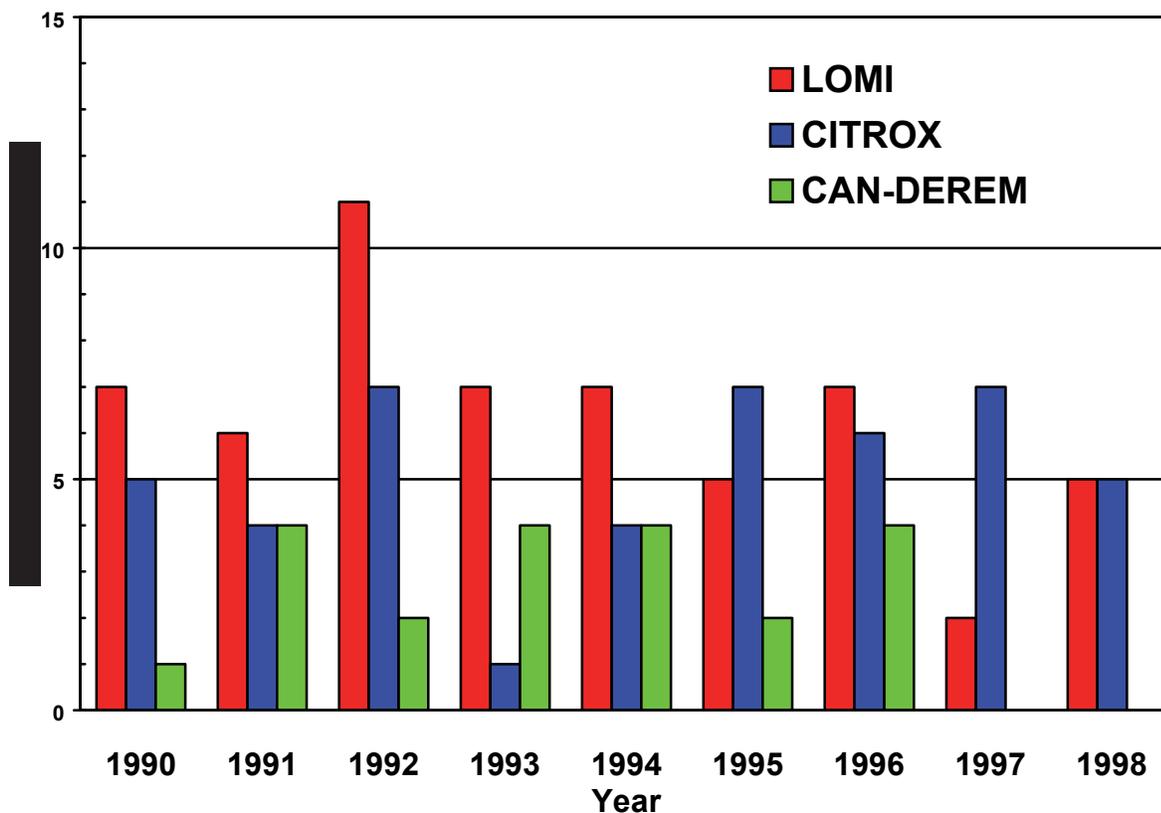


Figure 2. Types of Chemical Decontaminations Performed

CAN-DECON and CAN-DEREM Processes

The CAN-DECON chemical decontamination process was developed by AECL in the 1970s for use in CANDU heavy water reactors. This is a low concentration chemical decontamination process in which only radioactive waste generated is ion exchange resin. This is important in the use for the chemical decontamination of CANDUs, since they are heavy water moderated reactors. These reactors could not afford the loss of the expensive heavy water during the chemical decontamination process. CAN-DECON is composed of EDTA, citric acid, and oxalic acid in a molar ratio of approximately 2:1:1.

The CAN-DEREM process does not contain oxalic acid. The oxalic acid was eliminated from the CAN-DECON process due to some aggressive testing which indicated that the oxalic acid in the CAN-DECON solvent may lead to IGA/IGSCC in heavily sensitized SS 304. Ever since the indications that CAN-DECON could lead to IGA, only the CAN-DEREM process was utilized on these stainless steel systems.

The CAN-DECON and CAN-DEREM processes start with a solid powder that are typically dissolved in a mix tank. After the chemicals are dissolved in minimal water they are added to the chemical decontamination volume. There also have been instances where the chemicals are added to the decontamination volume in a flow-through basket and are dissolved as the decontamination volume is circulated through the basket. Enough chemicals are added such that the final concentration of the CAN-DECON or CAN-DEREM is on the order of 1,000 ppm or 0.1% by weight. Prior to the addition of the chemical, the decontamination volume has been heated to an operating temperature of approximately 200°F.

As the EDTA, citric acid, and oxalic acid dissolve in the decontamination volume, the oxide deposits begin to be solubilized and some crud burst may be observed due to loosening of the deposits by the decontamination chemicals. The low concentration of chemicals does not allow a large volume of deposits to be removed by the available chelant. Therefore on-line regeneration is required.

The on-line regeneration removes the iron from the chelant. In the case of CAN-DECON and CAN-DEREM the chelant is EDTA. The removal is accomplished by flowing the decontamination volume through cation exchange resin. The cation resin must be in the hydrogen form. Thus, as the iron is exchanged to the cation resin, it gives up to the solution two or three hydronium ions (H_3O^+) depending upon the oxidation state of the removed iron. Without this on-line ion exchange and regeneration of the active decontamination ingredients, the decontamination factors would be limited.

The recirculation and regeneration can continue indefinitely, however in practicality, the chemical decontamination is terminated with 12 to 24 hours after the addition of the chemicals.

Termination Criteria

The termination of the CAN-DECON and CAN-DEREM process is a subtle judgment call by the process engineer. Typically the iron concentration can be monitored during the chemical decontamination process and the removal rate by the cation exchange resin can be determined. As the soluble iron is reduced to the approximate value of the cation exchange resin outlet, the step can be successfully terminated. This statement assumes that the cation exchange resin has not been depleted.

At the Indian Point Unit 2 full system chemical decontamination performed in 1995, on-line radiation monitors were set up throughout the piping system. The dose rates were monitored continuously. If some of the dose rates were being reduced, the process was not terminated. Typically, during this chemical decontamination process all of the dose rates were stabilized significantly, prior to the termination of the process.

Once the step was terminated, anion exchange resin was brought on-line with the cation exchange resin. Therefore the flow path was through a cation exchange column followed by an anion exchange column. In lieu of these two columns a mixed bed column could be utilized.

The cation and anion resin column, or the mixed bed resin column, remove all of the remaining cations and anions which include all of the iron ions as well as the EDTA, citric acid, and the oxalic acid. The solution is passed through the columns until the water quality meets or exceeds the quality demanded by the site. Typically these specifications are on the order of a pH between 5 to 10, TOC < 10 ppm, and a conductivity of < 10 µmhos. Of these specifications the TOC, total organic carbon, is the hardest to achieve.

All of the organic acids utilized for chemical decontaminations are weak acids. Therefore as they pass through the ion exchange resin only a portion of them are removed due to their equilibria that are determined by their concentration and the equilibrium constant. If the pH can be increased to between 7 and 8, the pH will push the equilibrium to the dissociated state where the organic acids can be easily removed by the ion exchange resin. The equation below is a generic equation for the dissociation of weak organic acids. The observer can see that as sodium hydroxide is added to the solution the organic acid tends to be dissociated. The R⁻ is the part of the organic acid that leads to the TOC concentration. As can be seen in the equation below, as the acid becomes dissociated, the R⁻ can be removed on the anion exchange resin.



Decontamination factors of 5 to 20 have been observed with the use of the CAN-DECON and CAN-DEREM processes. If no oxidation step is utilized in the process lower decontamination factors will be found in BWRs. Alkaline Potassium Permanganate results in lower decontamination factors than Nitric Potassium Permanganate. The CAN-DEREM process is less aggressive due to the absence of oxalic acid and therefore can be used without corrosion concern on both stainless steel as well as carbon steel surfaces.

CITROX Process

The citrox reagent was developed by R.D. Weed and first utilized on the Plutonium Recycle Test Reactor (PRTR) located at the 300 Area of the Hanford Reservation (Weed, 1968). The reagent was composed of citric acid and oxalic acid thus its name CITROX. The original formulation for the PRTR chemical decontamination was approximately 0.3 M (25,000 ppm) citric acid and 0.2 M (58,000 ppm) oxalic acid. Inhibitors were also added to this solution due to its corrosive nature. Early in the history of the dilute chemical decontamination, PN Services modified this solution and applied it in the field at a concentration of approximately 0.2 weight percent. This product became known as PNS CITROX A that did not contain an inhibitor. PNS CITROX B included the use of an inhibitor and was utilized in carbon steel systems. This process is somewhat more aggressive than the CAN-DEREM or CAN-DECON solvents due to its higher

BWR and PWR component decontamination but has not been qualified for application on a full reactor recirculation system in a BWR or a reactor coolant system on a PWR.

The CITROX system is similar to the CAN-DEREM and CAN-DECON system in that it starts with a powder that is dissolved in a mix tank. After the chemicals are dissolved in minimal water the soluble chemical is slowly added to the decontamination volume. The rate of addition is such that the chemicals are added throughout one recirculation of the decontamination volume. These chemicals also could be added by flowing a bypass system through a basket or other container which holds the solid powder. Enough chemicals are added to result in a final concentration of CITROX in the total decontamination volume of 0.2 weight percent. Typically the molar concentrations of oxalic and citric acid approximately equal. Depending upon the results of any laboratory tests the ratio between the oxalic and citric acid can be slightly varied in order to optimize the decontamination factor.

The CITROX is regenerated on-line as are most dilute chemical decontamination reagents. In the case of CITROX, the on-line demineralization should be maintained at a high enough rate in order to keep the concentration of ferric ion to less than 10 ppm. Due to the elimination of the EDTA in the reagent the ferric ion is not as strongly complexed in the CITROX solution and therefore is available for ferric ion corrosion. This corrosion is substantially reduced if the ferric ion in solution is maintained at concentrations of less than 10 ppm.

During the decontamination operation the bulk solution can be analyzed for oxalic acid and various metals as well as pH. During the process, the effectiveness of the regeneration demineralization cation resin vessels should also be monitored. Once the iron concentration ceases to increase in value and the on-line radiation levels have stopped decreasing in value, the decontamination process should be terminated. During the chemical decontamination operation other metals such as chromium should also be monitored. If a increase in chromium concentration is observed in the decontamination solution after the initial injection, it is an indication that base metal corrosion may be occurring. At that time, the process engineer should evaluate the reactions that are occurring on the system surfaces and take the appropriate actions.

At the termination of the CITROX process, the solution can be demineralized with cation and anion resin to return the decontamination solution to demineralized water. All of the reagents added to the solution as well as all of the dissolved material are either cations or anions that will be removed on ion exchange resin. The weak organic acids are not totally dissociated at all pH units and therefore it will take some recirculation of the decontamination solution through the ion exchange vessels to totally clean the water. The time required to return the water to plant specified conditions of 10 μ mhos and 10 ppm TOC is typically 8 half lifes.

The recirculation of the decontamination solution can continue indefinitely but in practice, the chemical decontamination is typically terminated within 12 to 24 hours after the addition of the chemicals to the system volume.

CORD Process

CORD is an acronym for Chemical Oxidation Reduction Decontamination. It evolved from the OZOX process (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 (Wille, 1986).

The CORD process is actually a family of processes that utilizes permanganic acid (HMnO₄) as the oxidizing agent and oxalic acid as the dissolution and chelating agent.

Ultraviolet light as well as hydrogen peroxide is used to reduce the concentration of the oxalic acid to reduce total waste volumes. All of the waste generated by the CORD process is ion exchange resin. This process utilizes the permanganic acid as the oxidizing agent because its use also reduces the total ion exchange requirements.

The permanganic acid oxidizes the protective chromium in the corrosion film to the water soluble bichromate anion by the following chemical reaction:



Permanganate ion also tends to react with any oxidizable species contained in the water. This oxidation takes place in an acid medium. The reaction products of the permanganate are manganese dioxide, oxygen, and water. During the permanganic acid step in the CORD process, the process engineer must monitor the concentration of the permanganate ion. This concentration should be maintained in the range of 50-300 ppm for proper application. The application temperature is 190 to 200°F. Early in the reaction process, the permanganate concentration must be maintained at the higher end of the concentration range. As the step reaches the termination phase of the process, the concentration can be maintained at the lower end of the range. High concentrations of permanganic acid should not be added in the later stages of the process since it does not increase the amount of soluble chromium but it does add to the amount of waste generated during the chemical process.

During the oxidation phase of the CORD process, the chromium concentration also should be monitored. The chromium concentration will determine the termination of the process. The chromium concentration will increase rapidly and then the rate of increase will fall off sharply. When the rate of the chromium increase has reached diminishing returns, the oxidation phase of the CORD process can be terminated.

At the termination of the oxidation step, the excess permanganic acid and the resultant manganese dioxide must be destroyed prior to proceeding to the reduction step. The material is destroyed by reducing both species to the corresponding manganous ion (Mn⁺²). The reduction is performed by adding stoichiometric amounts of oxalic acid to the oxidation solution. This step is not a separate step from the decontamination step. The addition of oxalic acid for the reduction

of the remaining permanganic acid and the manganese dioxide as well as the decontamination process is added by one addition to the solution.

The decontamination step is achieved by adding an excess of oxalic acid for an ultimate concentration of approximately 1,500 ppm. The excess oxalic acid must be added for the destruction reaction of the permanganate and manganese dioxide reaction to occur. Without the addition of the excess oxalic acid, the pH will not be acidic enough for the destruction reaction to occur. The pH must be in the range of 3.5 to 4.0. For other processes described, the pH is achieved by passing the solution through a cation resin which will remove the cations in solution replacing them with hydronium ions (H₃O⁺).

Once the permanganate and manganese dioxide has been reduced to manganous ion the oxalic acid will dissolve the magnetite in the corrosion film by the following reaction.

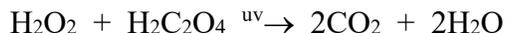


When the decontamination process is initiated, the cation columns must be placed on-line. The cation columns will remove all of the metal ions that have been dissolved by the oxalic acid and will regenerate the oxalic acid for further removal of the corrosion film. The regeneration of the oxalic acid will produce hydronium ions that will assist in sustaining the reaction. The temperature should be maintained at approximately 195°F for optimum conditions.

During this stage of the decontamination process the metal concentration as well as the oxalic acid concentration should be monitored to maintain the chemistry in the optimum concentration. If the amount of oxalic acid is substantially reduced at the same time that the iron concentration is reduced, the reaction may not be completed. In this case, the oxalic acid concentration may need to be spiked to optimize the reaction kinetics. The termination of the reaction will occur with optimum oxalic acid concentrations along with reducing metal concentration, especially iron concentration. It must be noted that the iron concentration should be monitored both before and after the ion exchange resin. The iron removal rate can be calculated from these analyses. The resultant buildup in concentration of the metals ions in the bulk solution from the dissolution of the corrosion film can be determined. These calculations then will lead to the optimum time for termination of the decontamination step.

At the termination of the decontamination step, the solution needs to be cleaned up to demineralized water quality. This can be accomplished in two ways with the CORD process. The original method of removing the oxalic acid was to use ion exchange resin. The oxalic acid was passed through an anion resin that removed the oxalate anion and the resultant hydroxide ions (two) released to the solution by the anion resin reacted with the hydronium ions from the oxalic acid and formed water. In the United States, the small amount of ion exchange resin resulting from this process was not a problem. However, in Europe, any ion exchange resin is difficult to dispose off site. For this reason the inventors of the CORD process developed a

decomposition method for the oxalic acid which uses hydrogen peroxide and ultraviolet light. The following reaction lists the products and reactants of the oxalic acid decomposition.



During this reaction the solution is passed through a light chamber in which intense ultraviolet light is used to decompose the oxalic acid to carbon dioxide and water (Bertholdt, 1994). If a CORD process is applied in a closed system, calculations should be performed in order to determine the increase in pressure that may be seen due to the generation of the carbon dioxide gas. Depending upon the venting system utilized, the carbon dioxide gas generated during the permanganate and the oxalic acid destruction process may exceed the system design pressure.

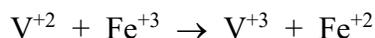
The anion resin required for a 10,000 gallon decontamination volume is typically in the range of 25 to 60 cubic feet per CORD step. Depending upon the system being decontaminated and the loading on the decontamination volume surfaces, the generated cation and anion resin may fit into a single 8-120 high integrity container for disposal in the United States.

The process described above is for a single CORD application. This application can be repeated until the decontamination factor goal is achieved. A typical CORD process takes from 4 to 16 hours if ion exchange cleanup is employed but can be extended to 10 to 36 hours if the hydrogen peroxide/UV oxalic acid decomposition is utilized.

The decontamination process engineer must work closely with the outage scheduler to determine the optimum treatment method. As can be seen above, the UV destruction process requires up to 20 additional hours. If the decontamination process is on critical path, it may be substantially cheaper to generate the ion exchange resin or use a combination of ion exchange and UV destruction to reduce the critical path time for the outage. Additional information regarding the CORD process may be found in the following references (Bertholdt, 1998) (Bertholdt, 1998a).

LOMI Process

The Central Electricity Generating Board in the United Kingdom developed the LOMI chemical decontamination process in the early 1980s with financial support from the Electric Power Research Institute (EPRI) (Bradbury, 1983). LOMI, an acronym for **Low Oxidation state Metal Ion** is considered to be fundamentally different from the other chemical decontamination processes described previously in this report. To a certain extent, this is correct in that the LOMI process employs a strong reducing agent to attack the ferric ion in the oxide matrix. The strong reducing agent is the vanadous ion that is in solution chelated with picolinic acid. The vanadous ion is oxidized to vanadic ion while reducing the ferric ion to ferrous ion as illustrated in the following reaction.



Once the various metal species are solubilized, they are complexed with picolinic acid, which is added to the solution at the beginning of the step. The process is utilized at a pH of between 4 to 5, therefore thus sodium hydroxide also is added to the concentrated chemicals prior to injection.

This process is identified as reduction dissolution and is much faster than acid dissolution. Typical LOMI applications involve a completed reaction in approximately 6 hours. The vanadous ion appears to be unstable in a carbon steel system and therefore it is not recommended for carbon steel piping systems.

A typical LOMI process utilizes about a 6 mMolar solution of vanadous ion. Prior to injecting the concentrated vanadous ion into the decontamination volume a solution of picolinic acid is mixed in the decontamination volume. The picolinic acid is mixed in a concentrated solution that is prepared in a manner such that 6 moles of picolinic acid is utilized for 1 mole of vanadous ion. Sodium hydroxide is also mixed with the picolinic acid prior to injection into the decontamination volume. Besides the obvious picolinic acid the vanadous formate contains formic acid as an impurity from the chemical reaction that produces the vanadous ion. When dissolving the picolinic acid, add the sodium hydroxide to the mix tank prior to adding the picolinic acid. This mixing method will significantly reduce the dissolution time for the picolinic acid.

The molar ratio of picolinic acid to vanadium ratio is rationalized by understanding that three atoms of picolinic acid are required to complex 1 atom of vanadium as well as 1 atom of iron. It is assumed that for every atom (or mole) of vanadous there will be one atom (or mole) of ferrous iron produced (see above equation). Some researchers have theorized that a lower molar ratio of picolinic acid could be utilized to maintain ion solubility but the majority of utilities have maintained the higher molar ratios during the decontamination process.

During the LOMI process both vanadous ion concentration as well as iron concentration is monitored to identify the termination point. The vanadous ion can be monitored spectrophotometrically and will decrease with time while the iron concentration will increase as the corrosion film is dissolved. Even though the vanadous ion concentration may be zero, there is still a driving force for the dissolution of the corrosion film by the oxidation potential of vanadic/vanadate oxidation couple. This couple also is found to be somewhat corrosive so the reaction should not run for more than 60 to 90 minutes in this mode. By this time the iron concentration should start to approach an asymptotic value that will result in the termination of the process.

At the termination of a LOMI process, the solution will be diverted to a cation and anion resin column that will remove the cations and anions respectively.

There are three disadvantages of the LOMI process; one disadvantage is that the vanadous ion is not stable in carbon steel systems. If there is a large amount of carbon steel in the

decontamination volume, a different process should be utilized. The second major disadvantage is the large amount of resin required for removal. The resin quantities can be somewhat reduced by reducing the molar ratio of 6:1 for picolinic acid to vanadous that is added to the system. However, the majority of the resin burden is from the three equivalents per mole for the vanadic ions that are in solution. The other decontamination processes do not have this resin burden. The last disadvantage is the cost of chemicals. The vanadous formate is made specifically for each client and has a short (6 month) shelf life. This is an expense that other processes do not have.

Even due to the resin burden and extra cost of chemicals, the LOMI process is the most frequently used by utilities within the United States (See Figure 2). The reason for its popularity is the reduced time for completion of the process. However, as the systems get larger, such as full system decontamination with a 100,000 gallon (378,000 liter) volume, the higher quantity of resin and cost of chemicals have pushed the economical evaluation away from the LOMI process. The only full system chemical decontamination process utilized to date on a commercial operating reactor was the AP/CAN-DEREM process.

DFD Process

The DFD process, a **Decontamination For Decommissioning** process, utilizes fluoroboric acid as the active ingredient (Bradbury, 1997) (Bradbury, 1998). The DFD process was developed to remove the radioactivity from metallic surfaces by corroding the metal surfaces. In theory, this general corrosion on the base metal would release any radionuclides deposited in pits or crevices within the base metal. After several cycles of DFD (eight to ten), the component's radiation levels are reduced and the component may be able to be free released.

The DFD process is licensed by the Electric Power Research Institute (EPRI). The process is multi-step and utilizes potassium permanganate to raise the oxidation potential of the solution to dissolve the protective chromium layer on some types of stainless steel. The process is initiated by heating the decontamination volume to 200°F. At that time, enough concentrated fluoroboric acid is added to the system to achieve a final concentration of 10mM (approximately 0.9 grams per liter) that results in a pH of approximately 2. The addition of the fluoroboric acid raises the pH of the solution due to the dissolution of the corrosion products. To maintain the pH of the solution in the 2.0 to 2.4 region for optimum performance of the fluoroboric acid, the solution is circulated through a cation resin column. The cation resin removes the dissolved metals from the solution, replacing them with the protons (H_3O^+) from the cation resin.

In order to remove the protective chromium layer, after the dissolution of the corrosion products has been substantially reduced, the flow through the cation columns is terminated and enough potassium permanganate is added to the decontamination volume to maintain an active concentration of the potassium permanganate of 100 ppm. Typically a total of 300 ppm is required to oxidize all of the exposed protective chromium to the solution chromate anion.

The next step involves the dissolution of any MnO_2 that is generated by the reduction or decomposition of the potassium permanganate. This dissolution is accomplished by adding a stoichiometric amount of oxalic acid to the solution. The pH of this solution must be in the area of 3.5 to efficiently drive this reduction reaction. The pH can be reduced during this step by passing the solution through a cation resin column. This ion exchange resin would remove the metal ions in solution (such as manganous ion, Mn^{+2}) and replace them with hydronium ions (H_3O^+). It must be noted that the Cr^{+3} can form a $\text{Cr}(\text{C}_2\text{O}_4)_3^{-3}$ compound with excess oxalic acid. The chromium ion will not be removed from this compound by the cation exchange resin and thus the chromium will tend to build up in solution during the course of a DFD application. The formation of this chromium compound is not a problem in other chemical decontamination applications because a mixed bed resin is inserted into the flow at the end of the oxalic acid destruction step. The anion portion of the mixed bed resin does an excellent job of removing this chromium oxalate complex.

If excess oxalic acid is present in the solution after all of the manganese dioxide is dissolved, a stoichiometric amount of potassium permanganate is added to the solution to remove it. With the cation resin column on line, all of the cations will be removed, achieving a chemical balance for the next fluoroboric acid step.

The Four DFD Steps

In summary, the DFD process consists of four discrete steps for each cycle. The first step initiates the chemical decontamination by adding the fluoroboric acid to the solution once the solution has achieved the DFD operating temperature of 200°F . The typical concentration of the fluoroboric acid is 10 millimolar. During this time, the solution is recirculated through a filter as well as a cation resin column until the particulate material has been removed and the dissolved metal concentration is below 10 ppm. At this point the cation resin columns are removed from the flow path.

After the cation columns are removed from the flow path, approximately 200 ppm of potassium permanganate is added to the fluoroboric acid solution to solubilize the chromium in the corrosion film. This reaction also is performed at 200°F and continues until the potassium permanganate is reduced to manganese dioxide. This reaction requires two to four hours.

The oxidation phase is followed by the destruction phase of the process that involves the addition on stoichiometric amounts of oxalic acid to dissolve the manganese dioxide. The cation resin columns are placed back on-line during the destruction phase of the process in order to maintain the optimum pH for the destruction as well as to remove the soluble ions in preparation for the next cycle. The purification half-life should be less than one hour with 30 minutes being the

preferred half-life¹. The completion of this step can be determined by the measurement of the soluble manganese ions in solution. These ions should be dissolved and removed by the ion exchange resin. Therefore when the concentration of the soluble manganese ions approach zero, the step can be terminated.

The final step in each cycle is the transition phase that returns the solution to the fluoroboric acid condition. In this phase, the oxalic acid concentration is determined by analytical methods and a stoichiometric amount of potassium permanganate is added to oxidize the oxalic acid to carbon dioxide and water. During this step the cation resin vessels are again placed in the flow path to remove the dissolved cations. After the dissolved cations are below a concentration of approximately 10 ppm the cycle is complete and additional cycles can be initiated. Typically 6 to 12 cycles are required to achieve the satisfactory decontamination factor. The number of cycles required will depend upon the ultimate decontamination goal at each individual facility.

At the termination of the DFD process the temperature is reduced to approximately 140°F and either mixed bed resin or a combination of cation followed by anion resin is required to remove the remainder of the dissolved metals along with the fluoroboric acid. The anion resin also will remove any of the accumulated chromium oxalate complex that was discussed earlier in this section.

Termination Criteria

All chemical steps are terminated by specific analytical termination criteria. Typically one or two parameters are used to terminate one of the chemical steps.

NP or AP Steps

The potassium permanganate steps are typically terminated by determining both the concentration of potassium permanganate as well as the concentration of chromium ions in the solution. As long as the concentration of the chromium ions is increasing, the step should continue. When the concentration of the chromium ions levels off with sufficient concentration of potassium permanganate, then the process should be terminated. Obviously this assumes that all process parameters, such as temperature, remain in the optimum operational range.

Oxalic Acid Destruction Step

¹ The purification half-life is defined as the time required to reduce the concentration of any species by a factor of 2 and assumes a 100% removal efficiency. It is calculated by multiplying the system volume by $\ln(2)$ and dividing by the flow rate through the ion exchange resin.

During the oxalic acid destruction step, the concentration of both the oxalic acid as well as the soluble manganese ion should be monitored. The solution will go through several color changes. At the start of the destruction step, there still may be a significant concentration of potassium permanganate that will produce a purple color in solution. As the oxalic acid is added, the potassium permanganate will be reduced to manganese dioxide resulting in a brown precipitate in the solution. When the solution turns water clear, the easily reduced manganese dioxide has been reacted and the remaining oxalic acid attacks the manganese dioxide on the surfaces of the metal pipe as well as the manganese dioxide in sludge piles in low flow areas.

Once the solution turns water clear, the concentration of manganese should be determined. If the concentration of soluble manganese levels off at the same time as the oxalic acid approaches zero, there is a possibility that there is more manganese dioxide in solution but the oxalic acid concentration reached zero prior to it reacting with the manganese dioxide. Therefore additional oxalic acid should be added to remove all of the solid manganese dioxide. At the termination of the oxalic acid destruction step there should be 50 to 100 ppm of soluble oxalic acid in solution to make certain that all of the manganese dioxide has been dissolved.

If the manganese dioxide is not totally dissolved, it could interfere with the next addition of chemical and some of the chemical could be depleted if enough manganese dioxide is still in the decontamination system. Some plants have found a strange brown substance in the pipes during startup after a chemical decontamination. Other plants have found a brown solid in piping systems after performing a chemical decontamination upon cutting out the pipe during replacement. All of the manganese dioxide is difficult to remove during a chemical decontamination and depending upon the conditions required after the chemical decontamination, a special effort should be made to remove as much as possible.

CAN-DEREM, CAN-DECON, CITROX and CORD

These decontamination steps are typically terminated by analyzing iron concentration or a specific radionuclide. Monitoring the radiation levels on a specific section of pipe during the chemical decontamination process also can terminate the steps. Since these processes are regenerative, the soluble cations are removed by recirculating the solution through cation resin on-line. The iron concentration does not build up but rather is continuously removed. Therefore as the concentration of the soluble iron in the influent of the cation resin column approaches the concentration of the soluble iron in the effluent of the cation resin column little if any new iron is being dissolved. If the process conditions are optimal at this point in the process, the step can be terminated.

LOMI

The LOMI process utilizes an active ingredient, vanadous ion, to help drive the reaction to completion. To determine the termination point for the LOMI process, at least two parameters need to be monitored. The first is the vanadous ion concentration. This concentration can be monitored by the use of an UV/Visible spectrophotometer. The iron concentration is a good choice for the second parameter to monitor. It also is a good idea to monitor total gamma activity for every sample. A graph can then be created of vanadous ion, iron, and total activity. It is the goal of each LOMI chemical decontamination to have the concentration of iron and total activity level off prior to the oxidation of the entire vanadous ion. If the vanadous ion approaches zero while the iron and total activity concentration is still increasing, not enough LOMI was added to remove all of the activity in the piping system. Additional vanadous ion could be added at this time up to a maximum concentration of approximately 10 mMolar.

When the concentration of vanadous ion approaches zero it is imperative that either more vanadous formate be added to the decontamination volume or that the demineralization to remove the LOMI chemical be initiated within an hour. After the vanadous concentration reaches a concentration of zero, the vanadium redox couple becomes corrosive to the material of construction. In order to reduce the chances for excess corrosion either the vanadium couple must be removed or additional vanadous ion should be added to change the redox couple to one that is not corrosive.

Recontamination

Prior to discussing the recontamination of core radiation levels one must understand that the water circulating through the BWR or PWR reactor coolant system is in a state of equilibrium and the corrosion products on the piping system is one portion of that equilibrium. Something such as a chemical or mechanical decontamination or chemistry change in the coolant will upset the equilibria and therefore result in changes in the system.

Some of the chemical conditions that can be changed in the coolant to upset the steady state equilibrium of the system are GEZIP, Noble Metal Additions, changing from normal BWR water chemistry to hydrogen BWR water chemistry, or other “improved water chemistries”.

When a chemical decontamination is performed, the corrosion products will tend to redistribute throughout the system to reestablish the equilibrium. The nuclear fuel has never been decontaminated with the reactor coolant surfaces and therefore there is a source of corrosion products available to reestablish the equilibrium. A report by Smee and LeSurf (LeSurf, 1991) details the recontamination data up to 1990. A report by Smee has updated the recontamination data from 1990 to the present (Smee, 1999).

The best information for full system chemical decontamination recontamination comes from a study of Indian Point Unit 2 1995 chemical decontamination program (Parry, 1998). This plant was chemically decontaminated with the fuel removed from the vessel in 1995. Figure 3 is a chart of the radiation levels at the secondary side hand holes on the steam generators. The first bar in each section is the dose rate just prior to the decontamination. The second bar is the dose rate immediately after the chemical decontamination with the third bar representing the dose rate one cycle after the chemical

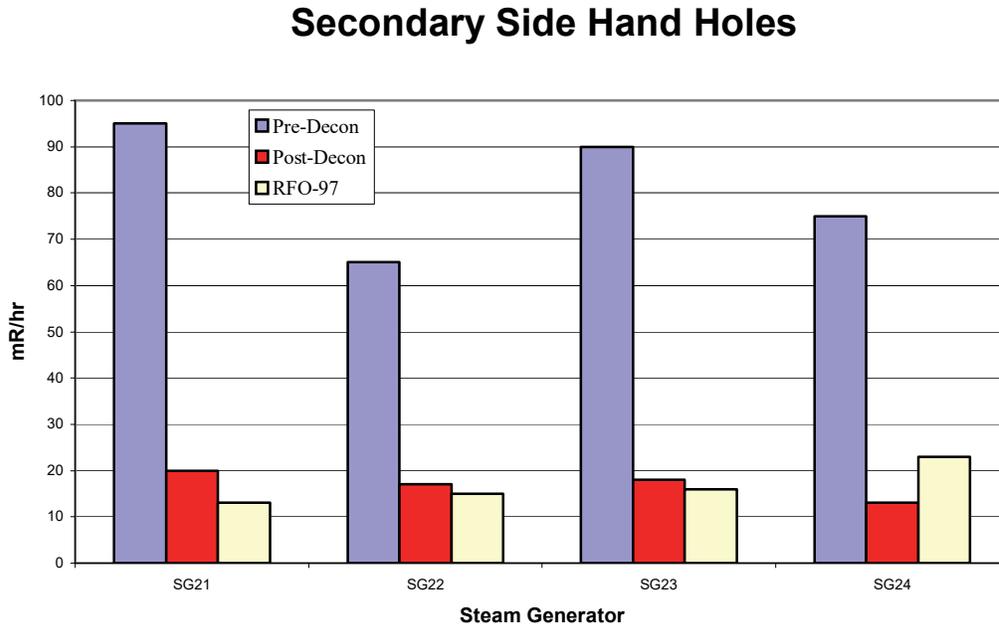


Figure 3. Steam Generator Secondary Side Hand Hole Dose Rates

RCS Loops General Area

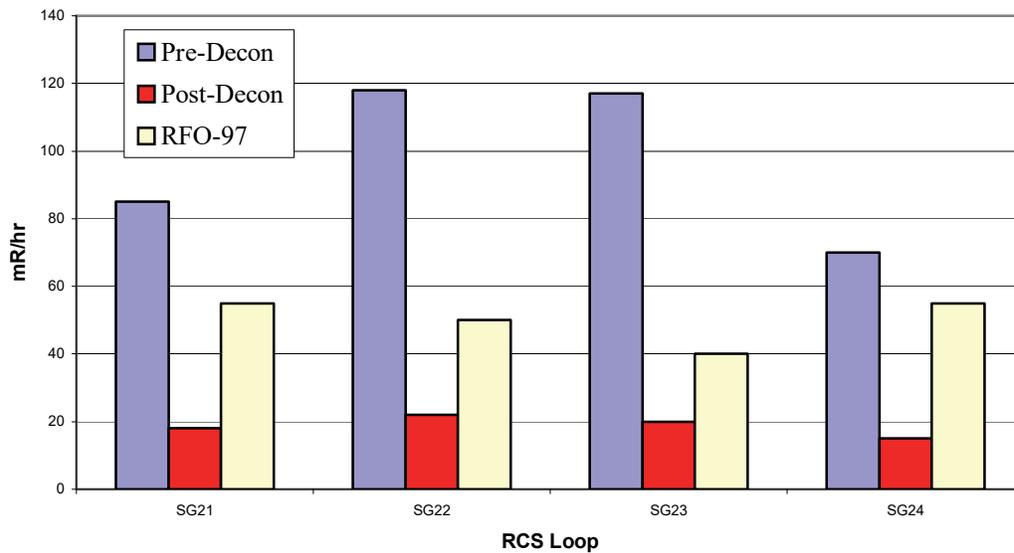


Figure 4. RCS Loops General Area Average Dose Rates

decontamination. In three out of four of the steam generators there was no appreciable change in the dose rates one cycle after the chemical decontamination. In SG24 the dose rate increased by approximately 50 percent during the first cycle after the chemical decontamination. Steam Generator 24 was the equipment utilized for the crud burst at the start of the 1997 outage. This could have resulted in the higher radiation dose rates on that piece of equipment. Figure 4 illustrates the general area dose rates for the pre and post chemical decontamination as well as the 1997 refueling. The general area radiation dose rates were substantially reduced during the chemical cleaning and were still considerably lower than the prechemical decontamination dose rates during the 1997 refueling outage.

The average decontamination factor obtained for the chemical decontamination was 7.8 determined by measuring the dose rate at 55 preselected points. The DF of 7.8 indicates a removal of 87 percent of the radionuclides. After one operating cycle the DF over the same 55 points was 6.4, which indicated an overall reduction of 84 percent of the radionuclides.

MECHANICAL DECONTAMINATION TECHNIQUES

In addition to the decontamination techniques based on chemical reactions, there are a number of mechanical methods that are available to remove contamination from various types of surfaces. There also are several review articles describing these techniques (Ayres, 1970) (Remark, 1981) (Irving, 1986) (Remark, 1989). These review articles present specifics how to remove the radioactive contamination from surfaces.

The techniques required in the removal of contaminated material are identical to the techniques required to remove dust, dirt, or corrosion products that are nonradioactive. The difference is that more waste may be generated in the cleaning of radioactively contaminated surfaces since cross contamination, the contamination of surfaces previously free of contamination, needs to be avoided. In order to avoid the potential for cross contamination, additional supplies are required such as rags or chemicals.

As dust becomes airborne, radioactive contamination also can become airborne. The surface of components can be wetted with water to reduce the possibility of airborne contamination. There are some aerosols that also can be applied to heavily contaminated surfaces to prevent the material from becoming airborne. Aerosols should be used in extreme measures for contamination control. To date, aerosols have just been utilized in decommissioning projects.

In the 1980s, there was a change in the direction of the use of mechanical decontamination techniques at nuclear power plants. In the early 1980s plants performed all of their own decontamination of parts and components. In the early 1980s Recycle Centers were first set up in Oak Ridge, TN. These Recycle Centers accept contaminated material for decontamination, volume reduction, and recycling. Since the establishment of these centers, the amount of decontamination performed at nuclear power sites has decreased.

When performing a decontamination, one must understand the reason for the decontamination. Is the component being decontaminated in order to reduce dose or the spread of contamination or is the part or component being decontaminated for free release? If free release is the criteria one must be concerned about leaching of radionuclides from crevices after the part has been surveyed and free released. Many investigators have found that some contamination resides in the cracks and pores of metals as well as concrete. Upon decontaminating the surface area and surveying it for free release, no radioactivity is found. After a period of time, radioactive material is again found on the surfaces that could only be the result of the radionuclides leaching from the interior of the surface. It is believed that the radionuclides are not found during the final survey because they are imbedded deep enough to be shielded from detection.

Decontamination of Exterior Surfaces and Removable Equipment

External surfaces of piping and process equipment, building floors and walls, equipment, and tools can become radioactively contaminated from coolant leaks and routine maintenance activities. Much of this contamination is spread and deposited in a manner similar to that for ordinary nonradioactive dust and dirt in any building where industrial processes are performed. That is, all exposed surfaces become contaminated to varying degrees, in keeping with certain common sense general principles (Irving, 1985).

Janitorial-Type Decontamination

Since the mechanisms for contamination of this type of cleaning are analogous to those of ordinary, nonradioactive dust and dirt, the processes, equipment, and procedures for janitorial decontamination have many similarities to those of good cleaning practices in nonradioactive industrial process plants. The only significant differences are:

1. Greater care is taken in monitoring and surveillance of the workers to prevent inadvertent overexposure to radioactive materials, and especially to guard against ingestion and accumulation of radionuclides on exposed skin areas.
2. Decontamination equipment is modified to retain for disposal a considerably larger fraction of the contaminant materials removal from the surfaces being cleaned.
3. Greater care is taken to prevent recontamination of decontaminated surfaces while performing remedial actions on the remaining contaminated surfaces.

The seven methods that are most commonly used to accomplish decontamination of the surfaces and structural members of buildings/facilities within the nuclear industry are as follows:

- a) Hand Wiping
- b) Hand Scrubbing
- c) Water Flushing
- d) High-Pressure Water Lancing
- e) Strippable Coating
- f) Steam Cleaning
- g) Cleaning with non-electrical conducting solvent.

Virtually all plants within the nuclear industry use at least the first three or four of these decontamination techniques for building and facility decontamination.

In summary, prior to using a new decontamination process that involves the utilization of new equipment the site personnel should contact experts in its use and application. It is very expensive to purchase and apply new equipment in the field without some knowledge of the usefulness of the process. Decontamination engineers have that understanding through their long-term experience in the field. Decontamination is a complex, demanding technical

discipline. Its success requires knowledgeable, experienced, and well-trained personnel to be able to select proper techniques and combinations of techniques for the plant application.

Decontamination Applicability

Prior to the decontamination of any removable component or part, the site should contact a decontamination engineer for help and advice on how to proceed. Many options exist in 2001 that did not exist 10 or 15 years ago and the economics of decontamination changes often. The flow chart below lists the thought process that should be considered at the site prior to proceeding with any type of decontamination with a removable part or component.

Some of questions that should be asked are:

1. Why is the component being decontaminated?
2. Can it be free released?
3. Can it go straight to disposal?
4. Which disposal site does it have to go to for disposal?
5. Is decontamination cost effective?
6. What decontamination method should be applied?
7. Has the site decontaminated this type of part or component previously?
8. What is the secondary waste generated?
9. Is the secondary waste hazardous, radioactive, or both?

Operational Considerations

All decontamination efforts have a common objective: the removal of contamination from their present undesirable location. Regardless of the nature or extent of the contamination, however, a variety of decontamination methods are available. An evaluation of several considerations will determine the specific methods to be applied.

These considerations may be generalized as follows:

- a) The radionuclides present and their physical state
- b) The surface and substrate material upon which the contamination is present
- c) The size, configuration, location and relationship to other surfaces of the contaminated surface
- d) Accessibility of the contaminated area
- e) Desired condition of the contaminated surface upon completion of the decontamination effort
- f) Desired degree of decontamination to be achieved
- g) Functional nature that must be retained following decontamination of the surface

- h) Equipment and materials available for use in decontamination, including those present at the site and available from other sources
- i) Worker safety and radiation dose minimization
- j) Cost-effectiveness of various alternatives, including the relative costs of disposal and replacement versus decontamination and reuse
- k) Quantity and nature of waste that will be generated, including disposal
- l) Manpower and training requirements

The weight given these individual considerations will vary greatly with the situation, with some requiring no consideration in many circumstances.

Experience has shown the desirability and benefits of providing hands-on training for decontamination workers and their supervisors and foremen. This training may include the use of mock-up facilities, simulating as closely as possible the thing to be decontaminated and the methods and equipment to be used during decontamination. Such training should be performed with the personnel dressed in the actual anticontamination clothing they will wear during performance of the work.

This training with mock-ups is generally at least as useful to the people charged with planning and scheduling the work, and with staging the equipment and material to the work area, as it is for the workers and their supervisors and foremen who will perform the decontamination activities. Such training activities are the best way to ensure that the safest, most effective, and most cost-beneficial results will be obtained from the work. They also provide assurances for complying with the regulatory requirement for accomplishing the required work with resultant worker radiation exposures maintained as low as is reasonably achievable (ALARA).

The decontamination operation must be based on a detailed action plan. Key elements of an action program include:

- 1) Preplanning all work, including specific activities to minimize the release of contaminants such as the use of catch basins, tenting and glove box construction, the strict observation of step-off-pads and other controls, and adherence to tag-out, draindown, flushing, and other maintenance prerequisites.
- 2) Minimizing the generation of contaminated items that must be transported through the station for cleaning or disposal, with the inherent potential for contaminating otherwise clean areas. Examples of this are the removal of all packaging materials prior to entry to a contaminated area, use of a “runner” to reduce the number of times dress-out and undress are required by maintenance and operation personnel, and careful selection of tools and equipment prior to start of work so that items are not unnecessarily exposed to contamination.

- 3) Emphasis at all times on the necessity for each individual to observe and deal with any discrepancy in system function or procedural operation. This should include the immediate reporting to maintenance of any leakage, the willingness of any individual to point out to another an error in procedure, open post-job debriefing, or any other activity that will correct or preclude errors in function of equipment or personnel.

Cost effectiveness of such a program is easily realized in reduction of labor and supplies used for decontamination, reduction in waste disposal costs, and reduction in total worker-rem expended per year.

SUMMARY

A person experienced in the use of decontamination processes and techniques should be the one that chooses the appropriate technique for each decontamination effort. Decontamination Engineers are not granted degrees in colleges or universities. These degrees are granted in the field after the experience is obtained by working with others on the process or technique. Critical tolerances can be damaged by the inappropriate application of a decontamination technique. The tolerances can be destroyed by corrosion or abrasive mechanisms.

The generation of secondary waste is dependent upon the process or technique utilized. The generation of secondary waste leads to the total cost of the process. Care must be taken in using any types of solvents in the generation of mixed waste. The elements removed during the decontamination must be identified so if mixed waste is generated it can be properly packaged and treated. Mixed waste contains both hazardous and radioactive materials.

Is the decontamination cost effective? The goal of the decontamination must be known and the process or technique chosen to reach the goal. Decontamination performed after the goal is reached may not be cost effective. The cost of the decontamination equipment is a major input into the decontamination method chosen. The initial techniques chosen should be the one in which the individuals performing the decontamination have the most experience and have the equipment. Consideration should be given to performing an individual technique, which may not be the optimum choice, but the equipment and personnel experience exists on site.

Decontamination techniques and equipment should be used by personnel experienced in the art. If not performed proper decontamination techniques may generate more contaminated material than was cleaned by the process.

References:

(Abrams, 1966) C.S. Abrams and E.A. Salterelli, “Decontamination of the Shippingport Atomic Power Station”, USAEC Report WAPD-299, Bettis Atomic Power Laboratory, January 1966.

(Ayres, 1970) J.A. Ayres, Editor, Decontamination of Nuclear Reactors and Equipment, The Ronald Press Company, New York, 1970.

(Ayres, 1970a) J.A. Ayres, “Decontamination of Pressurized Water Reactors”, in “Decontamination of Nuclear Reactors and Equipment”, The Ronald Press Company, New York, 1970.

(Beaman, 1982) T.A. Beaman and J.L. Smee “Experience With Dilute Chemical Decontamination” in Decontamination of Nuclear Facilities, September, 1982, ANS.

(Berry, 1979) W.E. Berry, “Survey of Corrosion Product Generation, Transport, and Deposition in Light Water Reactors”, NP-522, EPRI, 1979.

(Bertholdt, 1994) J. Lejon, X. Hermansson, H.O. Bertholdt, “A Full System Decontamination of the Oskarshamn 1 BWR”, Presented at the International Conference “Chemistry in Water reactors – Operating Experience and New Developments”, Nice, France, April 1994.

(Bertholdt, 1998) H.O. Bertholdt, “HP/CORD D UV – A New Decontamination Process for Decommissioning of NPPs”, Proceedings: 1998 EPRI Chemical Decontamination Conference, May 18-19, 1998, Greenville, SC, EPRI Report TR-110997, June 1998.

(Bertholdt, 1998a) H. O. Bertholdt, “A New Decontamination Process for Decommissioning of Nuclear Stations”, Nuclear Plant Journal, Volume 12, No. 4, July-August, 1998.

(Bradbury, 1997) D. Bradbury, G. Elder, EPRI DFD (Decontamination for Decommissioning) Process Evaluation, Electric Power Research Institute, TR-107707, December 1997.

(Bradbury, 1998) D. Bradbury, G. Elder, Review of Experience with the EPRI DFD Process: Decontamination for Decommissioning of Reactor Coolant Systems and Plant Components, Electric Power Research Institute, TR-109036, December 1998.

(Bradbury, 1983) D. Bradbury, M.G. Segal, R.M. Sellers, T. Swan, and C.J. Wood, “Development of LOMI Chemical Decontamination Technology”, EPRI Report NP-3177, July 1983.

(Cunnane, 1978) J.C. Cunnane, D.L. Uhl, A.J. Kennedy, “ Dynamic Corrosion Product Transport in Pressurized Water Reactors”, Paper 155, Corrosion/78, NACE, Houston TX, 1978.

(Greenman, 1986) W.G. Greenman, N. Nielsen, J.F. Remark “LOMI Decontamination of Indian Point III”, Paper 63F, Presented at AIChE Summer National Meeting, Boston, MA, 1986.

(Irving, 1985) B. Irving, “Decontamination” in Notes for ASME Short Course on Radioactive Waste Management for Nuclear Power Plants and Other Facilities, Alexandria, VA, May 1985.

(Irving, 1986) B. Irving and J.K. Allen, “Mechanical Decontamination Techniques” in Radioactive Waste Technology, The American Society of Mechanical Engineers, NY, NY, 1986.

(LeSurf, 1982) J.E. LeSurf and G.D. Weyman, “Cost Effectiveness of Dilute Chemical Decontamination”, Nuclear and Chemical Waste Management, Vol. 4, 1982.

(LeSurf, 1991) J.L. Smee and J.E. LeSurf, “Full-System Decontamination of a BWR Using the LOMI Process”. Volume 4: Full-System Decontamination Experience and Cost-Benefit Analysis. EPRI Report TR-100049, Volume 4, October 1991.

(Lister, 1989) D.H. Lister and R.D. Davidson, “Corrosion Product Release in Light Water Reactors”, NP-6512, EPRI, 1989.

(Lister, 1979) D.H. Lister, “The Accumulation of Radioactive Corrosion Products in Nuclear Steam Generators”, Corrosion, Volume 35, No. 5, Page 219, 1979.

(Lister, 1996) D.H. Lister, N. Arbeau, R. Campbell, M. Godin, “The Deposition of Cobalt on In-Core Surfaces During Boiling Heat Transfer”, Paper 10, “VII International Conference on Water Chemistry of Nuclear Reactor System”, Bournemouth, UK, October 1996.

(Osterhout, 1980) Marilyn M. Osterhout, Editor, Decontamination and Decommissioning of Nuclear Facilities, Plenum Press, New York, 1980.

(Nielsen, 1986) N. Nielsen, “Indian Point Unit No. 3 Decontamination” Paper 33, Proceedings: Seminar on PWR Water Chemistry and Radiation Field Control, Berkeley, CA, March 1986.

(Parry, 1998) J.O. Parry, “Recontamination Rates at Indian Point 2 Two Years After a Full System Decontamination” in Proceeding: 1998 EPRI Chemical Decontamination Conference, EPRI, TR-110997, May 1998.

(Perrigo, 1966) L.D. Perrigo, T.F. Demmitt, K.D. Hayden, R.D. Weed, and J.A. Ayres, “Plutonium Recycle Test Reactor Decontamination Following a MgO-PuO₂ Fuel Element Failure, USAEC report BWNL-SA-636, Battelle-Northwest Laboratory, March 31, 1966.

(Proceedings, 1998) Proceedings: 1998 EPRI Chemical Decontamination Conference, TR-110997, EPRI, May 1998.

(Proceedings, 1993) Proceedings: Fifth Workshop on Chemical Decontamination, NPD/M&C/93-1, EPRI, June 1993.

(Proceedings, 1991) Full System Chemical Decontamination Workshop, 91-WH-53, EPRI, June 1991.

Proceedings, 1995) 1995 Radiation Field Control and Decontamination Seminar, TR-106009, EPRI, December 1995.

(Remark, 1981) John F. Remark, Plant Decontamination Methods Review, NP-1168, EPRI, May 1981.

(Remark, 1984) John F. Remark, "Quadrex HPS LOMI Decontamination of the Mendocino Nuclear Power Station", presented at EPRI Seminar - BWR Corrosion, Chemistry, and Radiation Control, Palo Alto, CA, 1984

(Remark, 1986) John F. Remark, Low Oxidation Metal Ion (LOMI) Chemical Decontamination of Indian Point III, American Institute of Chemical Engineers 1986 Summer Meeting, Paper No. 63F. August 1986, Boston, MA.

(Remark, 1989) John F. Remark, A Review of Plant Decontamination Methods-1988 Update, NP-6169, EPRI, January 1989.

(Remark, 1993) John F. Remark & Tom G. Bengel, US Patent 5,305,360, "Process for Decontaminating a Nuclear Reactor Coolant System", Issued April 19, 1994.

Segal, 1983) M.G. Segal, T. Swan, *Water Chemistry-3* (1983); 61-70, London England, British Nuclear Energy Society.

(Smee, 1999) J. Smee, Decontamination Handbook, TR-112352, EPRI, July 1999.

(Weed, 1968) R.D. Weed, "Decontamination of the Plutonium Recycle Test Reactor (PRTR) Primary System", USAEC Report BNWL-711, Battelle Northwest Laboratory, March 1968.

(Wille, 1986) H. Wille, H.O. Bertholdt, W. Morell, "Development and Application of the OZOX/CORD Process", Paper 84, Fourth International Conference on Water Chemistry for Nuclear reactor Systems, British Nuclear Energy Society, London, 1986.

For Further Information Contact:

John F. Remark
TuDocs Group
jremark@gmail.com
434-229-5601