EPRI DFD (Decontamination for Decommissioning) Process Evaluation

Overview of EPRI DFD Process Applications

TR-107707

Final Report, February 1998

Prepared by
Bradtec, Ltd.
University of the West of England, Bristol
Coldharbour Lane
Bristol BS16 1QY
United Kingdom

Principal Investigators
D. Bradbury
G. R. Elder

Prepared for
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 94304

EPRI Project Manager
C. J. Wood

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS REPORT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS REPORT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS REPORT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS REPORT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS REPORT.

ORGANIZATION(S) THAT PREPARED THIS REPORT

Bradtec, Ltd.

ORDERING INFORMATION

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (510) 934-4212.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 1998 Electric Power Research Institute, Inc. All rights reserved.

REPORT SUMMARY

This report describes field results from a demonstration of the EPRI DFD (decontamination for decommissioning) dilute chemical decontamination process on several large-scale reactor components. In contrast to the decontamination processes used on operating plant systems that are to be returned to service, this process removes all radioactive contamination from metallic surfaces, permitting the majority of the metal to be released for recycling. Two different licensees have successfully used the process to decontaminate heat exchangers from BWR reactor water cleanup systems.

Background

Currently available dilute chemical processes used on operating plants do not generally achieve decontamination to the extent required for unrestricted release or recycling. On the other hand, concentrated reagents that provide the required degree of decontamination produce radioactive waste in an intractable form that is difficult to manage and dispose of.

The EPRI DFD process is a dilute chemical process that achieves complete removal of contamination by dissolving a thin layer of the base metal from the surfaces of retired components. At the same time, the contamination is collected on ion exchange resin that can be managed using established technology.

The process outlined in *Decontamination for Decommissioning: EPRI DFD Process* (TR-106386), has been patented and is now described in considerably more detail. This report includes all the information in TR-106386, additional qualification results and results from recent applications to reactor components.

Objective

To evaluate the EPRI DFD process for decontaminating retired components for unrestricted release or recycling.

Approach

This report describes the work carried out by two of the three vendors in the United States licensed to use the EPRI DFD process. They decontaminated and released stainless steel from regenerative heat exchangers that came originally from BWR reactor water cleanup systems. The DFD procedure involves circulating dilute

fluoroboric acid and potassium permanganate through the system to be decontaminated. Oxalic acid is added to remove manganese dioxide then any excess oxalate is destroyed by permanganate addition. Cation exchange removes dissolved metal ions. The cycle is repeated until the metal surfaces are clean. Final clean up is by mixed bed ion exchange. The report describes laboratory testing on reactor artifacts, materials corrosion data, waste management, and process safety and economics.

Results

Decontamination vendors can apply the process using existing equipment with only minor modifications; waste management characteristics are typical of sub-system decontamination. Alaron Corporation obtained an average decontamination factor exceeding 1000 on a 16 foot long by 2 foot diameter 304L stainless steel heat exchanger from ComEd's Quad Cities BWR plant. Residual activity levels were 400 dpm per 100 cm^2 and the tubes and shell were released after minor mechanical decontamination.

PN Services teamed with F. W. Hake and Associates to decontaminate two 27x2 foot heat exchangers from ComEd's Dresden BWR. Apart from some remaining hotspots in the area of the tube bends, a significant amount of the material was well below free release limits after limited further decontamination and is being recycled as non-contaminated scrap.

EPRI Perspective

This process provides a cost-effective alternative to storage or burial for retired components from nuclear power plants. The effectiveness of the process allows unrestricted release or recycling of non-activated material. Development using reactor artifacts and field testing on full-scale nuclear power plant components is complete. Non-exclusive licenses have been awarded to Alaron, PN Services and Framatome Technologies, Inc. A forthcoming report will describe the successful use of the process on the reactor coolant system of Consumers Energy's Big Rock Point BWR. Further applications on shutdown nuclear power plants and implementation on retired steam generators are planned.

TR-107707

Interest Categories

Decommissioning
Low level radioactive waste management
Radiation field control

Key Words

Low level waste disposal
Decontamination
Decommissioning

ABSTRACT

Recognizing that existing technology was not ideal for retired components and plant systems, EPRI initiated work with Bradtec in 1995 to develop a process that combined the operational advantages of dilute decontamination processes used on operating plants (such as LOMI) with the high decontamination factors achievable with concentrated, aggressive processes, which currently result in radioactive waste that presents difficult management challenges. The result, called EPRI DFD (decontamination for decommissioning) is a dilute chemical decontamination process for unrestricted release of stainless steel and alloy 600 components. The process can also be applied to other metals. Contamination levels can be reduced to background, with Decontamination Factors (DFs) exceeding 1000. The process uses standard equipment and conventional ion exchange technology for waste processing.

The development work on EPRI DFD was completed and reported in 1996; the process has been patented and licensed to qualified vendors. It has been demonstrated in two successful full scale projects by licensed vendors. The use of the process is currently being evaluated for large components and systems in the field, including retired PWR steam generators, heat exchangers, pumps and fuel racks. One major goal is to apply the process to full system decontamination of retired plants - the process has been chosen for the full system decontamination of the Big Rock Point BWR, a project due to take place at the close of 1997. Successful decontamination of a plant in this way would markedly reduce the costs and difficulty of dismantlement and open new options for the management of redundant plant components, for example through unrestricted release and recycle.

This report discusses the chemistry of the process, reports on recent large scale projects undertaken with it, and provides additional data in response to common questions concerning materials corrosion, waste management and safety.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

Chemical decontamination of sub-systems of operational LWR plants has now become relatively common, and recently full system decontamination has been demonstrated. This decontamination involves exposing parts of the reactor circuit to chemical solutions which dissolve the radioactive deposits which have accumulated on the process equipment, including piping. The spent decontamination solutions are then treated by ion exchange to retain all the chemical and radioactive burden of the decontamination solution on the resin, while clean water is returned to the system. An example of such a process is the LOMI process.

In decontamination processes used at operating plant the purpose is to remove the radioactive deposit to reduce the radiation exposure of plant workers. Because the processes are applied to items of plant which are returned to service, they are designed to avoid any damage to the materials exposed to the process. Such damage could occur as a result of corrosion during the application of the process, or as a result of exposure of plant items to the operating conditions of the nuclear plant subsequent to the decontamination. The restriction of avoiding damage has resulted in processes which do not attack base metal, but that operate by dissolving the overlying layer of corrosion product metal oxides. Because of this the effectiveness of such processes is limited - typically 80 - 95% of the radioactivity is removed - but this is nevertheless sufficient for the purpose of reducing radiation dose to workers.

The effectiveness of such processes is not, however, sufficient for the purpose of removing all the radioactivity from the surfaces, thereby allowing the items to be treated as nonradioactive waste. In order to achieve this it is necessary to remove a thin layer of the underlying base metal, so as to release radioactivity trapped in fissures in the metal (occurring, for example, as a result of mild intergranular attack of the metal surface). For decommissioning the restriction concerning plant damage is not so severe, because the plant items are not required for further operational duty. The only requirements with regard to damage are that the plant items must maintain their integrity against leakage during the operation of the process and must remain structurally sound. The removal of a thin layer of base metal is consistent with these requirements, although if too much metal is removed there will be a problem concerning the amount of radioactive waste generated.

Recognizing that existing technology was not ideal for retired components and plant systems, EPRI initiated work with Bradtec in 1995 to develop a process that combined the operational advantages of dilute decontamination processes used on operating plants (such as LOMI) with the high decontamination factors achievable with concentrated, aggressive processes, which currently result in radioactive waste that presents difficult management challenges. The result, called EPRI DFD (decontamination for decommissioning) is a dilute chemical decontamination process for unrestricted release of stainless steel and alloy 600 components. The process can also be applied to other metals. Contamination levels can be reduced to background, with Decontamination Factors (DFs) exceeding 1000. The process uses standard equipment and conventional ion exchange technology for waste processing.

The EPRI DFD Process is designed to be as similar as possible to existing decontamination processes which are routinely used on subsystems of operating nuclear plants. In this way the new process can utilize and build on the extensive experience which has already been gained with the latter type of process. The process relies upon circulation of very dilute chemicals to dissolve the radioactive deposits. Additionally the process is designed to remove progressively a thin layer of base metal to release radioactivity trapped in fissures. During application the solution is treated by ion exchange to recover released radioactivity and metals. After completion the solution is finally purified by ion exchange to leave the system full of clean water. The final waste form is conventional ion exchange, though further waste processing could be performed to reduce volumes and convert to different types of waste form if desired.

The development work on EPRI DFD was completed and reported in 1996; the process has been patented and licensed to qualified vendors. It has been demonstrated in two successful full scale projects by licensed vendors (these are described in outline below). The use of the process is currently being evaluated for large components and systems in the field, including retired PWR steam generators, heat exchangers, pumps and fuel racks. One major goal is to apply the process to full system decontamination of retired plants - the process has been chosen for the full system decontamination of the Big Rock Point BWR, a project due to take place at the close of 1997. Successful decontamination of a plant in this way would markedly reduce the costs and difficulty of dismantlement and open new options for the management of redundant plant components, for example through unrestricted release and recycle.

This report discusses the chemistry of the process, reports on recent large scale projects undertaken with it, and provides additional data in response to common questions concerning materials corrosion, waste management and safety.

2

PROCESS CHEMISTRY

General Theoretical Considerations

The overall objective of the EPRI DFD Process is to achieve conditions in which base metals are dissolved slowly and uniformly (together with their overlying contaminated oxide film) while at the same time the dissolved radioactivity and metals are removed on ion exchange resin.

The normal mechanism for cleaning metals is to employ acid dissolution by hydrogen (H^+) ions.

The overall reaction is:

$$x\ (\text{Metal}) + y\ (\text{H}^{+}_{x}\text{-Anion}^{x-}) \text{ - - > } \text{Metal}^{y+}_{x}\,(\text{Anion}^{x-})_{y} + (y*x/2)\ \text{H}_2$$

In many decontamination applications where avoidance of base metal corrosion is required, a relatively high pH is used coupled with the presence of chelants to keep dissolved metals in solution. These applications often take advantage of sophisticated chemical mechanisms such as reductive dissolution. In the case of decontamination for decommissioning the strategy is simply to use as low a pH as possible, to encourage uniform corrosion of the base metal. Chelants are then not necessary (an advantage from waste management considerations). Although dissolution of base metal can be retarded by the formation of protective films on the surface of the metals, the particular acid used and the conditions of application can be chosen to minimize this.

A pH of about 2 is the minimum which can be used for an acid cleaning solution in decontamination of a large reactor system for three reasons:

> Even if the acid used is a "strong" (ie completely dissociated) acid a pH of two requires the presence of 10 millimoles per liter of the acid. Much more than this concentration would require large quantities of chemical reagent. Besides the cost and inconvenience of purchasing and handling large quantities of chemicals, any residual chemicals not converted to the gas phase will end up as part of the radioactive waste resulting from the process. It is paramount to minimize chemical usage.

> There is an absolute requirement to ensure the structural integrity of all the many different types of components wetted by the decontamination solution in a large system. Some minor materials are capable of corroding extremely rapidly in concentrated acid, so highly acidic pH's should be avoided.
>
> The final reason relates to the requirements for continuous clean-up of the solution by ion exchange. This clean up removes the dissolved metals and radioactivity and regenerates the acid reagent. If concentrated acid is used in the formulation, the continuous circulation through the ion exchange column will drive the metals through the ion exchange resin leading to low capacity of the resin and hence excessive volumes of radioactive waste.

Many steels typically present in reactor systems are resistant to dissolution by typical acids at pH 2, even at the maximum temperature practically achievable in a non-pressurised system (ca 200°F). The desirable properties for an acid used in the metal dissolution system are that it should be a strong acid, the acid anion should have a minimal tendency to complex metals (complexation can cause binding of the anion to the metal surface with attendant problems in the metal dissolution mechanism such as localised attack) and the metal salts of the anion should be soluble in the prevailing pH of the solution. Excluding exotic chemicals (which would be costly for routine application in a decontamination process) the most superior acid according to these criteria is fluoroboric acid (HBF_4). However, it is not greatly superior to nitric acid on these criteria alone, and nitric acid is demonstrably unable to dissolve relevant metals at pH 2.

The benefits of fluoroboric acid as a decontaminant in concentrated small scale applications were first reported some years ago[1]. This work demonstrated empirically that fluoroboric acid was very effective as a dissolvant for many metals typical in the nuclear industry. Although the mechanism was not discussed, the reagent was shown (as was well known) to dissolve silica based materials. This may play some role in its surprising efficiency (minor silica impurities within the steel structure could form protective layers which prevent or slow dissolution by other acids). Also it is known that free fluoride enhances the nitric acid dissolution of stainless steels. It is possible that free fluoride in equilibrium with the fluoroborate anion plays some role in enhancing the dissolution. This previous work also showed that, particularly where lead metal was concerned, the dissolution was enhanced by presence of an oxidizing agent[2].

The concentrated fluoroboric acid process was developed to a sophisticated degree, including such features as manufacturing the acid in situ by reaction of free fluoride with boric acid present at the nuclear plant site and novel techniques for waste management including the recovery of the fluoroboric acid from waste solutions. The focus of all this work, however, was a "once-through" system in which the workpiece was contacted with the solution followed by the solution being treated for waste management when ion exchange purification was being employed.

This "once-through" concentrated methodology is acceptable for small components, but is not convenient for large scale systems. It is often thought that concentrated reagents are necessary in order to give adequate dissolution rates, but this question is often masked by the requirement of such systems to have enough acid capacity to complete the decontamination. The solution needs to be concentrated for the latter reason, which is why the validity or otherwise of the former reason is never investigated. In the early history of "oxide dissolving" operational reactor decontamination processes, highly concentrated solutions such as "APAC" (alkaline permanganate followed by acid citrate) were applied to reactor circuits to dissolve deposits, and when the decontamination was complete the solutions were removed and waste-managed[3]. In the late 1970's workers in Canada and elsewhere demonstrated that the established concentrated dissolution chemistries could be adapted for use with dilute recirculating ion exchange systems, in which the required reagent capacity was supplied by continuous ion exchange regeneration[4]. They then showed that with the aid of certain technical improvements the dilute solution could still be made to yield an oxide dissolution rate similar to the original concentrated process.

The EPRI DFD Process represents an exactly parallel development for fluoroboric acid metal dissolving chemistry to that described in the previous paragraph for oxide dissolving chemistries. The development has required certain technical advances to achieve success which are the subject of the proprietary information supplied by EPRI to its licensees for the process.

The Role of Oxidation

Early in the development program of the EPRI DFD Process it was found that, particularly for 300-series stainless steels, dissolution in dilute fluoroboric acid would not take place. It was also found that increasing the oxidation potential of the solution would then allow dissolution to take place. It is known that these steels are protected by a rapidly formed chromium rich film, in which the chromium is present as Cr (III). It was therefore suggested that when the oxidation potential of the solution is raised this film would not be stable, (chromium is then stable as soluble chromium (VI)). Accordingly the EPRI DFD Process employs an oxidizing reagent where necessary to allow dissolution of steels. Ozone can be employed, but it was found that although ozone can raise the bulk oxidation potential of solution to the required degree, nevertheless the oxidation potential at the steel surface (where it matters) can in certain circumstances be depressed. It was also reported to us that decontamination vendors consider the employment of ozone generators inconvenient. Potassium permanganate is a familiar oxidant employed in decontamination processes, and is very effective as the oxidant for this process. Quite small concentrations are employed and indeed 100 ppm or less is effective. Optimization of the concentration and application conditions has continued in dialog with the process licensees. The well established methodology of applying permanganate and then periodically removing the product manganese dioxide with an oxalate rinse has proved practical. Ion exchange can be dis-continued during the permaganate phase to avoid oxidative degradation of the ion exchange resins.

Process Chemistry of Application

This section is intended as a general outline of the EPRI DFD Process Chemistry only. In particular the values of parameters stated here should not be taken as limiting values for adoption in application procedures.

The following general procedure is appropriate for decontaminating 300 stainless steels.

Initially the system is filled with demineralized water and circulation through the chosen flowpath is established. The system is heated to 200° F.

1. When temperature and flow have been established fluoroboric acid is added to the system to achieve 10mM concentration (0.88 grams per liter). The pH should be maintained in the region 2.0 - 2.4 from now on until final clean-up. The solution is circulated.

2. Flow to the cation exchange column is opened up to remove any initial burst of metals or radioactivity released by the first chemical addition.

3. Once this phase is complete the ion exchange column is valved out and potassium permanganate is added to the system. Typically 300 ppm or less total addition is weighed out and added to the system gradually at a rate suitable to maintain a standing concentration of 100 ppm. This step continues until permanganate is no longer present. Permanganate lasts longer in the system in the later cycles as the metal surfaces become clean.

4. Oxalic acid is added to the system and the cation exchange flow re-established. The amount of oxalic acid should typically be 10% excess over the amount required to dissolve manganese dioxide resulting from reduction of the added potassium permanganate.

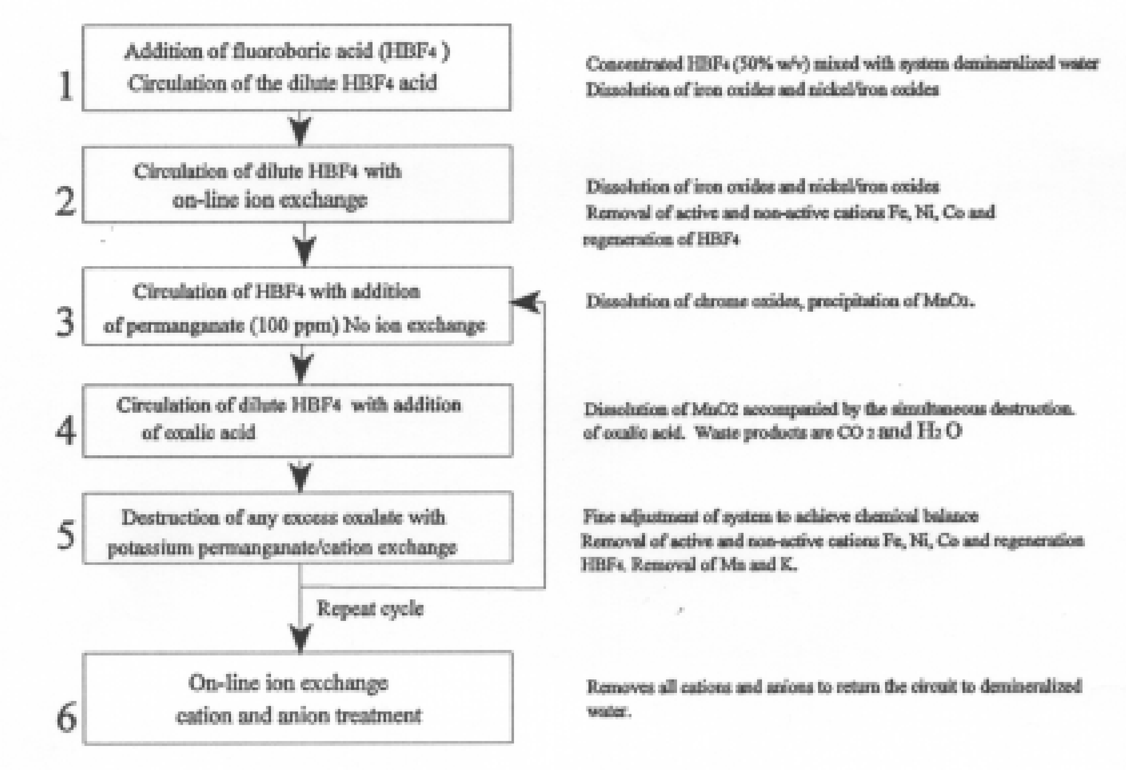
5. Any residual oxalate is destroyed by adding the amount of potassium permanganate necessary to convert it to carbon dioxide. Ion exchange flow is continued to remove residual potassium, manganese, metals and radioactivity. This continues until the pH and radioactivity measurements indicate completion.

The steps 3, 4 and 5 are now repeated for the required number of "cycles". A typical number of cycles required would be eight to achieve free release. The time required for each cycle depends on system parameters, but a typical value would be six hours per cycle. Completion is determined from a combination of direct dose rate readings on system components, radioactivity in solution or examination of system surfaces (or a removable artifact).

6. Fluoroboric acid is removed and water purity is re-established with anion or mixed bed ion exchange.

For other metals (such as carbon steel) decontamination can be achieved with milder conditions, in particular the temperature of application can be lowered to ambient.

The above scheme is summarized in Figure 2-1.



Concentrated HBF_4 (50% w/v) mixed with system demineralized water
Dissolution of iron oxides and nickel/iron oxides

Dissolution of iron oxides and nickel/iron oxides
Removal of active and non-active cations Fe, Ni, Co and regeneration of HBF_4

Dissolution of chrome oxides, precipitation of MnO_2.

Dissolution of MnO_2 accompanied by the simultaneous destruction of oxalic acid. Waste products are CO_2 and H_2O

Fine adjustment of system to achieve chemical balance
Removal of active and non-active cations Fe, Ni, Co and regeneration HBF_4. Removal of Mn and K.

Removes all cations and anions to return the circuit to demineralized water.

Figure 2-1
Schematic of the EPRI DFD Process

3

LABORATORY TEST PROGRAMS

Inactive Testing

Initial development work was performed on inactive test coupons. Two construction materials, 304 L stainless steel and Inconel 600 were chosen for the testwork. The samples were air oxidized to produce a surface oxide representative of those developed during reactor operation over a number of years [5, 6].

Samples were monitored visually for the destruction and removal of the oxide coating with the final surface analysis being confirmed by the use of a Scanning Electron Microscope (SEM) coupled with an energy dispersive X-ray analysis facility.

Samples were considered "cleaned" when no oxide was discernible using the SEM, and surface analysis gave the same alloy composition as that of the bulk metal.

The development of the EPRI DFD Process Chemistry took place using tests of this type.

Having developed the EPRI DFD solvent in this way the ion exchange properties were also examined. Analysis of the spent solvent before and after cation ion exchange demonstrated the removal of all metals from solution to below detection limits (50 ppb).

Active Test Program

Two active test specimens were used to determine the effectiveness of the DFD solvent on real reactor oxides. These were a stainless steel coupon from a PWR manway cover (Indian Point 2) and a piece of Inconel 600 steam generator tube (North Anna 2). Both samples were decontaminated to free-release levels and achieved very high DFs, see Table 3-1.

A further sample of carbon steel boiler tube from a UK gas cooled reactor was also decontaminated to free release levels after the removal of tritium by baking, Table 3-1.

Testing was also performed by Rolls-Royce & Associates (UK) using a redundant stainless steel steam generator tube. The tube was successfully decontaminated to free-release levels. Figure 3-1 shows the decontamination achieved with each individual cycle of the process application.

Larger scale laboratory tests were conducted at the ALARON Corporation Northwest facility at Wampum, Pennsylvania. During these tests a number of artifacts were free-released including samples of stainless steel plate from fuel racks and a 400 series stainless steel pump impeller, see Table 3-1. Figure 3-2 shows a number of the artifacts which have been free-released after decontamination in the laboratory.

Laboratory tests have also been performed by PN Services at their Richland facility in Washington State. These comprised a selection of metal artifacts from various reactor sources, see Table 3-2.

The success of the laboratory programs led to the application of the DFD solvent at full scale. Full scale testing was performed on regenerative heat exchangers by ALARON at their facility and by PN Services at the HAKE facility.

Table 3-1
Active Test Samples Decontaminated to Below Free-Release Levels by the EPRI DFD Solvent

Material	DF
Steam Generator Tubing (I-60)	680,000
PWR Stainless Steel Manway Cover	90,000
Fuel Racks Beaver Valley DC Cook	 200 50
Pump Impeller (400 Series SS)	>7.5
Carbon Steel Boiler Tube (ex UK Gas Reactor)	6,500*

* After first stage pre-treatment

Table 3-2
Active Artifact Test Results at PN Services

Artifact Description	DF	Comments
IP-2 SG Tube (Inconel 600)	>1000	Free released, 7 cycles
SG Tube (Inconel 600)	>2900	Free released, 7 cycles
Perry RRS 304 Stainless Steel	459	Not complete on 7 cycles
Barsebeck-2 RHR 304 Stainless Steel	>600	Free released

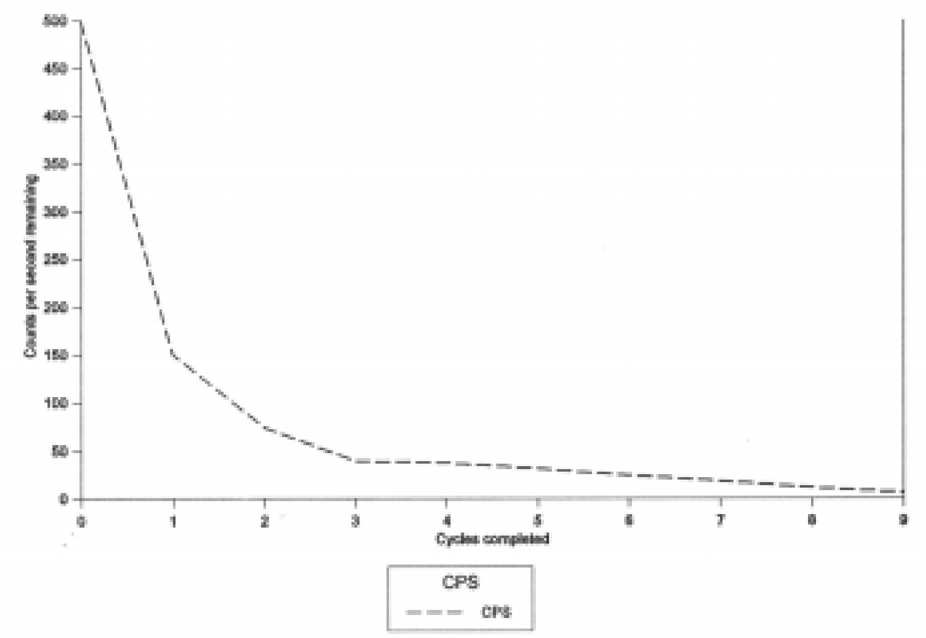


Figure 3-1
Stainless Steel SG Tube Decontamination using EPRI DFD Solvent

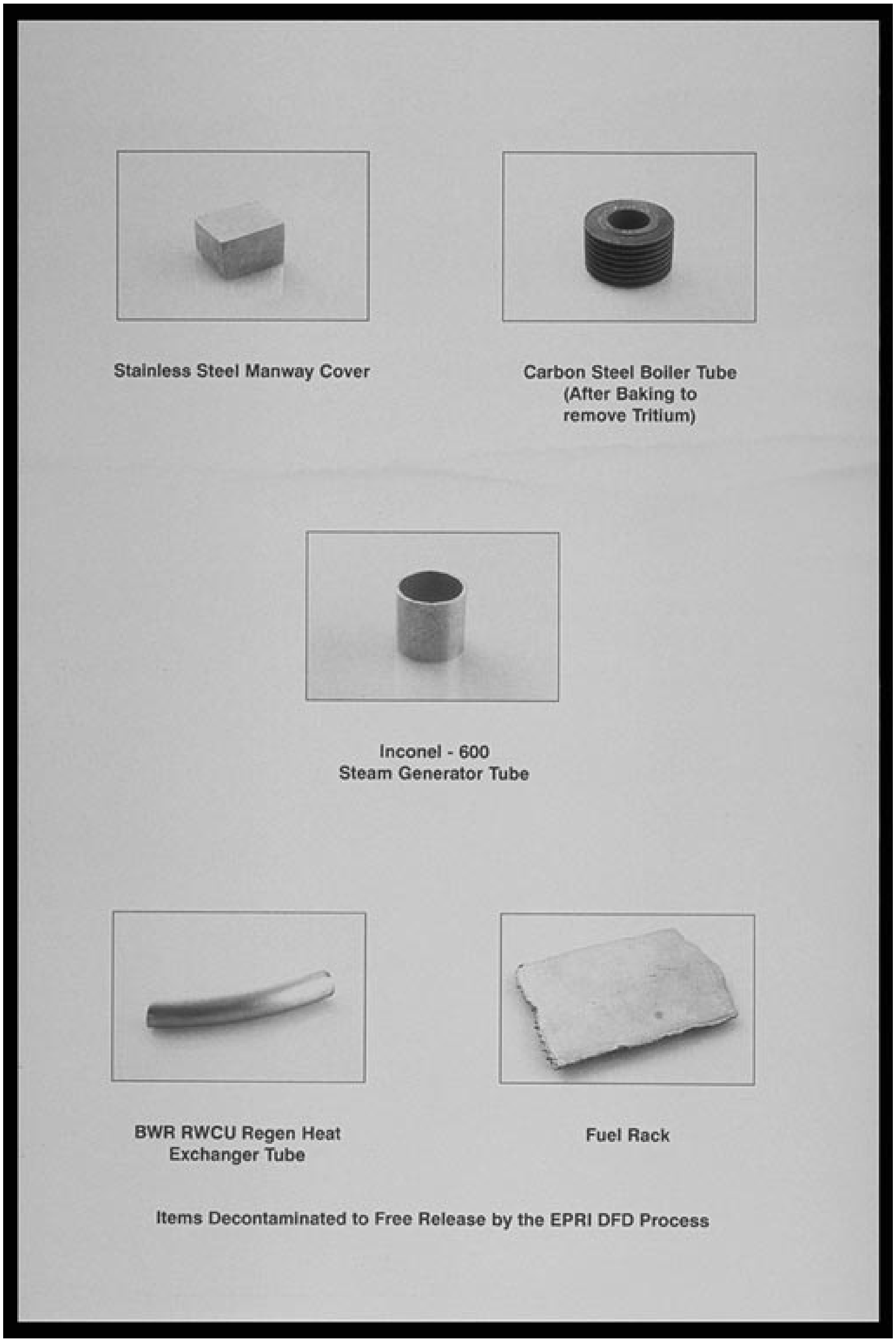


Figure 3-2
Items Decontaminated to Free-Release by the EPRI DFD Process

4

ALARON FIELD TESTS

Twelve stainless steel (type 304L) regenerative heat exchangers (HXs) were replaced in the 1995 maintenance outage at Commonwealth Edison Quad Cities Nuclear Power Plant. These HXs were a part of the Reactor Water Clean-Up unit. As a result of its regenerative function each HX is contaminated on both the primary and secondary sides.

Each exchanger contains some 7,750 lbs (3,523 kg) of stainless steel and has exterior dimensions of approximately 24 inches (60 cm) diameter and 16 feet (490 cm) long. Before being removed from site the HXs were decontaminated using a triple application of CITROX. This reduced the radiation fields on average by a factor of five from 1 R/hr (10 mSv hr^{-1}) to 200 mR/hr (2 mSv hr^{-1}).

The HX chosen for the trial had a high spot of 1 R/hr (10 mSv hr^{-1}) and general reading of approximately 50 mR/hr (0.5 mSv hr^{-1}).

Process Layout and Equipment

The equipment requirements for the process were uncomplicated and could all be met by standard "off the shelf" products. The process circuit consisted of a chemical make up tank with heaters (36 KW), a pump, a valve manifold, an ion exchange column, bag filters and the heat exchanger. A circuit diagram of the layout is given in Figure 4-1. The valve manifold allowed the process flow to be altered as required by the decontamination chemistry or by the physical requirements of the process.

The solvent flow could be directed through the HX via the primary side only, the secondary side only or the primary and secondary sides in series. The flow directions could also be reversed. The return flow from the HX (in forward or reverse mode) could be directed to bypass or flow through the filter or the ion exchange column.

The process equipment and the heat exchanger were connected by 2 ½ inch diameter hoses with stainless steel quick connect fittings. The entire system was rated to a working pressure of 150 psi and a temperature of 250o F. The total system volume was approximately 475 US gals (1.8 m^3) divided between the components as follows; HX

132 gals (500L), IX 132 gals (500L), hoses 40 gals (150L), filters 30 gals (115L) and chemical tank 150 gals (565L).

Process Application

The HX was surveyed prior to decontamination and twelve places marked as survey points for monitoring progress throughout the trial.

Pre-oxidised stainless steel coupons were submerged in the chemical make up tank and examined at intervals between the chemical cycles to estimate the surface condition of the HX internals.

The DFD chemical cycle time averaged just over eight hours for each cycle over a series of eight cycles.

Temperatures were maintained between 150oF and 175o F. Flow rates were in the region of 130 gpm. The system's running pressure was 10 to 15 psi. The flow paths were switched during running to enhance removal of air from the system and to aid the exposure of all parts of the system to fresh process chemicals. The decision to halt the process was based on the corrosion coupon losses, the reducing radiation fields and the opportunity to examine the internal surfaces using a boroscope and abrasive surface wipes while the system was shutdown.

Monitoring of the process was achieved by sampling the solvent at appropriate stages during the process and performing a simple titration. Visual examination of the sample throughout the oxidation cycle was an additional and important method for estimating the condition of the solvent.

Results

An average decontamination factor of greater than 1000 was achieved overall. During the initial fill and flush of the HX considerable solids were removed from both the primary and secondary sides of the HX. Some of this dissolved readily on addition of the fluoroboric acid and was removed by ion exchange, the majority remained in the filters where they gave readings of 300 mR/h (3 mSv hr^{-1}) on average.

On filling the HX, most of the radiation readings fell giving the indication that the source was far enough away from the shell wall to be shielded by the water. During the process run the readings fell steadily, although some were more affected than others.

The pre-oxidised coupons lost the oxide coating after four cycles. By the end of the run the coupons had lost 10 µm from the surface. Similarly, a boroscope inspection of the secondary side and below the tube sheet in the primary side, showed the metal to be gray and lustrous with no evidence of oxide.

After draining, the HX shell was cut around its circumference close to the tube sheet and pulled from the tube bundle. Some particulate debris remained in the shell and was flushed out with a water spray. All the tubes had a clean, bright appearance, Figure 4-2. Samples were taken from the shell and the tubes and were measured at below free-release levels.

A tube sample was removed and subjected to a further decontamination cycle in the laboratory apparatus. This reduced the remaining activity by a further factor of 3. The sample of tube was then used for surface analysis studies. Analysis by energy dispersive X-ray techniques confirmed the removal of the oxide coating and demonstrated that the metal surface had a composition the same as that of the bulk metal, see Figure 4-3. The absence of the oxygen peak and the similar peak heights of chrome (Cr) and Iron (Fe) are typical of a clean metal surface.

In one or two small areas fixed activity remained on the surface (typically areas between 2 to 10 square inches). This was readily removed by the brief application of an electropolishing wand.

Gamma spectroscopy showed the residual cobalt-60 on the tube specimen to be 0.06 Bq cm^2 and 0.08 Bq g^{-1}. For cobalt-60 this equates to 400 dpm per 100 cm^2. The free release limit is 5,000 dpm $\beta\gamma$ per 100 cm^2.

The secondary waste generated was in the form of contaminated cation exchange resin. This amounted to some 4 cu ft which is approximately 5% of the original waste volume.

Chemical demands were very low due to the dilute nature of the process and were 4.4lbs (2 kg) of potassium permanganate and 3.8lbs (1.7 kg) of oxalic acid (di-hydrate) for the whole process. The fluoroboric acid was regenerated and will be used for further heat exchanger decontamination.

Dismantlement and Free-Release

After removal of the tube bundle from the shell, the shell was cut along its lateral axis to produce two boat shaped pieces which could be easily surveyed for surface contamination. Surveying revealed activity on the outside surface in addition to several small areas (2 - 10 in sq) inside. The inside areas responded to electropolishing or simply rubbing with a cloth to remove particulate debris.

To ensure the outside was thoroughly decontaminated the two shell pieces were treated by an abrasive metal grit blasting process. This was successful and both pieces were free-released.

The tube bundle was dismantled by cutting the tubes away from the tube sheet working sequentially from the outside perimeter pairs to the central pairs. The tubes were wiped on the outside and monitored. A statistically meaningful number of samples were taken for splitting and monitoring of the internal surfaces. All the tubes were free-released using this method.

The stainless steel diaphragm and external carbon steel pressure plate were free-released after treatment by the metal grit process. The tube plate remains to be monitored and released. Approximately 90% of the material has been free-released to date.

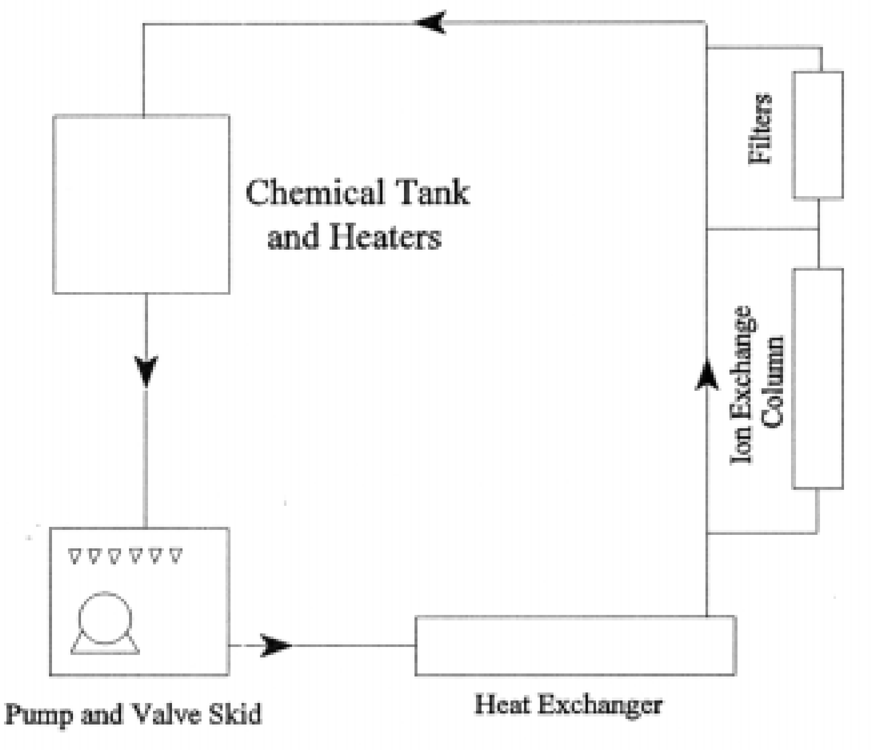


Figure 4-1
Flow Diagram of Process Equipment

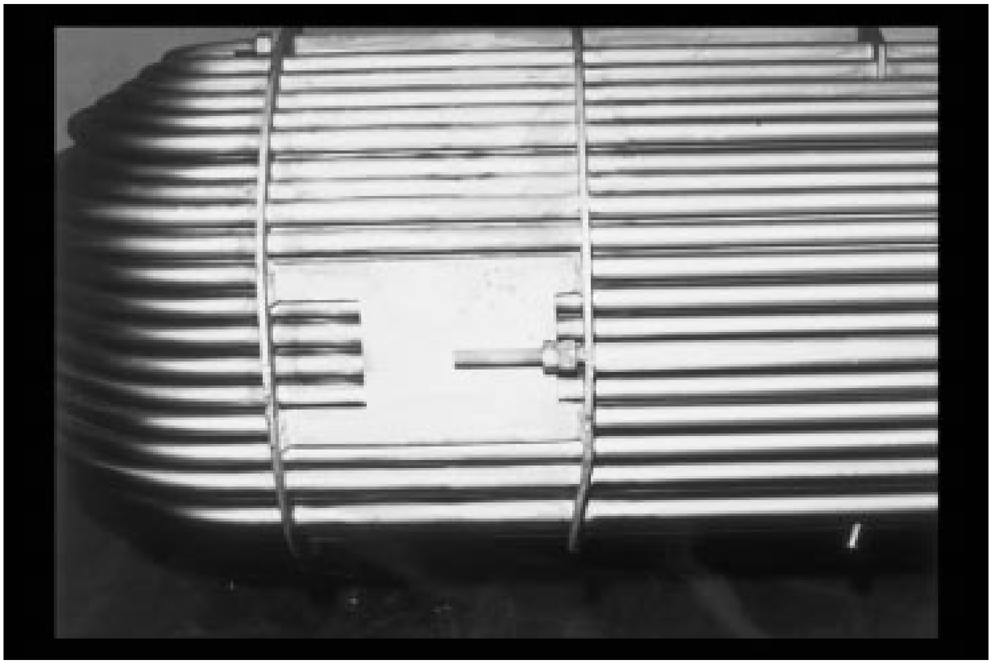


Figure 4-2
Photograph of Heat Exchanger Tubes

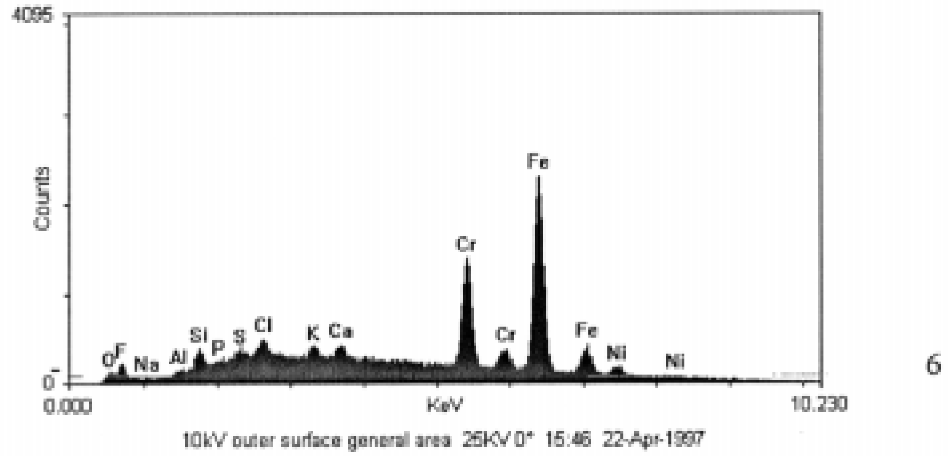


Figure 4-3
Surface Spectrum of Cleaned Tube

5

PN SERVICES / HAKE FIELD TESTS

PN Services and F.W. Hake and Associates teamed together to decontaminate dismantle and release two BWR RWCU Regenerative Heat Exchangers (HXs) removed from the Dresden BWR Plant.

The Heat Exchangers were of 304 Stainless Steel construction and weighed 22,000 lb each (flooded).They were set up side by side at the Hake facility. Initial contact dose rates were generally 15- 100 mR/h with hot spots up to 8R/h.

The dimensions were as shown in Figure 5-1. Flanged joints were welded to the inlet and outlet connections and a flow path established with 6" diameter 304 stainless steel piping. The flow path was from the process equipment to shell in / shell out of HX #1, shell in / shell out HX #2, through a 180° bend, tube in / tube out HX#2, tube in / tube out HX #1 and return to process equipment.

PN Services supplied equipment for the decon for connection to the heat exchangers, namely a circulating pump, heaters, a chemical mix tank, a flow reversal skid (for periodic reversal of the direction of flow through the heat exchangers). A cation exchange column (30 cu. ft capacity, 25 cu.ft resin used) and a mixed bed column (5 cu.ft capacity, 4 cu.ft used) were provided. Full flow filtration was also provided. Filter elements were changed out once during the process. Process equipment other than the 6" main circulation loop was interconnected with flexible hoses.

Process Application

The system was filled with mains water and demineralized using the mixed bed column. The water was then heated to 200°F.

The EPRI DFD Process application commenced and a total of nine cycles were applied between 10:30 on 9/5/97 and 22:00 on 9/7/97. Circulation was lost temporarily on two occasions during the application, but the process was restarted without difficulty. After completion the solution was demineralized with the mixed bed column and the water cooled and drained from the system.

Dismantlement

The heat exchangers were dismantled by removing the removing the top half of the shell beyond the tube sheet, cutting off and removing the tubes and then cutting and removing the remaining pieces. Prior to dismantlement some recalcitrant hot spots of activity had been noted, and after dismantlement it was discovered that the worst hot spots were associated with the inside surfaces of some of the tubes in the area of the tube bend at the end of the heat exchanger. These sections were removed and sent for disposal as radwaste. The remainder of the material was either below free release levels, or was lightly contaminated and could be processed to below free release levels by simple wiping or passage through a shot blaster. At the time of writing significant quantities of the material have been free released for recycle as non-contaminated scrap.

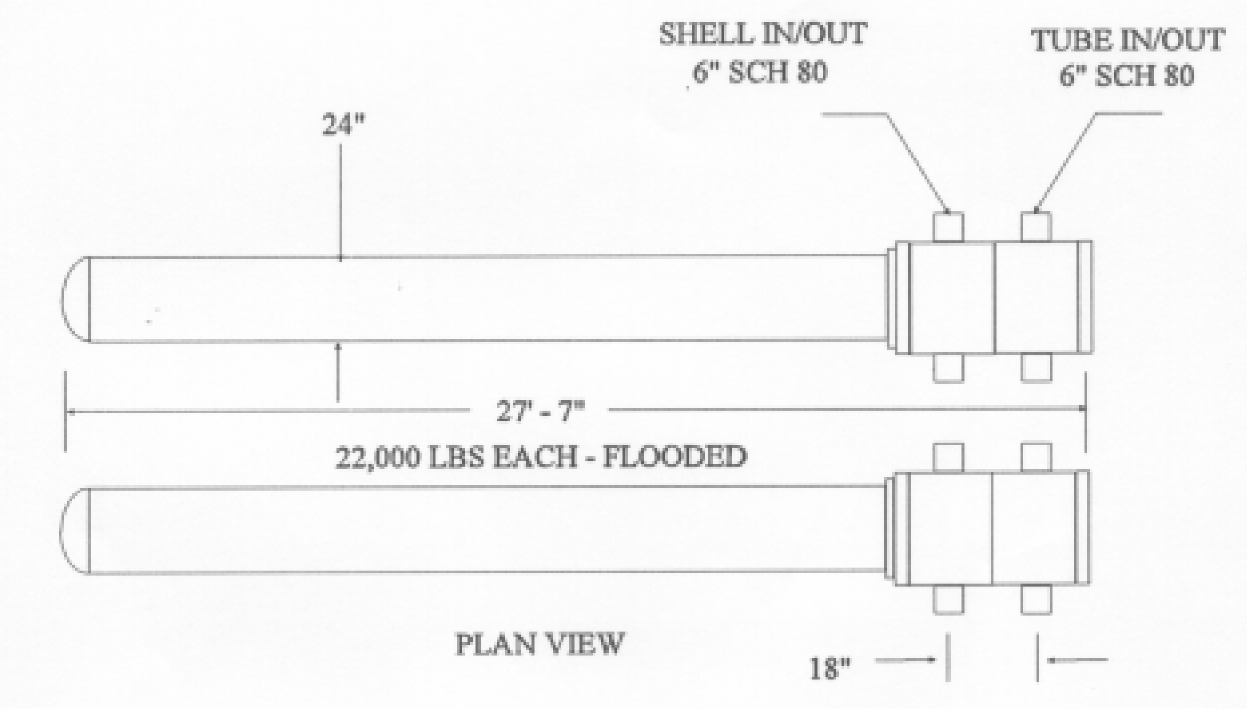


Figure 5-1
Dresden Heat Exchanger Dimensions

6

MATERIALS CORROSION DATA

The corrosion data gathered to date is as a result of coupon exposure during the field tests at the ALARON Northwest facility and artifact testing by PN Services in their test loop at the Richland facility and in a corrosion chamber at the HAKE field test.

Corrosion data has been generated to give information for system integrity assurance, equipment construction materials and process waste estimates.

Metals such as carbon steel, 400 series stainless and aluminum all exhibit high corrosion rates at higher temperatures, 60° C - 94° C (140° - 200° F), but can be successfully decontaminated at lower temperatures with a concomitant reduction of corrosion rate.

A number of non metallic materials have been exposed to the DFD solution, these have comprized ring seals, gaskets, valve seats, valve packing and valve diaphragms. Visual examination of the materials detected no obvious deterioration. Parameters such as elasticity or surface finish all appeared to be unaffected by the exposure. The materials are listed in Table 6-1.

Tables 6-2, 6-3 and 6-4 summarize the metal corrosion data available to date. A further laboratory test program including surface analysis studies is planned for early 1998 at the Bradtec facility.

Table 6-1
Non Metallic Materials Tested

RCP Seals 9.4”
RCP O Ring 7.7”
Asbestos Seal 7.2”
RHRP Seal Plate O Ring 5”
Charging Pump Gasket 4.7”
Charging Pump O Ring 2.9”
1” Ball Valve Seat
Valve Diaphragm EPDM
Valve Packing

Table 6-2
Results from an Initial Material Test Program At ALARON

Sample ID	1 Cycle g/m2	5 Cycles g/m2	1 Cycle Metal Loss um	5 Cycles Metal Loss um	Material Description
C61-43 C29-42	754.82 796.90	ND ND	97.40 102.83	ND ND	Stainless 420
CO8-83 CO8-62	1190.59 1148.14	ND ND	146.99 141.75	ND ND	Low alloy carbon arrived badly corroded
CO2-21 CO2-22 VO2-1	674.19 646.67 653.00	4236.38 4128.30 4080.83	86.99 83.44 84.26	523.01 509.67 503.81	Stainless 410
CO6-2 SO6-1 SO6-2	23.13 25.40 31.81	678.88 667.68 716.65	2.86 3.14 3.93	83.81 82.43 88.48	17-4 PH
D1 SO3-D6 SO3-D8	5.51 5.37 5.41	52.78 145.96 94.88	0.68 0.66 0.67	6.52 18.02 11.71	CF8 w/w Weld
O3X2 O3X5 O3X6	6.63 5.28 4.90	71.47 47.44 54.00	0.82 0.65 0.61	8.82 5.86 6.67	CF8 w/o Weld

Sample ID	1 Cycle g/m2	5 Cycles g/m2	1 Cycle Metal Loss um	5 Cycles Metal Loss um	Material Description
SO1-1 VO1-3 VO1-5	7.61 10.91 13.91	227.55 289.99 0.00	0.94 1.35 1.72	28.09 35.80 0.00	Sensitized 304 stainless
C56-42 C56-43 V56-42	0.11 0.15 0.11	9.74 10.83 10.25	0.01 0.02 0.01	1.06 1.18 1.12	HAYNES 25
C10-42 V26-4	6.41 16.18	131.69 177.11	0.79 2.00	16.26 21.87	Stellite 156
V26-64	0.62	23.46	0.08	2.90	Stellite 6
AL1100 6061/143	619.76 491.21	2819.56 2774.51	228.69 181.26	1040.43 1023.80	ALUMINUM
CDA110	8.53	206.68	1.05	23.25	COPPER
CDA443	10.89	223.36	1.28	26.22	Cu 72%-Zn 27%-Sn 1%
CDA706	29.45	282.36	3.29	31.58	Cu 90%-Ni10%
LEAD 9	188.21	382.50	16.60	33.73	LEAD
PTFE 0 PTFE 1 PTFE 2	-0.37 0.37 0.44	-0.37 0.37 0.44	-0.05 0.05 0.05	-0.05 0.05 0.05	PTFE (TEFLON)
I-26 I-27	ND ND	254.60 258.95	ND ND	30.20 30.70	Inconel 600 (pre-ox) TOTAL 8 CYCLES
S-127 S-128	ND ND	69.87 62.62	ND ND	8.63 7.73	Stainless 304L (pre-ox) TOTAL 8 CYCLES

ND Means no data generated

Table 6-3
Artifact Test Results

Sample ID	3 Cycle Metal Loss µm	Material Description
HC-04 -1 -2	1.1	Hastelloy C20004
HC-28 -1 -2	0.8	Hastelloy C22-28
-21 -24	12.9	Inconel-600
04	2.5	Stainless 316
06	2.3	Stainless 316L
09	2.5	Stainless 304
10	3.3	Stainless 304L
5	3.9	Stainless 304 U-bend
304 -9 -10	85	Sensitized 304 U-bend

Table 6-4
Corrosion data from the Hake Field Test

Material	Corrosion (microns)
304-308 (weld) - 304	1.88
I-182 weld metal	11.1 / 14.6
Inconel 600 (flat coupon)	5.8 / 5.4
Inconel 600 (SG Tube, mill annealed)	7.8 / 8.0
Inconel 600 (tubing)	3.1 / 3.4
Incoloy 800 (flat coupon)	2.7 / 2.0
Incoloy 800 (tubing)	3.6 / 3.5
321 stainless (flat coupon)	2.8 / 1.2
321 stainless (tubing)	6.8 / 6.7
410 stainless	489.2 / 527.2

Specimens were flat coupons, unless otherwise noted

NB: Specimens were exposed throughout the decontamination

7

WASTE MANAGEMENT AND PROCESS SAFETY

Chemical and Radiation Safety Issues

Material safety data sheets for the chemicals used are provided in Appendix A.

Significant problems have been encountered in applying *concentrated* fluoroboric acid processes due to the corrosive nature of fluoroboric acid and its volatility. Extensive personnel and equipment protection is necessary, particularly where raised temperatures are involved. The EPRI DFD, however, uses fluoroboric acid in very *dilute* concentration, and once the stock chemical has been diluted into the process system as the first stage of the process, the hazards of handling the circulating solution have been shown (in the full scale demonstration programs) to be no greater than those encountered in typical sub-systems applications. Precautions necessary are typical of those required for handling hot mildly acid solutions. Respiratory protection is not normally required, even when the process solution is open to atmosphere.

Other chemicals used in the EPRI DFD Process are familiar and are regularly used in commercial decontamination projects.

Concentrated fluoroboric acid is highly corrosive towards Zircalloy. Corrosion of zircalloy proceeds at a slightly greater rate than carbon steel in the hot EPRI DFD solution, but much less than in concentrated fluoroboric acid. The total inventory of fluoroboric acid for any project is extremely small (e.g. one 55 gallon drum for a full system decontamination). By limiting the inventory of chemical in this way, any concerns about deleterious effects of inadvertent exposure of zircalloy to the chemical can be avoided.

Radioactivity is removed from the circulating solution by ion exchange on a continuous basis. The circulating concentration of radioactivity during the decontamination is unlikely ever to exceed 10^{-2} microcurie per ml. During system heat-up or towards the end of the process, (which are the most likely time that a system leak would occur) the circulating radioactivity is likely to be two orders of magnitude below this level. Radiation levels in contact with process equipment during the decontamination are well within the experience typical of commercial decontaminations.

Mechanical Safety

The similarity of the EPRI DFD Process to other decontamination processes means that the mechanical safety issues are familiar. The only new issue which has emerged in the testing work is that care should be taken to exclude or remove small threaded carbon steel fittings from the flow system if the most aggressive conditions are being employed for decontamination of 300 series stainless steel. Threaded fittings of this type could, in the worst case, lose sufficient metal to allow the fitting to be ejected, causing a system leak.

Materials of construction for equipment is an issue which has been addressed by process vendors. Although some changes to traditional equipment materials have proved necessary, no serious problems have been encountered.

Waste Volumes

The volume of ion exchange waste generated by any particular application has to be calculated by the process vendor. An approximate guide to the expected waste volume is that 1 liter of ion exchange resin waste will be generated per square meter of surface area decontaminated (1 cu. ft resin per 300 sq. ft. surface area decontaminated). A small fraction of the total resin waste will be anion exchange resin, the volume of which is dependent on the volume of the system being decontaminated.

Where a production line situation exists, the same fluoroboric acid solution can be used for many decontaminations, all but eliminating the need for anion exchange resin.

Ion exchange resin will normally be buried as the final waste form from the process. However, chemical regeneration and reuse of the ion exchange is feasible. In this case the regeneration solution obtained can be treated by other methods (e.g. neutralization, precipitation and stabilization). This type of processing can be expected to lead to significant volume reduction.

We have found that the ion exchange waste volumes generated for full system decontamination with the EPRI DFD Process match quite closely the maximum curie loading which can be tolerated on ion exchange resin due to radiolysis and "Greater than Class C" limitations. Reducing further the volumes of ion exchange resin waste would not therefore be beneficial.

Mixed Waste Issues

The major concern with regard to the potential classification of the waste as "hazardous" is the presence of chromium initially present in the oxide films and metal, and subsequently removed by ion exchange resin.

Toxic Characteristics Leaching Procedure (TCLP) testing has recently been completed on resin waste arising from a number of different applications of the EPRI DFD process. In all cases anion resin shows less chromium leached than the 5 ppm RCRA limit defined in 40 CFR 261. In the case of the cation resin, however, the leachable chromium was sometimes less and sometimes marginally greater than the 5 ppm limit.

The RCRA limit is intended to apply to hexavalent chromium and on theoretical grounds it can be stated that hexavalent chromium is extremely unlikely to be present in the cation resin, since the form of any hexavalent chromium would be anionic in the prevailing chemical conditions.

Work by PN Services has confirmed this, showing, for example, that chromium leached from the cation resin is not hexavalent according to the diphenylcarbohydrazide analysis method Good evidence now exists that leachable chromium is in the form of trivalent chromium mono-oxalate complex, formed due to traces of oxalate running through the cation exchange column during the process application. This complex is cationic, and is weakly held by the cation resin.

The extent of chromium leachability is dependent on the control of process parameters, the more care which is taken to exclude oxalate from the cation exchange column, the less leachable chromium there will be. If the resin is not fully loaded and there is spare capacity this will also reduce the chromium leachability. These strategies are unlikely, however, to guarantee that the 5 ppm leachability limit will not be breached in every case.

The best approach may be to apply for "Trivalent Chromium Exclusion" from the 5 ppm RCRA limit, since there is now ample evidence that no hexavalent chromium is leached from waste resins arising from the EPRI DFD Process.

8

PROCESS ECONOMICS

Although the EPRI DFD Process may be considered to have benefits in the reduction of worker radiation exposure or environmental improvements, it is nevertheless only likely to be applied when it can be demonstrated that there are clear economic benefits in doing so. Analysis of the economics of application cannot be done on a generic basis, but must take account of the specific circumstances of a particular project. Each point in the analysis is stated and then discussed.

The benefits to be gained are:

> reduction in waste management costs, i.e. avoidance of packaging, transportation and disposal costs of the material, but offset by the costs of processing, transportation and disposal of secondary waste from decontamination.
>
> the scrap value of the material recovered "free release".
>
> reductions in the costs of dismantlement due to the mitigation of radiological conditions during dismantlement (where relevant).

Against these benefits must be set:

> The labor, facility and equipment costs of preparing for and conducting the decontamination.
>
> The costs of chemicals consumed in the decontamination
>
> The cost of monitoring the material for free release (and any secondary decontamination required).

The cost savings associated with waste disposal can be calculated easily in the light of options pertaining to the storage and disposal of radioactive waste in the country concerned. The volume and characteristics of secondary waste can be predicted with reasonable accuracy prior to the decontamination. The scrap value of recovered material can be determined from market information. Cost savings in dismantlement, if applicable, can be calculated by predicting the radiological conditions which will pertain following decontamination, based upon the assumption that surfaces of material exposed to the decontamination solution will be clean but must be "suspected" of minor contamination after treatment.

The costs of process preparation and application are highly dependent on the size of the system decontaminated. In general cost per unit mass of material treated can be minimized by applying the process to as large a system as possible, and by operating the process on a production line basis when applied at a fixed base facility. Chemical costs are largely surface area dependent and are not therefore subject to such economies of scale. However, the chemicals are not exotic and only small quantities are consumed, so that this item is unlikely ever to be a significant item in the overall cost base.

The costs of monitoring are dependent on the methods employed which in turn are dependent on the regulations in force in the country of application. Monitoring is often a labor intensive operation, but where large volumes of material are routinely being processed, more sophisticated automated monitoring systems can be considered. A key factor in reducing monitoring costs in future years will be demonstration to regulatory authorities that methods based on gamma spectroscopy coupled with statistical sampling and "fingerprinting" techniques can be used with confidence to assure regulatory compliance with free release criteria.

Economic analysis by ALARON Corporation, using parameters derived from the heat exchanger decontamination, described in this report, has shown that decontamination for free release is cheaper by a considerable margin when compared with immediate direct disposal for management of a variety of redundant components from LWR plants (under conditions prevalent in the US). Where delay store is an option instead of immediate disposal, the economic case for decontamination for free release can still be made in some circumstances on the basis of avoided future costs of storage and ultimate disposal. Where exceptionally high value alloys are concerned (e.g. Inconel), the recovered scrap value may even cover the costs of decontamination and secondary waste disposal, allowing the material to be dealt with free of charge.

9

CONCLUSIONS

1. High Decontamination Factors have been achieved using the EPRI DFD Process on a wide range of artifacts, demonstrating that the process can be used to achieve free release of redundant nuclear plant components.

2. Large Scale Field Tests have confirmed that the process can be safely, practically and economically applied, and that the high decontamination factors achieved at lab scale can be repeated under field conditions. The majority of material from the large scale field tests has now been recycled as non-radioactive scrap.

3. Issues such as Safety, Waste Management, Materials Corrosion and Process Economics have been addressed, and relevant data is provided in this report.

4. The next step is to continue to commercialize the types of application which have already been demonstrated, and to expand the use of the process to new applications such as PWR Steam Generators and Full System Decontaminations of shut down LWR plants.

10

REFERENCES

---

1. Hanulik, J., US Patent 4,828,759, May 1989.

2. Hanulik, J., US Patent 5,340,505, August 1994

3. Ayres, J. A., "Decontamination of Nuclear Reactors and Equipment", The Ronald Press, New York, 1970.

4. Petit, P. J., Le Surf, J. E., Steward, W. B., Strickert, R. J., Vaughan, S. B., Materials Performance, 1980, <u>19</u>, 1.

5. Allen, G. C., Dyke, Harris, s. J. and Morris, A., "The oxidation of Inconel 690 alloy at 600 K in air". Central Electricity Generating Board, Technology Planning and Research Division, Berkeley Nuclear Laboratories, Berkeley, Gloucestershire, GL 13 9PB, TPRD/B/0996/R87, September 1987.

6. Allen, G. C., Dyke, Harris, s. J. and Morris, "A surface study of the oxidation of stainless steel type 304L at 600 K in air", ibid. TPRD/B/0994/R87, September 1987.

A

MATERIAL SAFETY DATA SHEETS

PRODUCT: **OXALIC ACID**

HAZARD CLASS: NR **UN No CAS No** 6153-56-6

PHYSICAL DATA

Description: Colorless crystals

M Pt(deg C) 101 **B Pt(deg C)** n/a **Specific Gravity** n/a
Solubility in water soluble
Vapor pressure n/a **mmHg at Deg C**
Vapor density n/a **(air=1)**

FIRE AND EXPLOSION HAZARD Not applicable

Flash point (deg C) n/a
Explosive limits (%): lower n/a, **upper**
Auto-ignition temperature (deg C) n/a

Firefighting measures Not applicable

HEALTH HAZARD

Harmful by ingestion and if inhaled as dust, irritating to skin and eyes. May cause burns and dermatitis if contact is prolonged. If ingested causes severe internal pain followed by collapse.

Toxicity data LD50 375 mg/kg oral, rat

Carcinogenicity No evidence of carcinogenic properties
Mutagenicity/Teratogenicity Evidence of reproductive effects
Exposure limits OES,mg/m3 1 **(Long-term, 8 hour TWA)**

FIRST AID

Eyes:	Irrigate thoroughly with water for at least 10 minutes. OBTAIN MEDICAL ATTENTION.
Lungs:	Remove from exposure, rest and keep warm. In severe cases OBTAIN MEDICAL ATTENTION.
Skin:	Wash off skin thoroughly with water. Remove contaminated clothing and wash before re-use. In severe cases OBTAIN MEDICAL ATTENTION.
Mouth:	Wash out mouth thoroughly with water and give plenty of water to drink. OBTAIN MEDICAL ATTENTION.

REACTIVE HAZARDS

Stability stable

Reaction with water none

Other known hazards Mixtures with sodium chlorite can explode on the addition of water.

Avoid contact with :	**Water** (no)	**Acids** (no)	**Bases** (no)
	Oxidizers (yes)	**Combustibles** (no)	

SPILLAGE DISPOSAL

Precautions Wear appropriate protective clothing

If local regulations permit, mop up with plenty of water and run to waste, diluting greatly with running water. Otherwise transfer to container and arrange removal by disposal company. Wash site of spillage thoroughly with detergent and water.

For large spillages liquids should be contained with sand or earth and both liquids and solids transferred to salvage containers. Any residues should be treated as small spillages.

If material has entered surface drains it may be necessary to inform local authorities, including fire services if flammable.

PROTECTIVE MEASURES as appropriate to quantity handled

Respirator	Dust respirator
Ventilation	Extraction hood
Gloves	Rubber or plastic

Eye protection	Goggles or face shield
Other measures	Plastic apron, sleeves, boots - if handling large quantities

STORAGE AND HANDLING

Special requirements none

PRODUCT: **TETRA-FLUOROBORIC ACID**
(about 50%)

HAZARD CLASS: 8 **UN No** 1775 **CAS No** 16872-11-0

PHYSICAL DATA

Description: Colorless liquid

M Pt(deg C) n/a **B Pt(deg C)** n/a **Specific Gravity** 1.31
Solubility in water miscible in all proportions
Vapor pressure n/a **mmHg at Deg C**
Vapor density n/a **(air=1)**

FIRE AND EXPLOSION HAZARD May evolve toxic fumes in fire

Flash point (deg C) n/a
Explosive limits (%): lower n/a, **upper**
Auto-ignition temperature (deg C) n/a

Firefighting measures Not applicable

HEALTH HAZARD

Causes burns to eyes and skin. Extremely irritating to respiratory system. If ingested causes severe internal irritation and damage.

Toxicity data no data

Carcinogenicity No evidence of carcinogenic properties
Mutagenicity/Teratogenicity No evidence of mutagenic or teratogenic effects
Exposure limits OES,mg/m3 2.5 F **(Long-term, 8 hour TWA)**

FIRST AID

Eyes: Irrigate thoroughly with water for at least 10 minutes. OBTAIN MEDICAL ATTENTION.

Lungs: Remove from exposure, rest and keep warm. In severe cases or if exposure has been great, OBTAIN MEDICAL ATTENTION.

Skin: Drench the skin thoroughly with water. Remove contaminated clothing and wash before re-use. Unless contact has been slight, OBTAIN MEDICAL ATTENTION.

Mouth: Wash out mouth thoroughly with water and give plenty of water to drink. OBTAIN MEDICAL ATTENTION.

REACTIVE HAZARDS

Stability stable

Reaction with water none

Other known hazards Can react violently or explosively with acetic anhydride.

Avoid contact with :	**Water** (no)	**Acids** (no)	**Bases** (yes)
	Oxidizers (no)	**Combustibles** (no)	

SPILLAGE DISPOSAL

Precautions Wear appropriate protective clothing

Spread soda ash liberally over the spillage. If local regulations permit, mop up cautiously with plenty of water and run to waste, diluting greatly with running water. Otherwise transfer to container and arrange removal by disposal company. Wash site of spillage thoroughly with water.

For large spillages liquids should be contained with sand or earth and both liquids and solids transferred to salvage containers. Any residues should be treated as small spillages.

If material has entered surface drains it may be necessary to inform local authorities, including fire services if flammable.

PROTECTIVE MEASURES as appropriate to quantity handled

Respirator	Self-contained breathing apparatus
Ventilation	Fume-cupboard
Gloves	Rubber or plastic
Eye protection	Goggles or face shield
Other measures	Plastic apron, sleeves, boots - if handling large quantities

STORAGE AND HANDLING

Special requirements none

PRODUCT: **POTASSIUM PERMANGANATE**

HAZARD CLASS: 5.1 **UN No** 1490 **CAS No** 7722-64-7

PHYSICAL DATA

Description: Dark purple crystals

M Pt(deg C) 240d **B Pt(deg C)** n/a **Specific Gravity** 2.70
Solubility in water soluble
Vapor pressure n/a **mmHg at Deg C**
Vapor density n/a **(air=1)**

FIRE AND EXPLOSION HAZARD May ignite combustible material

Flash point (deg C) n/a
Explosive limits (%): lower n/a, **upper**
Auto-ignition temperature (deg C) n/a

Firefighting measures Water spray

HEALTH HAZARD

Harmful by ingestion and if inhaled as dust, causing nausea, vomiting and kidney damage. Extremely irritating to eyes and irritating to skin. Solutions have a caustic effect.

Toxicity data LD50 1090 mg/kg oral, rat

Carcinogenicity No evidence of carcinogenic properties
Mutagenicity/Teratogenicity No evidence of mutagenic or teratogenic effects
Exposure limits OES,mg/m3 5 Mn **(Long-term, 8 hour TWA)**

FIRST AID

Eyes: Irrigate thoroughly with water for at least 10 minutes. OBTAIN MEDICAL ATTENTION.

Lungs: Remove from exposure, rest and keep warm. In severe cases OBTAIN MEDICAL ATTENTION.

Skin: Wash off skin thoroughly with water. Remove contaminated clothing and wash before re-use. In severe cases OBTAIN MEDICAL ATTENTION.

Mouth: Wash out mouth thoroughly with water and give plenty of water to drink. OBTAIN MEDICAL ATTENTION.

REACTIVE HAZARDS

Stability stable if kept away from combustible materials

Reaction with water none

Other known hazards

Spontaneously flammable in contact with glycerol and with ethanediol. Can react vigorously or explosively with acetic acid, acetic anhydride, ammonia/sulphuric acid mixtures, ammonium nitrate, antimony, arsenic, hydrogen peroxide, hydroxylamine, phosphorus, sulphur or titanium powder.

Avoid contact with :	**Water** (no)	**Acids** (no)	**Bases** (no)
	Oxidizers (no)	**Combustibles** (yes)	

SPILLAGE DISPOSAL

Precautions Wear appropriate protective clothing

If local regulations permit, transfer spillage into containers of water, stir to dissolve or suspend and run to waste, diluting greatly with running water. Otherwise mix with wet sand, transfer to container and arrange removal by disposal company. As contact with any oxidant can render organic matter (paper, wood, textiles) dangerously combustible, wash area of spillage and contaminated clothing thoroughly with water.

For large spillages liquids should be contained with sand or earth and both liquids and solids transferred to salvage containers. Any residues should be treated as for small spillages.

If material has entered surface drains it may be necessary to inform local authorities, including fire services if flammable.

PROTECTIVE MEASURES as appropriate to quantity handled

Respirator	Dust respirator
Ventilation	Extraction hood
Gloves	Rubber or plastic
Eye protection	Goggles or face shield
Other measures	Plastic apron, sleeves, boots - if handling large quantities

STORAGE AND HANDLING

Special requirements

In accordance with health and safety guidance notes. Store away from combustible materials.