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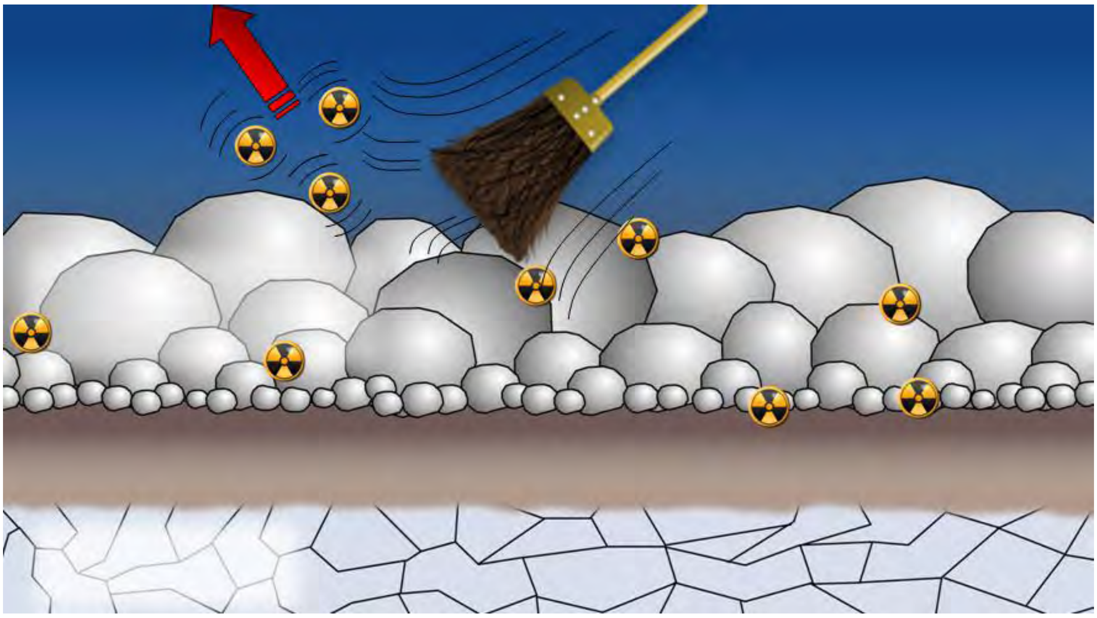

FP6-036367 ANTIOXI

ANTIOXI - Decontamination techniques for activity removal in nuclear environments

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ANTIOXI - Decontamination techniques for activity removal in nuclear environments

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Summary

In this literature survey the most used chemical, electrochemical and mechanical decontamination techniques to remove activity from system inner surfaces have been evaluated. The evaluation is separating between in-situ chemical methods (e.g. to be applied to big components like main coolant pumps or subsystems like reactor water clean-up system, reactor heat removal systems, etc. and eventually to full systems) and ex situ mechanical or electrochemical methods. The in-situ procedures are mainly chemical methods because of the necessary access to the inner surfaces of the system. In case of a removal of parts from the system there are multiple mechanical, chemical, and electrochemical methods which can be applied.

The water chemistry history and the type of oxide on material surface are the determining factors for selection of a suitable chemical decontamination technique. The basic steps in chemical and electrochemical decontamination are:
(1) dissolution of Cr-rich oxide layers,
(2) dissolution of Fe- and Ni- rich oxide layers.

After repeating some cycles of these basic steps, a final repassivation of the surface may be necessary. From a historic perspective, different oxidation-reduction techniques, based on several combinations of chemicals (e.g. LOMI, CANDECON™, HP/CORD) had been used in various modifications.

In case of removable parts, mechanical techniques different water jet and ultrasonic applications are the most used techniques in the decontamination shops of nuclear power plants. The main advantages of mechanical techniques are that they are rather easy to use, easily available, inexpensive and effective. The main disadvantage is that they usually remove also the protective oxide layers and wear the material surfaces exposing them to different corrosion phenomena.

Confidentiality	Public

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Preface

The work discussed in the present report has been carried out as in the Work Package 3 of the project FP6-036367 A deterministic model for corrosion and activity incorporation in nuclear power plants (ANTIOXI) in 2006 - 2007. The ANTIOXI project is a part of the EURATOM FP6 Programme “Advanced tools for nuclear safety assessment and component design”.

The ANTIOXI project in EURATOM FP6 concentrates on development of modelling tools for the prediction of activity incorporation and corrosion phenomena into oxide films on construction materials in light water reactor environments.

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Espoo, Finland, March 12th 2008

Author

Contents

1 Introduction

Decontamination is an optional countermeasure against activity build-up on inner surfaces of reactor systems. The application of decontamination techniques to reactor components, equipment, and systems is essential for reducing occupational exposures, limiting potential releases and uptakes of radioactive materials, permitting the reuse of components, and facilitating waste management. Decontamination processes are carried out both during service breaks and in decommissioning of a nuclear power plant. The decision to decontaminate should be weighed against the total dose and cost. Especially at the component level the benefits of decontamination and of a replacement with a new component have to be carefully evaluated.

Decontamination methods have been developed for a number of years for different types of reactors. Practically two main ways to decontaminate exist: mechanical and chemical/electrochemical. The selection of the decontamination process in the in-situ case depends on the achievable decontamination factor, the material compatibility and the amount of waste that will be generated. Mechanical decontamination is usually applied to single components and includes tens of different techniques. Chemical decontamination, on the other hand, has been applied on both component and system level decontaminations (electrochemical decontamination mainly for components). Chemical decontamination processes are also numerous but during the years a few techniques have turned out to be more applicable than the others. Both ways to decontaminate have gone through a massive development work during the years and also totally new techniques and processes are developed all the time.

In this survey different decontamination techniques are briefly described summarising the studies presented in numerous reports and scientific publications over the last thirty years. The main goal has been to build-up an awareness of the many decontamination processes and techniques used in nuclear industry during the last decades. The purpose of this work has not been to rank the techniques but to collect the descriptions of the most used techniques and to evaluate their advantages and disadvantages. Even though both mechanical and chemical (and electrochemical) decontamination techniques are included, the main focus is set to chemical decontamination processes. Due to the huge amount of data about different decontamination processes and applications presented in literature, the study has been limited mainly to describe the practical implementation of the techniques. Therefore, for example waste management issues and economical aspects related to each technique have not been included in this survey.

2 Goal

The goal of this work was to collect together brief descriptions of the decontamination techniques used in nuclear power applications.

3 Limitations

In this literature survey only the different techniques used to decontaminate component and system surfaces in nuclear environments are studied and described. The purpose has not been to rank the techniques but to give an overview on different technical approaches that have been applied. The study is limited to the description of techniques and no thorough description or conclusions on e.g. costs or amounts of waste produced for different techniques have been included. The study is also limited to decontamination methods for operating power plants. Therefore the methods for decommissioning power plants (e.g. melting of components) are not treated in this study.

4 Results

Definition of decontamination

Decontamination means removal of radionuclides from the inner surfaces of primary coolant loop or its components in nuclear power plants.

On a wider scale decontamination also means removal of oxide layers from material surfaces e.g. in process plants. However, in process industry the more used term for oxide removal is mechanical or chemical cleaning instead of decontamination. In this work decontamination is studied only in nuclear environments.

The target in decontamination can be either a component (e.g. main coolant pump), a subsystem (e.g. residual heat removal system) or a full system (e.g. whole PWR or BWR primary coolant loop with or without fuel). For the components that can be easily removed from the system the most usual option is to use either mechanical or electrochemical decontamination, whereas in all other cases the chemical decontamination is the only viable method.

The selection of a proper decontamination technique is not straightforward but must be based on several selection criteria that have been established to rationalise this selection. The criteria are briefly described in the following chapter.

4.1.1 Evaluation criteria for decontamination techniques

The effectiveness of decontamination is usually measured with a decontamination factor (DF) defined as

DF = initial activity/residual activity

This is not, however, the only definition for the decontamination factor. In some papers it can be found defined as the ratio between initial and residual dose rates, i.e. *the dose rate reduction factor*, or between initial and residual activity of some specific isotope. Therefore, care must be taken when comparing the decontamination factors determined by different authors.

To rank the applicability of the different decontamination techniques, it has been first necessary to establish a suitable set of evaluation criteria, which are regularly

- the decontamination factor,
- the material compatibility and
- the waste volume.

These are definitely the most important factors to be taken into account when selecting a proper decontamination technique.

However, especially in chemical decontamination the selection of a proper technique is also related to commercial values. The main target compatible methods described in this work have a strong commercial impact. For example, one of the most important chemical decontamination techniques, HP/CORD UV developed originally by Siemens, is not qualified to be used in the U.S. markets. Furthermore, the licensing of the techniques has lead to the development of several different processes that do not contradict with the immaterial property rights of the original processes.

If the comparison between different decontamination methods is looked on a more detailed scale, the selection criteria can be also categorised as (1) decontamination effectiveness, and (2) impacts and constraints associated with the use of the technique [1]. These criteria are also applicable to all industrial cleaning, i.e. not only to nuclear applications. Even though in this work no thorough ranking between different methods will be made, some rankings based on the various criteria presented in the literature are included in the text.

4.1.1.1 Decontamination effectiveness [1]

The different decontamination methods considered have been usually developed to satisfy particular industrial cleaning requirements. There are seven different requirements which should be satisfied for effective decontamination.

1. Loose debris removal

   This criterion includes removal of both the loose particles which have deposited at the bottom portions of the system in low spots and dead volume spaces, and the loosely adherent, smearable material which may be attached to the internal surfaces of the system being cleaned. The loose particles most probably include a range of particle sizes including fuel fines. For satisfactory decontamination, it must be possible to remove the loose debris as well as the smearable material.

2. Adherent particle removal

   This classification includes the radioactive material which adheres tightly to a surface, more tightly than the smearable film discussed above. Also included is a corrosion layer if that layer contains radioactive material. It is possible that successful removal of the adherent particle layer requires the removal of some of the base metal.

3. Particle removal from crevices

   Many components in a reactor coolant system such as valves, demineralizers, pumps, tanks with internal parts, and filter housings can contain narrow spaces, like cracks or crevices. Radioactive particles, including fuel fines, can migrate into such crevices, and must be removed. Some of the decontamination methods evaluated will penetrate the crevices and remove particles and some will not. If a particular technique will not remove particles from crevices, then it may have to be followed by a process that will, in order to effectively complete the decontamination.

4. Effect of internal components

   Some of the tanks, vessels, and other items to be decontaminated contain internal components, which can have a marked effect on the applicability and effectiveness of a particular decontamination technique.

5. Production Rate

   The rate at which a particular method will effectively decontaminate a component (production rate) is important, because it is significant to both cost and radiation exposure. However, since production rate is not as important as the effective removal of contaminated material, the weighting factor given to production rate is not usually so high than that assigned to the other requirements.

6. Remote Operation

   One of the more important considerations in selecting a decontamination method is the ALARA requirement for minimum exposure to operating personnel. This requirement can greatly reduce the applicability of some otherwise promising decontamination method. The need to protect personnel from excessive exposure will increase the difficulty of the cleaning operation, add to its cost, and increase the time required. The extent of these difficulties will vary inversely with the degree of remoteness of operation of a given decontamination method, i.e., in the extreme, if the technique lends itself to remote operation, there will be no "hands-on" requirement (except for the initial setup) and thus no need for shielding of personnel.

7. Degree of Development

   Degree of development is defined as the extent that the decontamination technique has been developed for industrial use. The technique may have been developed to the point where it is 1) used routinely and the equipment is essentially "off the shelf" in availability, 2) proven, but is still in the developmental stage, and has been employed only on an experimental basis, or 3) still in the experimental stage, and the equipment required for its application requires development rather than refinement.

4.1.1.2 Impacts and constraints of a technique

In addition to the seven criteria relating to the effectiveness of the different decontamination techniques discussed above, there are 10 criteria concerned with impacts and constraints associated with use of the techniques. With respect to impacts, some of the techniques may produce large amounts of secondary waste, i.e. material added to effect the decontamination may mix with the contaminated material to produce a large amount of radioactive waste. Also, some of the techniques may alter or damage the surface of the item treated to the point where the item cannot be reused. To a lesser degree, the surface finish may be modified to the point where subsequent recontamination may occur more rapidly than the original contamination, and this recontamination may be more difficult to remove. [1]

In addition to these types of impacts, there are definite constraints on the application of many of the techniques studied. Some can be used to decontaminate equipment while it remains in place in the reactor coolant system, but others can only be used to clean items or pieces of a certain maximum size after their removal from the system. The effect of any chemical residue (e.g. chlorides) which could remain after decontamination must also be considered as a constraint.

Radiological safety

- The radiological safety aspects of a particular cleaning technique can greatly influence its latitude for use.

Waste generation

- All of the waste produced during a decontamination operation must be reduced in volume, if possible, and properly packaged for storage, transport and disposal. The radioactive waste that is removed from the contaminated surfaces can be expanded in volume by the decontamination agent during the decontamination process. Any increase in the total volume of resultant radioactive waste increases the cost of disposal. The total amount of difficult-to-dispose-of-waste resulting from decontamination is very important and has a high weighting factor in determining a suitable decontamination method.

Need for disassembly

- Some of the components to be decontaminated would have to be disassembled to some degree to provide access to the interior surfaces. Both the degree of disassembly required and the relative difficulty of disassembly would impact the applicability of a particular decontamination technique. The need for disassembly, along with waste generation, has very high weighting factor in considering a proper technique.

Accessibility

- Since the radioactive material will generally be on the inside of the reactor coolant system, the area to be decontaminated must be accessible. Depending upon the technique considered one or more openings may be required to decontaminate the system at hand.

Size of item

- For off-system decontamination, an item that is too large to fit off-system decontamination equipment, e.g. an ultrasonic tank, must be sectioned. The size of the component becomes then an important factor to be considered.

Capital cost

- The initial cost of the decontamination equipment and supporting systems, plus the expected life of that equipment, can be an important factor in the selection of an appropriate decontamination method. The capital cost would include the total cost of all the needed equipment, amortized over the expected useful life and being less the salvage value.

Operating cost

- This criterion includes the labour cost plus the cost of consumable supplies. A labour intensive decontamination technique, and/or one which requires a large amount of expensive material is unfavourable. It should be noted that the operating cost for the purpose of decontamination can be quite different from the cost of ordinary industrial cleaning. The costs associated with personnel shielding and waste disposal can add considerably to the cost that would result from an application of the same technique to a non-nuclear cleaning project.

Re-qualification

- The feasibility of reusing a component/system after decontamination can be affected by a number of different factors. One is the cost of decontamination and re-qualification compared with the cost of replacement. Another factor is the effect of access or sectioning operations that require excessive repair work and re-qualification tests. Some decontamination techniques result in the removal of a significant amount of metal from the surface being cleaned. Such removal might affect the reusability of the item. The surface quality after cleaning is also important, since a rough surface is much more subject to rapid recontamination. All of these factors can affect re-qualification.

Corrosiveness

- This refers to the tendency to corrode a surface as a result of the reaction between the decontamination agent and the item being cleaned, both during the decontamination and as a residual effect later on.

Industrial safety

- This criterion relates to the inherent safety characteristics of the decontamination technique. In deciding on a proper decontamination technique, the level of safety precautions and their effects on the costs need to be considered.

Non-chemical decontamination techniques

Non-chemical or mechanical decontamination techniques are techniques that use either mechanical removal of the contaminated oxide or use chemicals that are not traditionally used in decontamination. From an application standpoint, an additional distinction exists in that some of the techniques are amenable to in-place use on a reactor cooling system, while some can only be used to decontaminate components removed from the system.

Non-chemical decontamination techniques have been used especially in cleaning components in conventional process plants but many of them have been developed also for nuclear environments. The points to be taken into account in selecting a proper technique are the ones listed above. In the history many extensive literature surveys on these techniques have been published [1-5]. Therefore in this survey these techniques are described only briefly in Appendix 1 stating the advantages and disadvantages of each of them [1-9]. It is also worth mentioning that in this work the conventional hand scrubbing is not considered as a modern and safe decontamination method.

Gardner et al. [1] have ranked the non-chemical decontamination techniques based on the criteria mentioned above: decontamination effectiveness and impacts and constraints associated with the use of the technique. Since each criterion will have a different influence on applicability considerations, each was given a grading scale and weighting factor in accordance with its perceived effect or importance. Final ranking was obtained by summing up the products of these two factors for each criterion. According to them the highest scoring techniques for both in-place and off-system decontamination are:

- Mechanical methods, propelled devices
- Mechanical methods, ”pigs”
- Mechanical methods, rotated brushes/hones
- High-pressure water

- Ultrahigh-pressure water
- Pumped abrasive slurries
- Water abrasive cleaning
- Vibratory finishing
- Ultrasonics
- Freon cleaning

However, in real decontamination processes the target of decontamination usually determines the final selection of the technique. For example, the fuel bundles cannot be cleaned with mechanical brushes but some pressurised water jet techniques or ultrasonics can be used. Therefore the ranking of the techniques has to be treated with caution. In the following text two often used mechanical techniques are described in more detail.

4.1.2 Ultrasonic cleaning

One of the most often used techniques in decontamination, especially in that of fuel rod bundles and simple shaped components is ultrasonic cleaning. EPRI has developed this technique extensively for fuel rod decontamination [10-12]. The EPRI ultrasonic fuel cleaning technique uses an optimum arrangement of special transducers. The resulting ultrasonic energy field is able to “see around” the intervening fuel rods into the very centre of the assembly, in effect producing an energy field of relatively uniform intensity throughout the fuel matrix. The interior rods of a fuel assembly can thus be cleaned effectively, while limiting the energy intensity on peripheral rods to maintain pellet and cladding integrity. A scheme of an ultrasonic fuel cleaning system is presented in Figure 1.

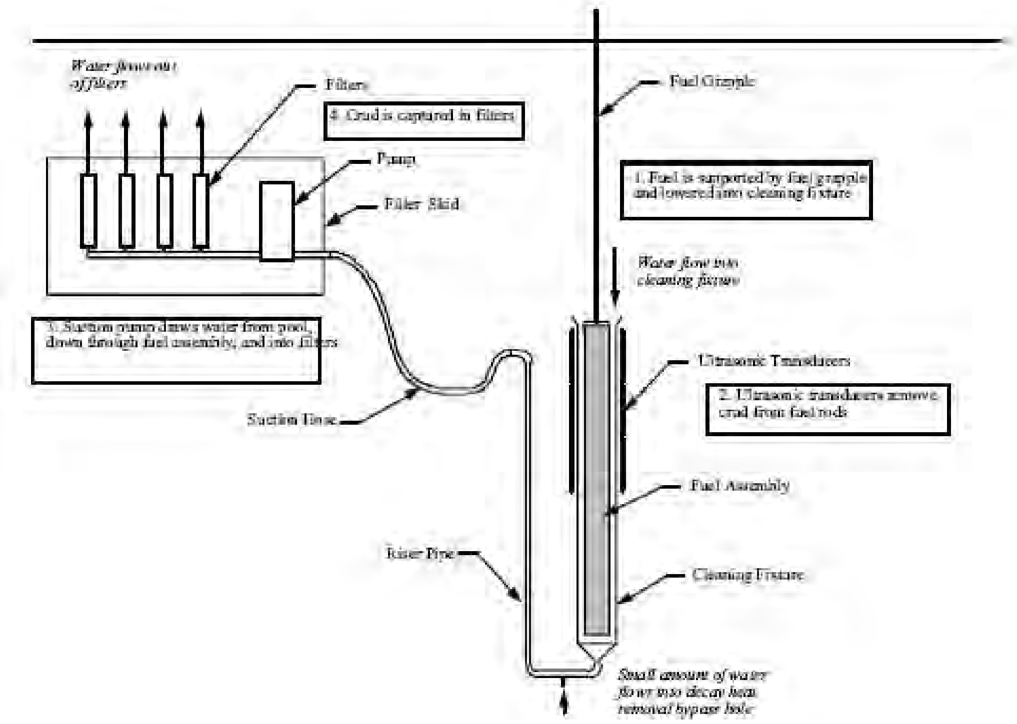


Figure 1. A scheme of an ultrasonic fuel cleaning system [12].

The equipment was successfully demonstrated on discharged Callaway NPP fuel in April and August 1999, followed by cleaning of sixteen reload assemblies during cycle 11 in 1999 and the entire reload inventory prior to loading the core for cycle 12. The sixteen cleaned assemblies were found to perform well during October 1999, with neither fuel failures nor evidence of local axial offset anomaly (AOA). The cleaning efficacy of the prototype cleaner was definitively demonstrated on spent fuel assemblies at Callaway NPP during October 2001. These tests consisted of sampling the fuel deposits on a discharged (uncleaned) fuel assembly, cleaning the assembly with the prototype ultrasonic cleaner followed by a second sampling of the cleaned assembly. Comparison of the activity of deposits before and after cleaning provided a measure of the degree of removal of corrosion products from actual fuel. The percentage of activity removed from the various rods and spans used in the comparison ranged between 41 and 100%, with many values of 75% or higher. The percentage of activity removed from the four highly crud-loaded spans of each rod was averaged, and the averages indicated that over 75% of the activity was removed from each rod. For some rods over 90% was removed. The combined averages of the activity removed from the two sampled assemblies indicate that about 86% of the initial activity was removed by use of the ultrasonic cleaning process.

Based on the excellent performance of the sixteen cleaned reload assemblies in Cycle 11, AmerenUE elected to clean the entire reload inventory prior to loading the core for Cycle 12. These 96 once-burned fuel assemblies were returned to the reactor with feed fuel to constitute the Cycle 12 core. The fuel cleaning operation was generally trouble-free and effective in removing corrosion products from the once-burned fuel assemblies. Approximately 48 hours were expended for cleaning the 96 assemblies, including retrieval of the assembly from the spent fuel storage rack and insertion into the cleaner, the actual cleaning operation, and return of the cleaned assemblies to the storage rack.

Ultrasonic cleaning has been also developed for steam generator secondary side cleaning [13]. Rootham et al. wanted to test the cleaning effectiveness and structural integrity using ultrasonic cleaning with laboratory scale mock-ups. Based on the results, they concluded the following:

Effectiveness testing

- In the absence of a significant inventory of suspended solids hydrophone measurements have been demonstrated to correspond with deposit removal for tests run under the same conditions of temperature and frequency.
- Steam generator deposits can be removed from tube surfaces by ultrasonic energy in reasonable time. This is based on both deposit stimulant tests and tests with pulled tubes.
- Higher power levels correlate with more efficient deposit removal (cleaning).
- The power densities required to clean deposits are judged to be achievable in an operational steam generator using specially designed push pull transducers operating at an energy density of 30 to 60 watts per gallon.
- Effective cavitation has been observed penetrating as far as 42 rows deep within the tube bundle.
- Cleaning efficiency improves when the temperature is below 60^{o}C.
- The presence of moderate amounts of suspended solids (i.e. 1%) has a minor effect on cleaning effectiveness.
- The use of dilute chemical agents can dramatically enhance deposit disruption.

Integrity testing

- The limiting consideration is tube wear at tube support plates.
- Work rate due to the alternating component of wear is small and relatively insensitive to contact force.

- The calculated wear rate is controlled by the constant, or direct, loading component of the tube against the tube support plate.
- Tube displacements are very small. There is no potential for tube to tube contact.
- Induced tube stress is small.
- Impact loads are considered insignifigant.

Even though ultrasonic cleaning is not the most highly scored technique in the list by Gardner et al. (see above) it is used quite often due to its rather easy installation and capability to clean components with very different shapes.

4.1.3 Dry ice blasting [14]

Dry ice blasting together with ultrasonics is rather much used in process and power plants to purify material surfaces. Dry ice blasting, or carbon dioxide (CO_2) blasting, is an industrial cleaning process for surfaces that uses carbon dioxide pellets as the blasting medium. Carbon dioxide pellets are about 1-3 millimeters in size but may be as long as about 4.5 millimeters. The pellets are very cold (below -38°C).They are housed in a machine where they are typically accelerated by compressed air with pressures in the range of 100 – 150 psi, although lower and higher pressures of up to 300 psi may be used in certain circumstances. To remove the contamination, the pellets are fired at the contaminated surface. In dry ice blasting, contamination is removed by three mechanisms which occur nearly simultaneously. In the first mechanism, the accelerated carbon dioxide pellets drive the contamination off of the surface because of their impact at high velocities. This mechanism of removal is similar to that of sandblasting. In the second mechanism, the cold pellets create a thermal difference between the contaminant material and the surface. This thermal difference may cause the contaminant and the surface to contract at different rates, thereby weakening the bond between them. In the third mechanism, the carbon dioxide pellets lift the contamination off of the surface when they expand into a vapour. This expansion occurs when the pellets are exposed to room temperature and when they collide with the surface. The carbon dioxide gas rapidly expands, and, as it does, it lifts the contamination off of the surface.

Dry ice blasting machines are commercially available. The machines are either electric or pneumatic, and they store the pellets for use. The rate of pellet delivery is adjustable. Some machines use one hose, delivering the pellets and high-pressure air down the same path. Other machines use two hoses with the first one used to transport air of about 40 psi to carry the pellets and a second hose for delivering the high pressure air to the nozzle gun where the pellets and high-pressure air are combined. All of these machines operate on the principle that the CO_2 gas returns to the atmosphere and leaves only the contaminant and particles removed from the surface as waste. Therefore, they are usually used with other systems that filter the CO_2 gas and collect the waste material. For blasting in radioactive environments, support systems such as an air compressor, air dryer, and containment hut with a HEPA filtered ventilation system may be advisable to use. In general, dry ice blasting requires superior off-gas treatment systems and has been described as a slow technique.

Chemical decontamination

4.1.4 General considerations [15, 16]

Chemical decontamination is usually carried out by circulating the selected reagents in the system. However, segmented parts may be decontaminated by immersing them in a tank containing the reagent, which is then agitated.

When selecting a suitable chemical decontamination process, in addition to the general considerations and in view of the variety of chemical decontamination processes available, several criteria must be considered in a detailed analysis based on site-specific conditions. Most of the criteria are related to the specific features of a nuclear installation, such as:

- location of the contamination (e.g., inner versus outer surfaces of closed systems);
- physical integrity status of the systems;
- materials (e.g. steel, concrete);
- history of operation (to determine contamination-strata profile);
- nature of the contamination (e.g. oxide, crud, particulate, sludge);
- effectiveness of previously used chemical decontamination processes;
- distribution of contamination (e.g. surface, cracks, homogeneous distribution in bulk material);
- exposure to humans and the environment;
- safety, environmental, and social issues;
- exposure-level-reduction requirements (e.g. recycling versus disposal);
- quantity and type of secondary waste from decontamination and conditioning;
- ultimate fate of decontaminated materials;
- time;
- costs.

Chemical decontamination is mainly applied to decontaminate a subsystem or the whole system. Chemical decontamination normally consists of consecutive treatments of contaminated surfaces with different chemicals that dissolve the oxide layer by layer. In some cases either electrical or mechanical surface cleaning processes have been combined with the chemical treatments. Chemical decontamination where the concentrations of different chemicals are less than 1 wt% is called dilute (or mild) concentrate decontamination (DCD, see Chapter 4.1.9.1).

In chemical decontamination the composition of the contaminated surfaces has to be known. The selected decontamination method has to be able to dissolve mixed oxide layers. Based on experiences from the plant conditions the typical thickness of an oxide layer is a couple micrometers at the time when decontamination is usually applied. Depending on the water chemistry history and used construction materials the protective oxide layer consists mainly of different amounts of Fe, Ni and Cr (see Figure 2). As seen in Figure 2, in WWER (and PWR) conditions the oxide film on stainless steel is enriched in Cr and partly depleted in Fe. In BWR environments the oxide film consists mainly of Fe and Ni and is depleted in Cr. This Cr content is the determining factor for the resistance of an oxide layer towards chemical exposures. Therefore, the decontamination process is usually different in PWR/WWER conditions when compared to that in BWR conditions.

The oxides of these elements are practically insoluble in pure neutral water, which is overcome by adding chelating agents to decontamination solutions. These chelating agents can be e.g. complexing organic acids (oxalic acid, citric acid, ethylenediaminetetraacetic acid (EDTA) and nitrilo-tri-aceticacid (NTA)). An alternative to chelating agents would be to lower pH, but the risk of base metal corrosion limits the use of this method (except if corrosion inhibitors are used). In most cases the most crucial step for chemical decontamination to be successful is the removal of the Cr enriched layer of oxide. Especially in PWR/WWER conditions, the decontamination process calls for oxidation of these Cr ions from trivalent to hexavalent, which form more easily soluble species. This is usually accomplished by adding permanganate solution (see also Chapter 4.1.6.1 for a description of AP/NP preoxidation) [17]:

$$Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCrO_4^- + 2MnO_2(s)$$
$$MnO_2 + H_2C_2O_4 + 2H^+ \rightarrow Mn^{2+} + 2CO_2 + H_2O.$$

Any remaining MnO_4^- and the MnO_2 formed are destroyed in most cases using oxalic acid rinse.

After removing the protective Cr layer, the next step is the actual decontamination step during which the Fe and Ni rich oxide layers are removed. The used chemicals in the decontamination step vary from process to process and in case of the most used processes the chemical combinations are patented or otherwise commercially protected. After the oxide removal the surface needs to be passivated properly in order to prevent the degradation of the base material.

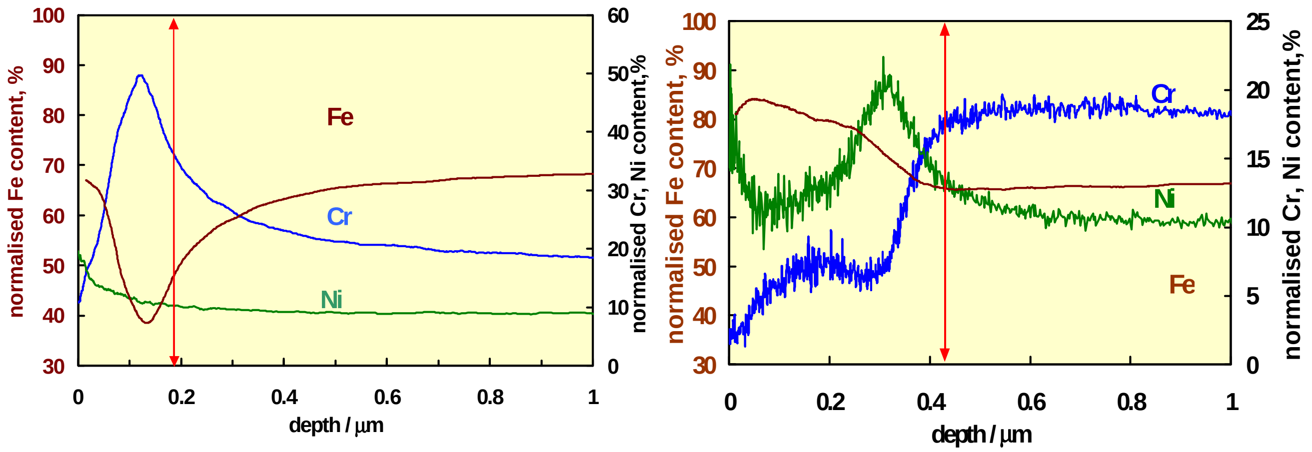


Figure 2. GDOES analysis of the AISI 316 samples after ca. 12 months of exposure to WWER (Loviisa 1, left) and BWR (Olkiluoto 1, right) environments. Vertical arrows indicate the oxide film thicknesses.

In the last 30-40 years several different procedures for accomplishing these steps have been developed and chemical decontamination has been extensively studied. Several excellent summaries of different techniques exist in literature [e.g. refs. 16 and 18 and references therein] and in this work the main features presented in those summaries have been collected together.

Factors considered for in-line chemical decontamination are also valid for the immersion process. However, because the tanks are usually open at the top, a proper ventilation system must be installed, and special care must be taken to avoid contact between the operators and the highly corrosive reagents. It should be noted that chemical reagents at excessively high temperatures may result in undesirable effects, such as toxic or explosive gases, e.g., hydrogen. Chemical decontamination requires efficient recycling of reactive chemicals, as insufficient recycling of decontamination products may increase the amount of secondary waste which may be difficult to treat. It may generate mixed waste, and it may result in corrosion and safety problems when misapplied. In addition, it requires both different reagents for different surfaces, and drainage control. For large jobs, it generally requires constructing a chemical storage and collecting equipment as well as addressing criticality concerns, where applicable.

In general, knowledge of chemical cleaning methodology is a prerequisite for assessing decontamination technology as most of the procedures and chemicals used to decontaminate nuclear materials and equipment are also used for cleaning equipment and materials in the chemical process industry. Both chemical cleaning and decontamination require the same areas of knowledge and experience: chemistry of fouling, corrosion technology, and waste-generation/removal techniques. Furthermore, the same engineering knowledge is required to devise suitable procedures for mixing, pumping, as well as heating solvents and other chemical-cleaning constituents. Compliance with basic health and safety practices regarding chemical agents is required, in addition to the radiological safety aspects. Additional safety equipment depends on the toxicity of contaminants.

The main advantages and disadvantages of chemical decontamination can be listed as:

Advantages

- Chemical decontamination is relatively simple and similar to classical cleaning in the conventional industry for which a lot of experience exists. It may also be relatively inexpensive where additional equipment is not required.
- Chemical decontamination is a known practice in many nuclear plants and facilities.
- With proper selection of chemicals, almost all radionuclides may be removed from contaminated surfaces. Problems of recontamination may be reduced by continuously rinsing the surface with water.
- With strong mineral acids, a decontamination factor of more than 100 may be achieved, and in many cases, the item may be decontaminated up to releasable levels.
- Chemical decontamination may also remove radioactivity from internal and hidden surfaces. However, in this case, its effectiveness may be low, and measurement at release levels will be a problem.
- Chemical decontamination involves relatively minor problems of airborne contamination, similar to those of the closed-system approach.

Disadvantages

- The main disadvantage of chemical decontamination is the generation of secondary liquid waste, resulting in relatively high volumes compared to other processes, such as electropolishing. The treatment and conditioning of this secondary waste requires appropriate processes to be considered when selecting the decontamination option. Moreover, in some cases (e.g. internal and hidden surfaces), the effectiveness of the decontamination may be relatively low.
- Usually the solution must be heated up to 70 to 90°C in order to increase the rate of the decontamination process.
- A further disadvantage in obtaining high decontamination factors is that corrosive and toxic reagents may need to be handled.
- Chemical decontamination is mostly ineffective on porous surfaces.

Decontamination chemicals

Chemical decontamination calls for combination of several chemicals in sequential steps during the decontamination process. The mostly used decontamination chemicals and chemical decontamination techniques are briefly listed below in Table 1. More detailed information of the usage of these chemicals is included in Appendix 2. [14, 16].

Table 1. Chemicals or processes used in chemical decontamination

CHEMICAL	**EXAMPLES**
Strong mineral acids	nitric acid, sulphuric acid, phosphoric acid
Acid salts	sodium phosphates, sodium sulphate
Organic acids	formic acid, oxalic acid, citric acid
Bases and alkaline salts	potassium hydroxide, sodium hydroxide
Complexing agents	picolinic acid, ethylenediaminetetra-acetic acid (EDTA)
Bleaching	calcium hypochlorite
Detergents and surfactants	
Organic solvents	kerosene, tetrachloroethane
Multiphase treatment processes	See Appendix 2

DIFFERENT CHEMICAL DECONTAMINATION TECHNIQUES

Several chemical decontamination procedures and processes have been developed during the last thirty years. However, nowadays practically only three of them have noticeable commercial impact: *HP/CORD UV* originally developed by Siemens KWU, *LOMI* developed by Central Electricity Generating Board (CEGB) for Electric Power Research Institute (EPRI) and *CAN-DECON* developed by Atomic Energy of Canada Limited (AECL).

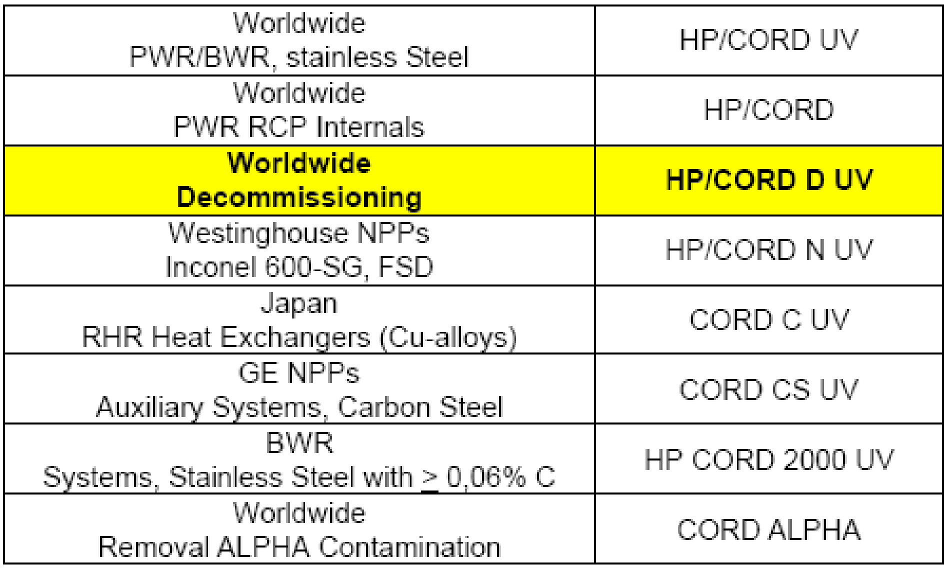
In the following chapters these most often used multistep chemical decontamination processes together with some modifications are described in more detail. The modifications are usually done to get another commercially usable process and to avoid patent restrictions. Also a brief comparison of these techniques and descriptions of some other techniques are included.

4.1.5 HP/CORD UV Process

The most recent decontamination procedure that has been applied widely in many decontamination campaigns, is the HP/CORD UV process originally developed by Siemens KWU (nowadays AREVA NP GmbH) [19, 20]. Currently almost all system decontaminations (not in the U.S.) are performed either with the CORD technique or with modifications from it. The abbreviation HP/CORD UV stands for

HP	**P**ermanganic acid
C	**C**hemical
O	**O**xidation
R	**R**eduction
D	**D**econtamination
UV	**U**ltra-**V**iolet light

Actually, AREVA NP GmbH has developed a whole family of different decontamination procedures to be applied for different types of plants and water chemistries (see Figure 3).



Worldwide PWR/BWR, stainless Steel	HP/CORD UV
Worldwide PWR RCP Internals	HP/CORD
Worldwide **Decommissioning**	**HP/CORD D UV**
Westinghouse NPPs Inconel 600-SG, FSD	HP/CORD N UV
Japan RHR Heat Exchangers (Cu-alloys)	CORD C UV
GE NPPs Auxiliary Systems, Carbon Steel	CORD CS UV
BWR Systems, Stainless Steel with ≥ 0,06% C	HP CORD 2000 UV
Worldwide Removal ALPHA Contamination	CORD ALPHA

Figure 3. Processes of the Cord family developed by AREVA NP GmbH (formerly Siemens AG) [21].

The idea of the HP/CORD UV process is based on (see also Figure 4):

1. preoxidation aimed at the dissolution of oxides containing Cr by oxidizing Cr^{3+} to Cr^{6+} by means of permanganic acid ($HMnO_4$) (see the reactions above),
2. reduction of permanganic acid (manganese is reduced from Mn^{7+} to Mn^{2+}) using oxalic acid
3. decontamination using oxalic acid
4. decomposition of decontamination chemicals to water and CO_2 using ultra-violet light and H_2O_2.

It is worth mentioning that the whole HP/CORD UV process is applicable to PWR surfaces whereas in case of BWR decontamination the preoxidation is not necessarily needed (This actually applies to all three decontamination processes mentioned in Figure 4). Also, in the HP/CORD UV process no transition step is needed between preoxidation and decontamination steps. This of course makes the process faster.

PWR decontamination

Process	**LOMI**		**CAN-DECON**		**HP CORD UV**	
	Process steps	*Chemicals in solution*	Process steps	*Chemicals in solution*	Process steps	*Chemicals in solution*
Preoxidation	**AP-Oxidation** •$KMnO_4$ **NP Oxidation** •HNO_3+$KMnO_4$ •Circulation •Discharge or go to transition step	MnO_4^- K^+ $HCrO_4$- By NP Oxidation like AP+NO_3^-	**AP-Oxidation** •$KMnO_4$ (AP) injection •Circulation •Discharge or go to transition step	MnO_4^- K^+ $HCrO_4^-$	**HP Oxidation:** •$HMnO_4$ injection •Circulation	MnO_4^- $HCrO_4^-$
Transition to dissolution step	•$H_2C_2O_4$ injection •Circulation •Discharge or •Ion exchange	$C_2O_4^{2-}$ Cr^{3+}	•$H_2C_2O_4$ injection •Circulation •Ion exchange	$C_2O_4^{2-}$ Cr^{3+}	*No specific action*	
Dissolution step (decontamination)	•LOMI reagent ($V^{II}(pic)_3^-$) injection •Circulation	$V^{II}(pic)_3^-$ $Fe^{II}(pic)_3^-$	•EDTA •Citric acid	$EDTA^{4-}$ $C_3H_5O(COO)_3^{3-}$	**CORD® decontamination**: •$H_2C_2O_4$ injection •Circulation •Ion exchange (Activity Ni^{2+}, Mn^{2+}, Fe^{2+})	$C_2O_4^{2-}$ Cr^{3+}
Cleaning	•Discharge to waste •Intermediate storage or •Ion exchange		•Discharge to waste •Intermediate storage or •Ion exchange		**UV Decomposition:** •H_2O_2 injection •Circulation •Ion exchange (Cr^{3+})	

BWR decontamination
may start here ↓

Figure 4. Description of the most important commercial chemical decontamination processes

Typically, the conditions for the decontamination with HP/CORD UV are as follows:

- Temperature 95°C +/- 2°C
- $HMnO_4$ concentration 200 ± 50 ppm
- Oxalic acid concentration 2000±200 ppm
- H_2O_2 solution of 30% concentration.

Figure 5 shows how oxidation-reduction potential and amount of cations released change during sequential cycles with the HP/CORD UV process as the surface becomes decontaminated.

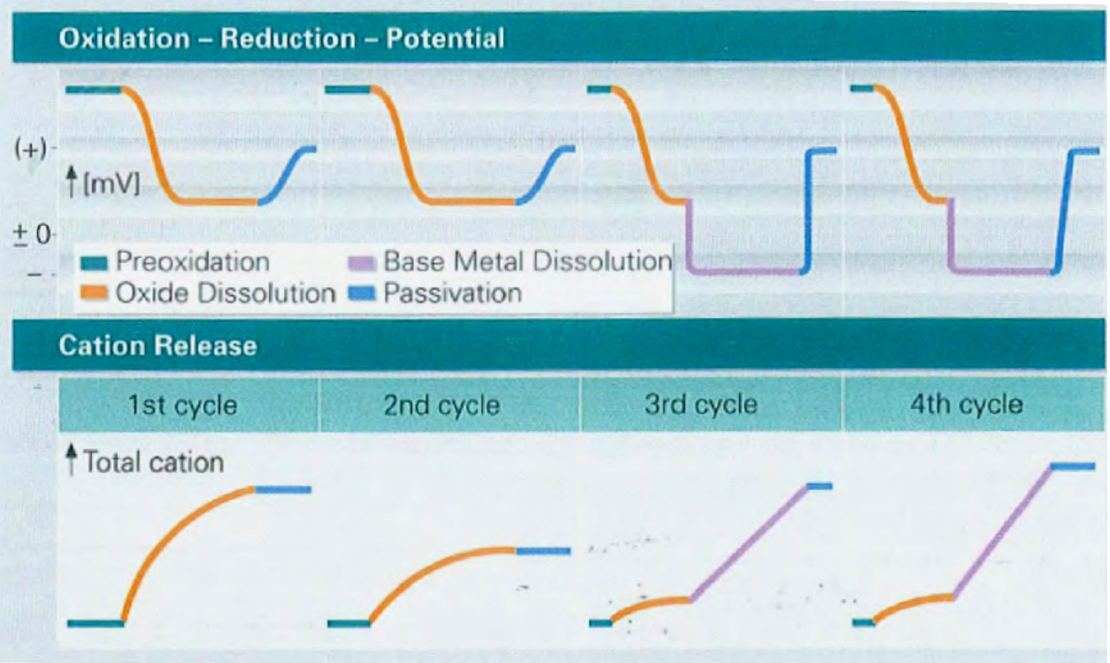


Figure 5. Oxidation-reduction potential and the cation release during the HP/CORD UV process. [19]

The benefits of the HP/CORD UV technique are

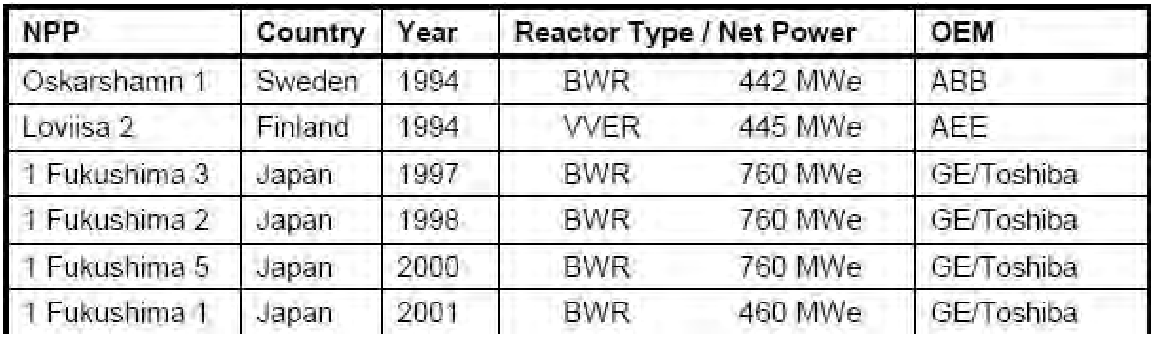
- High material compatibility
- HP as oxidation agent
- A single decontamination chemical for reduction and decontamination
- Entire decontamination is performed with only a single fill of water
- Regenerative process
- High decontamination factors for all reactor types and water chemistries
- In-situ decomposition of the decontamination acid to carbon dioxide and water
- Chelate-free waste (no decontamination chemicals in waste)
- Minimum waste generation

The main disadvantages of HP/CORD UV are the observed IGA sensitivity on some materials after this process and on the other hand the risk of oxalate formation during the decontamination step, which makes the process purification more difficult.

One of the main features in the HP/CORD UV process is that it can be easily cycled as many times as necessary in order to remove all activity from the surfaces. A “special case “of the base process is the process for decommissioning of power plants, HP/CORD D UV. In this process the oxide film is totally removed from the surface using HP/CORD UV process. After this the exposed base material is uniformly dissolved with a final decontamination cycle until the residual activity still present in the base material has been removed (HP/CORD D UV). This reversal from surface protection to surface attack is done by reducing the redox-potential of the decontamination solvent and also by lowering the corrosion potential of the base material. From a process engineering point of view this is done by the removal of all oxidative constituents (e.g. Fe^{3+}, oxygen) from the decontamination solvent. When enough base material has been dissolved, the dissolution process can be terminated at any time by the addition of oxidative constituents (e.g. air or H_2O_2). Additional chemicals or a change of decontamination solvent are not necessary and the dissolution rate of material can be quite easily controlled.

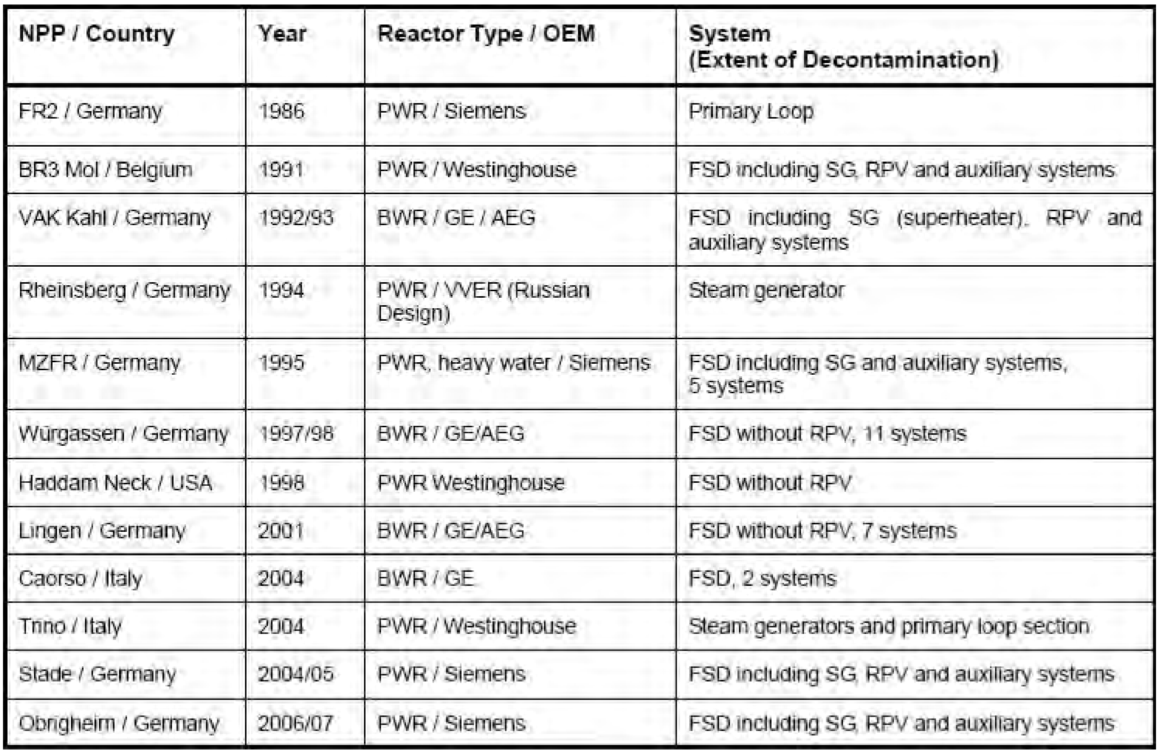
The CORD family of processes has been widely applied in full system decontaminations, component decontaminations as well as in decommissioning campaigns (see Table 2 and Table 3). In general the decontamination factors for CORD family processes have been rather high, from few tens to several thousands using only the base HP/CORD UV process and depending to some extent on the power plant application.

Table 2.References for CORD family of processes for decontaminations in operational plants. [21]



NPP	Country	Year	Reactor Type / Net Power		OEM
Oskarshamn 1	Sweden	1994	BWR	442 MWe	ABB
Loviisa 2	Finland	1994	VVER	445 MWe	AEE
1 Fukushima 3	Japan	1997	BWR	760 MWe	GE/Toshiba
1 Fukushima 2	Japan	1998	BWR	760 MWe	GE/Toshiba
1 Fukushima 5	Japan	2000	BWR	760 MWe	GE/Toshiba
1 Fukushima 1	Japan	2001	BWR	460 MWe	GE/Toshiba

Table 3. Usage of CORD family processes for decontamination prior to decommissioning [21].

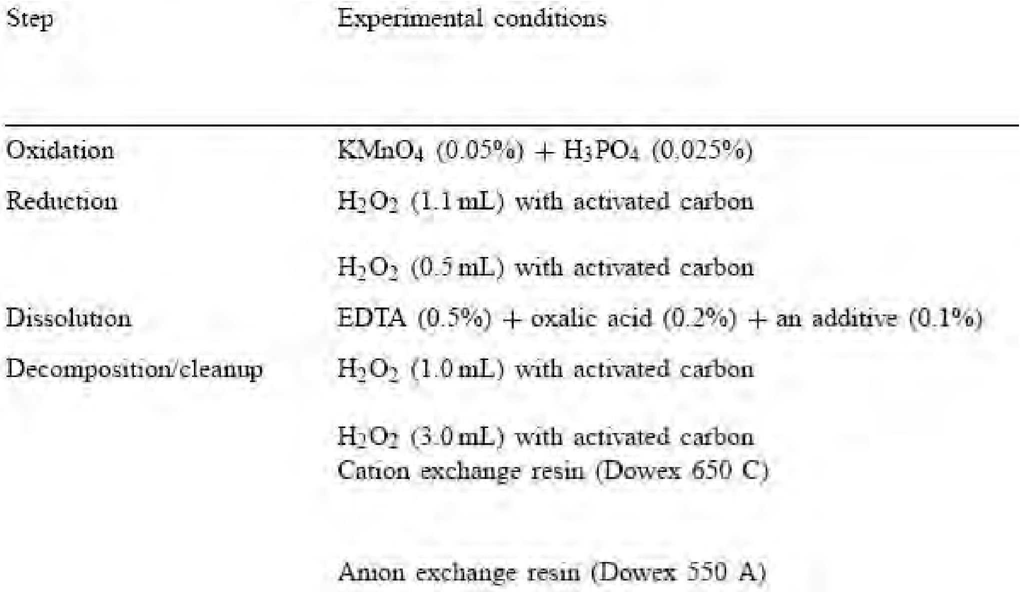


NPP / Country	Year	Reactor Type / OEM	System (Extent of Decontamination)
FR2 / Germany	1986	PWR / Siemens	Primary Loop
BR3 Mol / Belgium	1991	PWR / Westinghouse	FSD including SG, RPV and auxiliary systems
VAK Kahl / Germany	1992/93	BWR / GE / AEG	FSD including SG (superheater), RPV and auxiliary systems
Rheinsberg / Germany	1994	PWR / VVER (Russian Design)	Steam generator
MZFR / Germany	1995	PWR, heavy water / Siemens	FSD including SG and auxiliary systems, 5 systems
Würgassen / Germany	1997/98	BWR / GE/AEG	FSD without RPV, 11 systems
Haddam Neck / USA	1998	PWR Westinghouse	FSD without RPV
Lingen / Germany	2001	BWR / GE/AEG	FSD without RPV, 7 systems
Caorso / Italy	2004	BWR / GE	FSD, 2 systems
Trino / Italy	2004	PWR / Westinghouse	Steam generators and primary loop section
Stade / Germany	2004/05	PWR / Siemens	FSD including SG, RPV and auxiliary systems
Obrigheim / Germany	2006/07	PWR / Siemens	FSD including SG, RPV and auxiliary systems

4.1.5.1 Modifications to CORD processes and processes resembling to it

The main reason for the modifications of e.g. HP/CORD UV has been that this process is tightly patent restricted and the storage and transportation of permanganic acid seems to be difficult. One of the many modified versions of the CORD process has been developed for Korean PWRs [22]. As seen in the table below, the main differences in this procedure compared to the HP/CORD process are that in the oxidation stage $KMnO_4$ together with phosphoric acid have replaced permanganic acid. On the other hand, in reduction only H_2O_2 with activated carbon have been used instead of oxalic acid. The actual decontamination step contains not only oxalic acid but also EDTA and an additive, the roles of which in the process have not been, however, clarified. Temperature for the whole process is 85°C, i.e. ten degrees lower than in the HP/CORD process, and the duration of the whole process ca. 24 hours.

Table 4. Korean modification of the CORD process [22].



Step	Experimental conditions
Oxidation	$KMnO_4$ (0.05%) + H_3PO_4 (0.025%)
Reduction	H_2O_2 (1.1 mL) with activated carbon
	H_2O_2 (0.5 mL) with activated carbon
Dissolution	EDTA (0.5%) + oxalic acid (0.2%) + an additive (0.1%)
Decomposition/cleanup	H_2O_2 (1.0 mL) with activated carbon
	H_2O_2 (3.0 mL) with activated carbon Cation exchange resin (Dowex 650 C)
	Anion exchange resin (Dowex 550 A)

HOP method

Japanese decontamination approach, based on rather similar treatments as CORD and developed in FUGEN nuclear power station, is called the HOP technique [23]. In FUGEN several decontamination campaigns have been performed during the years. In 1989 and 1991 decontamination was performed by a reduction method using a reducing agent KD-203 (composition has not been given), which lead to significant reduction in radiation levels and average DFs of 3.4-5.1 [24]. However, after one year of operation, activity had built up again to approximately 70% of the pre-decontamination level. Long term hydrogen injection had been used in FUGEN as a countermeasure for stress corrosion cracking. This injection had raised the Cr concentration in the oxide films so it was considered unfeasible to achieve high DF by means of the reduction method. Therefore the HOP method (hydrazine, oxalic acid and potassium permanganate) was introduced. In the HOP method sequential oxidation and reduction steps are used to dissolve first Cr-rich layer and then Fe-Ni rich layers. Oxidation is performed using potassium permanganate with the concentration of 500ppm, (in CORD permanganic acid is used at this step) and the reduction using 200ppm oxalic acid and hydrazine to set pH to 2.5. Otherwise the project is almost identical to CORD processes. The DFs obtained with this method varied between 3 and 20 depending on the component decontaminated.

NPOX decontamination system

Archibald et al. [25] have developed a modification called the NPOX process. The NPOX system uses more common chemicals than HP/CORD UV and is a hybrid of many decontamination processes that use nitric acid, potassium permanganate, oxalic acid, ion-exchange resins, and ultraviolet light with hydrogen peroxide to achieve the desired decontamination, removal of the radionuclides from solution, and destruction of the remaining solution components. For example, the oxidation step can be conducted using any of several strong oxidizing compounds, mixtures of strong oxidizing compounds, or electrochemical methods. Archibald et al. used nitric acid/potassium permanganate solutions in this process. However, according to them, perchloric acid, nitric acid/potassium periodate, or permanganic acid solutions could just as easily have been used. Similarly, oxalic acid is only one of several organic acids that could be used for the reductive step. Tartaric acid and citric acid are two others that could work well.

As there are numerous reactions that oxalic acid participates in, it is necessary to control its concentration to achieve the desired result. Excess permanganate in the system without excess oxalic acid will result in the formation of MnO_2 precipitate that will potentially absorb other metal species, plug system hardware, and deplete the solution of oxalic acid needed to solubilise the scale on the parts to be decontaminated. With excess oxalic acid, the MnO_2 dissolves alleviating some of the aforementioned problems; however, the metal solubility increases making it more difficult to remove them in the cation-exchange columns. Alternatively, the oxalic acid is destroyed *in situ* by one of two methods. Permanganate may be added to destroy the oxalic acid after the oxalic acid has had sufficient time to dissolve the scale. Another method for the oxidization of oxalic acid is the use of ultraviolet light. This operation uses peroxide or peroxide with an iron catalyst to destroy the oxalic acid.

Archibald et al. found out in the tests that use of the NPOX process without ultrasonics resulted in 95% removal of the cesium and 80% removal of zirconium from the SIMCON II coupons (i.e. steel coupons containing a coating of cesium and zirconium oxide), However, use of the NPOX system with ultrasonics resulted even in 100% removal of both the Cs and Zr.

4.1.6 LOMI technology (<u>L</u>ow-<u>O</u>xidation-state <u>M</u>etal <u>I</u>on)

LOMI technology has been developed for EPRI in the early 1980's [26-29]. The main decontamination techniques used before LOMI had been alkaline permanganate treatment followed by a mixture of oxalic and citric acids and the so-called CAN-DECON™ treatment employing low concentrations of complexing organic acids (see Chapter 4.1.7). The alkaline permanganate treatment had two main drawbacks: it lead to a very large volume of radioactive effluent requiring a sizeable facility for handling and due to the aggressive chemicals used some material compatibility uncertainties existed. On the other hand, the CAN-DECON™ treatment employed low concentrations of organic acids that dissolved BWR crud only slowly and PWR crud hardly at all. The main objective for developing LOMI technology has been to obtain a technique that is more efficient but produces less waste and reduces corrosion problems in comparison to earlier techniques.

In the LOMI technique the oxide formed on a construction material is dissolved by reducing the iron in the oxide from trivalent to divalent and binding the divalent Fe with an appropriate ligand to keep the Fe ion in the solution. The challenge in the technique development has been to find out appropriate chemicals on both BWR and PWR oxides as well as for deposited and grown-on oxides.

Already at an early stage of the development it was found out that the LOMI process is more easily developed for BWR oxides than for the PWR oxides due to the high concentrations of Cr(III) PWR oxides. Therefore the development of the LOMI process has been done mainly for BWRs, even though some tests for PWRs have also been performed.

Typical conditions for the decontamination using the LOMI technique are:

V^{II} (the reducing agent)	$2\text{-}4 \times 10^{-3}$ M
Picolinic acid	$1\text{-}2 \times 10^{-2}$ M
Formate	$1\text{-}2 \times 10^{-2}$ M
pH	4-5
Temperature	80-90°C
Process duration	Up to six hours

The key chemical in LOMI is the vanadonous picolinate solution. The V^{II} can be manufactured for example by dissolving $VOSO_4$ in H_2SO_4. The reaction sequence in the decontamination is the following.

$$Fe^{3+}(\text{oxide}) + V^{II}(\text{pic})_3^- \rightarrow Fe^{2+}(\text{oxide}) + V^{III}(\text{pic})_3$$

i.e. vanadonous picolinate reduces Fe^{3+} in the oxide producing Fe^{2+}, which is unstable in the oxide lattice and will be transported to solution:

$$Fe^{2+}(\text{oxide}) + 3\ \text{pic-} \rightarrow Fe^{II}(\text{pic})_3^-.$$

The rather low pH of a value 4-5 is needed to ensure solubility of V^{II}. The low pH also calls for extra picolinic acid in the solution to ensure Fe^{2+} solubility.

The reason for adding formate in the solution is that it prevents the attack on the V^{II} by oxidising radicals formed in water radiolysis ($H^{\bullet}$,$OH^{\bullet}$, $HO_2^{\bullet}$, H_2O_2).

4.1.6.1 Preoxidation and corrosion aspects

As mentioned above, the typical LOMI process is not suitable for PWR oxides as such. The V^{II} as a reducing agent is not able to reduce chromium based oxides due to the fact that the redox potential of V(III)/V(II) couple complexed with picolinic acid is -0.41 V_{SHE}. This is almost equal to the redox potential value of the uncomplexed Cr(II)/Cr(III) system in aqueous solution. In the oxide lattice the redox potential of this system is apparently slightly lower since the vanadium has insufficient thermodynamic reducing power to reduce Cr^{3+} to Cr^{2+} in that system. Thus oxides containing significant amounts of chromium are immune to attack by the vanadonous picolinate system.

This finding has lead to e.g. separate investigations concerning the dissolution of chromium using chromous-based LOMI reagents (e.g. $Cr^{II}(EDTA)^{2-}$) instead of the expensive vanadonous picolinate. However, the competing reaction of the reagent with water complicates the usage of this reagent. According to investigations performed in Hungary (Paks NPP), by experimenting with the V(II)/Cr(II) ratio the dissolution of the magnetite oxide film can be catalysed to some extent [30]. However, the kinetics of the dissolution reactions of magnetite is still not clear.

As the replacement of decontamination chemical in LOMI has turned out to be difficult, the solution has been the development preoxidation processes before the LOMI decontamination step. As an outcome from this development several different options based on dilute acid permanganate / citric oxalic acid (CITROX), the NP-LOMI (NP: nitric acid and potassium permanganate) process and the AP-NP-LOMI (AP: alkaline permanganate followed by NP) process have been presented for decontaminating systems which contain chromium rich oxides.

The dissolution of Cr(III) and MnO_2 by the NP or AP solvents is as given in Chapter 4.1.4. Although NP and AP are non-regenerative solvents, the oxalic acid rinse is regenerative by passing the solvent through cation exchange resin during the process to remove the Mn and most other dissolved metals and radionuclides. The extensive development work has led to the following conclusions about preoxidation [28]:

- vanadonous picolinate / formate LOMI reagents are suitable as such for iron-rich oxides.
- NP-LOMI is used with high chromium oxides on stainless steels.
- Also NP-CITROX can be used for stainless steels.
- AP-LOMI is the process usable for high-chromium oxides on Inconel 600 and
- AP-NP-LOMI for mixed-alloy systems containing high-chromium oxides.

Decontamination factors for the reagent combinations have been [28]

	Stainless steel	Inconel 600
• NP-LOMI	10-20	1.5-3
• AP-LOMI	2-10	2-4
• NP-CITROX	5-10	1.5-3
• AP-CITROX	2-5	2-4
• AP-NP-LOMI	-	4-8

The usage of many different chemicals in removal of oxides has raised concern whether the base metal is exposed to different forms of corrosion immediately after decontamination. The corrosion sensitivity has been studied using prefilmed type 304 stainless steel and Inconel 600 samples in autoclaves in simulated BWR and PWR conditions. Summarising, none of the treatments appeared to increase the SCC susceptibility of sensitised, or solution-annealed, type 304 stainless steel or Inconel 600. The combination of a preoxidation treatment, followed by a LOMI treatment, was needed to completely remove the prefilm. The uniform metal penetration during decontamination was slight. Post-decontamination exposure to simulated reactor conditions appeared to repassivate both the stainless steel and Inconel 600, including the superficial pits on the Inconel 600 that formed during several of the decontamination processes.

As an example of using different LOMI-family processes can be mentioned the decontamination campaign run at Browns Ferry BWR Unit 1 in the U.S. [31]. The power plant unit was taken into use again after 17 years from the shutdown. At this plant reactor systems were decontaminated by using e.g. LOMI, NP-LOMI and NP-CITROX processes. The LOMI process was also used in the Monticello Nuclear Generating Plant (BWR), where this process was found to reduce the radiation fields in the two recirculation loops by factors ranging from approximately 4 to 60 [32]. Recontamination after LOMI and NP-LOMI treatments has been studied in Winfrith BWR [33]. Inconel 600, AISI 304 and Zircaloy-4 samples were exposed to primary coolant for 75 days after which they were decontaminated using either LOMI or NP-LOMI techniques. Good decontamination factors were obtained on stainless steel but on Inconel decontamination was less effective. Recontamination was allowed to happen during 148 days exposure to primary coolant. The main finding was that recontamination of stainless steel increased up to predecontamination levels and material treated with LOMI alone exceeded predecontamination levels. Thus decontamination on stainless steel surfaces using these techniques was concluded to offer only a temporary remedy, dose rates rapidly returning to predecontamination levels in step with the formation of a new oxide film.

One of the main disadvantages of NP/LOMI (and also CITROX, see below) technique is that this process produces more waste than other mostly used processes. An extensive set of results obtained with different LOMI processes in power plant artefact tests is given in ref. 17.

4.1.6.2 CITROX processes

CITROX processes are in many references included in the “LOMI-family” of processes. However, the development of this process has been done separately from the conventional LOMI processes, but with rather similar process parameters. Typically the CITROX process contains also the AP (or NP) step to pretreat the surface with permanganate solution. A typical composition of the AP solution is 10wt% sodium hydroxide and 3wt% potassium permanganate. The AP step removes most of the Cr-51 as well as small amounts of Mn-54, Co-60, Co-58 and Fe-59. The AP solution is usually applied for 4 hours at 90^{o}C. [34, 35]

After AP the surfaces are rinsed usually with hydrazine and boric acid after which the actual CITROX process takes place. The rinsing is continued until the pH of the rinse falls below 10. All of the AP solution must be rinsed from the system as it will react with the chemicals in the actual CITROX step reducing the effectiveness of decontamination [34].

CITROX contains a combination of organic chelating agents and acids (2.5 wt% oxalic acid, 5wt% dibasic ammonium citrate, and 2 wt% ferric nitrate). Diethylthiourea, 0.1 wt%, may also be added as a corrosion inhibitor when using CITROX with carbon steel systems. Also ferric nitrate can be used as a corrosion inhibitor [34, 35]. Organic acids dissolve and complex the corrosion products and the chelating agent chemically binds the released or dissolved corrosion products. The concentration ratio of oxalic acid to dibasic ammonium citrate must be less than or equal to 0.5 to prevent secondary film formation. This is important because citrate ions complex iron and inhibit the formation of an oxalate precipitate. The formation of a precipitate film could interfere with subsequent exams. Ferric nitrate, ferric sulphate and diethylthiourea are often used as corrosion inhibitors to prevent pitting of carbon steel surfaces. CITROX is usually applied for ca. eight hours at 80^{o}C. [34]

The flow rate of the decontamination solution during the AP-CITROX process has been observed to affect the decontamination effectiveness [36]. The studies performed in Hungary have indicated that by increasing the flow rate from the average normal value of 0.5 m/s to values close to 3 m/s the effectiveness of the process is significantly increased. On the other hand, during the re-passivation of the stainless steel surfaces the flow rate should be kept as low as possible.

CITROX process has been also applied in a dilute version with 0.1% AP solution and 0.25% PNS CITROX solution (PNS = Pacific Nuclear Services) [37]. Dilute solutions enable the use of multistep treatments. However, multistep treatments may result in significant degradation of IGSCC resistance on stainless steels, which may be due to the presence of excessive dissolved iron in the CITROX solution. On the other hand, it has been also reported that the AP-CITROX decontamination procedure, performed even in three consecutive cycles, does not exert detrimental corrosion effects, but rather substantially improves the passivity of the surface oxide-layer and increases the surface roughness on austenitic stainless steel 08X18H10T [38]. Moreover, reducing decontamination solution of citric acid and EDTA have been found to be reasonably effective in decontaminating nickel-free Type 410 stainless steel, but a process involving preoxidation with alkaline permanganate solution before dissolution with oxalic acid was required for the Types 316 and 316L stainless steels. In addition, if Zn additives are used in the BWR coolant, the austenitic steels become considerably more difficult to be decontaminated [39].

Another modification of the CITROX process is so-called OPG-AP-CITROX process that was developed for post-accident chemical decontamination mainly for TMI-2 [40]. The OPG solvent is composed of oxalic acid, sodium oxalate, gluconic acid, sodium gluconate and boric acid and it is used in the presence of hydrogen peroxide. The role of the sodium gluconate – gluconic acid solution combination is that it buffers the solution and prevents decomposition of hydrogen peroxide in systems where large metallic surfaces are present as well as increases complexing capacity of the solvent. OPG has been successfully used as part of the decontamination process for recovery of systems that have been contaminated with uranium fuel. The OPG-AP-CITROX process has been tested either in concentrated form at 40^{o}C or in a dilute form at 80-95^{o}C. There seemed not to be noticeable differences in effectiveness between these two forms of the process. However, a dilute process is cheaper to use as the waste processing costs are lower. The OPG-AP-CITROX solvent has shown satisfactorily low corrosion rates on materials typical of those at TMI-2 and has been found to be effective at removing corrosion-product radioisotopes from sample surfaces.

Despite of many good results obtained with CITROX processes, a replacement for this process has been studied especially in Czech Republic and Slovakia. [41] Due to some negative effects observed in material behaviour after CITROX decontamination, the so called AP/NP- NHN process has been applied to decontaminate primary circuit parts of Russian type reactors VVER 1000/440. The abbreviation proprietary NHN comes from mineral acid + reduction agent + complexing agent combination (the exact composition is not given). Decontamination efficiency of the new procedures AP/NP-NHN together with their practical applicability were verified at NPPs EDU, ETE (Czech Republic) and EBO, EMO (Slovak Republic). In pilot plant decontaminations comparable or higher DF was achieved using AP/NP-NHN solutions than using the AP-CITROX procedure (ca. 44 for NHN vs. 16 for CITROX. It was found that the use of the alkaline oxidation (AP) was better than acidic oxidation (NP) as the primary circuit internals often are soiled by greases and graphite. Values of the average DF over 100 were achieved after 2 cycles of the AP-NHN decontamination application on the main circulation pump internals at the NPP Temelin during standard decontamination services.

4.1.7 CAN-DECON™ and CAN-DEREM™

(AP/)CAN-DECON™

CAN-DECON™ process [42-45] was originally developed in Canada by AECL and was used for deuterium uranium-pressurised heavy water reactors (CANDU-PHWRs) and later BWRs and PWRs. CAN-DECON™ process is often used with alkaline permanganate (AP) treatment.

Typical conditions for the decontamination are: 85-125°C, 0.1-0.2 wt% LND-101A reagent concentration, pH = 2.7 – 2.8, duration 24-36 hours. Furthermore, ferric ion (50-500 ppm) and some other chemicals can be used as corrosion inhibitors. The key factor in the CAN-DECON™ process is the decontamination chemical LND-101A (in some references mentioned also as LND-101 and LND-104), the chemical composition of which is mentioned in ref. 46 to be EDTA + citric acid + oxalic acid with a molar ratio 2:1:1. CAN-DECON™ has undergone extensive testing to determine the degree of corrosion of construction materials of reactor components, especially intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC). Tests have indicated that the CAN-DECON™ process does not contribute significantly to the general corrosion of BWR system components. The corrosion test data has shown that carbon steels are the most susceptible to such corrosion. Nonsensitized specimens of BWR materials (especially stainless steel 304) show no increase in susceptibility to IGSCC as a result of decontamination with this technique. However, sensitized BWR materials exposed to 500-h treatments have shown a significant increase in IGSCC when the solvent contained no ferric ions. For example, in the tests performed at the Maanshan NPP in Taiwan IGA on sensitized 304 after the four-step AP-CAN-DECON process has been observed [46]. In the presence of 50-80 ppm ferric ions, BWR and PWR materials have not shown any evidence of IGA. Therefore the presence of ferric ions during the decontamination with the CAN-DECON™ process is a necessity [42-45].

(AP/)CAN-DEREM™

The AP/CAN-DEREM™ (Canadian Decontamination and Remediation process) consists of several consecutive steps: dissolution of iron oxide with organic acids using citric acid and EDTA (ethylenediaminetetraacetic) as chelating agent (CAN-DEREM™ step) and, oxidation and dissolution of the chromium with an oxidizing alkaline permanganate followed by a rinse step using dilute oxalic acid (AP step) [47]. The main difference between CAN-DECON™ and CAN-DEREM™ processes is that CAN-DEREM™ does not contain oxalic acid as the acid has been found to increase the susceptibility to IGA/IGSCC on sensitised stainless steels [48]. AP/CAN-DEREM™ process has been used e.g. at Indian Point 2, where the systems decontaminated were: the entire primary reactor coolant system (RCS) with fuel removed, residual heat removal system (RHR), chemical and volume control system (CVCS), portions of the primary sampling system. The process used was a five-step combination of the CANDEREM and AP processes in the order CANDEREM-AP-CANDEREM-AP-CANDEREM [14].

Altogether, CAN-DECON/CAN-DEREM processes had been used in either full system (CANDUs) or subsystem (BWRs/PWRs) decontaminations ca. 40 times by the year 1992 [49].

4.1.8 Short comparison between LOMI processes, CAN-DECON™ and HP/CORD UV

The decontamination "network" for LOMI, CAN-DECON™ and HP/CORD UV is shown in Figure 6. LOMI and CAN-DECON™ processes have been originally licensed to PN-Services (nowadays a part of Westinghouse). On the other hand, Siemens as a developer of the CORD processes has also had a license to CAN-DECON™ and LOMI.

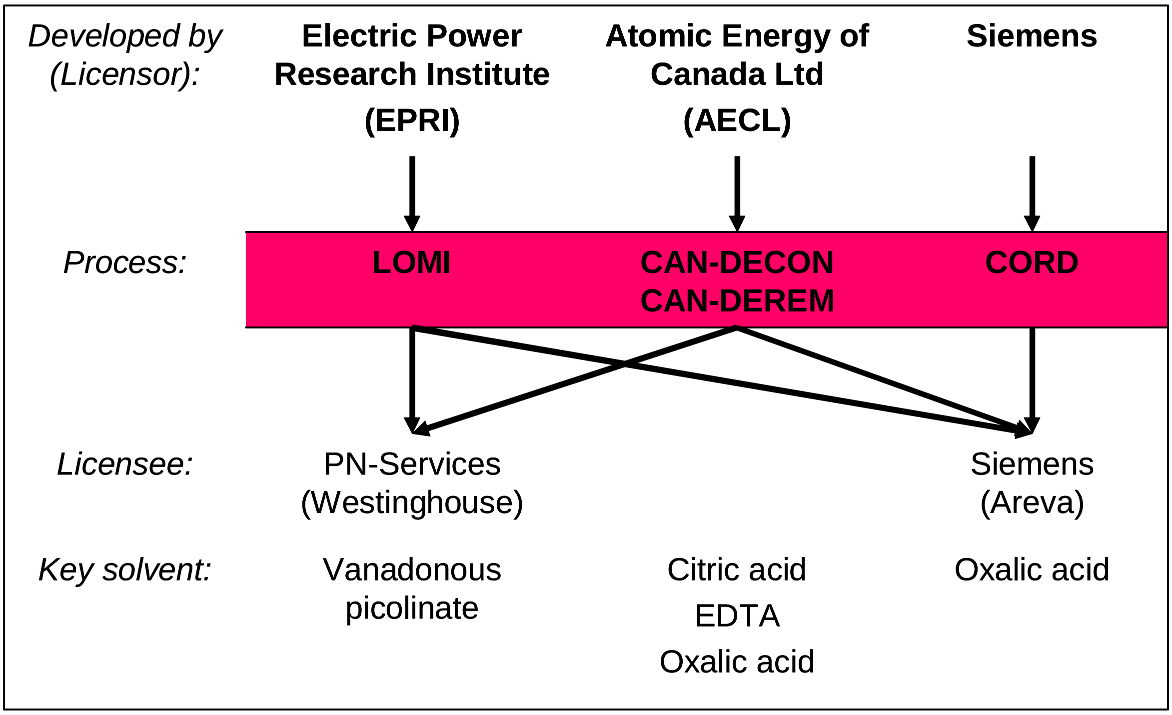


Figure 6. Decontamination "network" for LOMI, CAN-DECON™ and HP/CORD UV

Table 5 summarises briefly the main advantages and disadvantages of LOMI, CAN-DECON™ and HP/CORD UV.

A common feature for all three processes is that they all require several cycles (usually three) to accomplish the decontamination, which is due to low chemical concentrations and high Cr content oxides especially in PWR and WWER environments.

From the chemical point of view the main difference between these three processes is that LOMI and CAN-DECON™ use complexing agents in decontamination whereas in HP/CORD UV only oxalic acid is used (see Figure 4).

Other main difference between these techniques is that the permanganic acid preoxidation in HP/CORD UV is advanced in whereas for LOMI and CAN-DECON™ especially the AP preoxidation has been to some extent problematic. This has led to a search of more advanced preoxidation (e.g. NP or ozone) increasing the costs of the processes. Also, there is a noticeable difference in waste volumes; HP/CORD UV process produces waste the least. This is a remarkable benefit for the process as it decreases the costs noticeably.

When the CAN-DECON™ has been compared with the LOMI processes using BWR fuel and core materials it has been found that LOMI-treated specimens show low general corrosion and no IGA or pitting, and no increase in IGSCC susceptibility or corrosion attack on samples with crevices [50-52]. CAN-DECON™ treated specimens, on the other hand, indicate formation of shallow pits on creviced specimens. In some studies CAN-DECON™ has been observed to cause intergranular attack on stainless steels (see above) and some fuel bundle components fabricated from Inconel X-750 [53]. Furthermore, the CAN-DECON™ process seems to remove more metals than the LOMI process. The IGA sensitivity is to some extent also a risk with HP/CORD UV.

The main difference between the processes is, however, that HP/CORD UV is not qualified for the U.S. markets. This limits the commercial impact of the process and gives a huge benefit for the other two processes.

Table 5. Comparison between LOMI, CAN-DECON™ and HP/CORD UV

ADVANTAGES / DISADVANTAGES		
LOMI	**CAN-DECON**	**HP CORD UV**
High DFs if Fe_3O_4 surface	Moderate DFs	Moderate DFs
	No oxalate formation	Oxalate formation a risk
Solution must be O_2 free →risk for application error →equipment cost	No advanced preoxidation available	Advanced preoxidation step $HMnO_4$ (patented)
Qualified in the US	Qualified in the US	Not qualified in the US
The key chemical is expensive		
Waste volume large	Waste problem due to preoxidation	Waste volume small
If AP enhanced →MnO_2 formation	MnO_2 formation is a risk IGA sensitivity if no ferric ions used	IGA sensitivity
Modification of AP has not been successful		

An interesting practical comparison especially between LOMI and CAN-DECON™ processes has been made for Three Mile Island Unit 2 (TMI-2) coolant system decontamination [35]. A total of seven different chemical decontamination processes were subjected to laboratory screening tests. Cleanup of the TMI-2 reactor coolant system was more difficult than routine PWR decontamination because the system was contaminated by both radioactive fuel and radioactive corrosion products. The investigated techniques and observed results were:

Table 6. Comparison of decontamination techniques for TMI-2 coolant system decontamination [35].

Technique	**Key process parameters**	**Results**
AP-CITROX	CITROX: diammonium citrate, oxalic acid, ferric nitrate, diethylthiourea, (boric acid)	Fair performance in uranium oxide dissolution and good DF. Slightly higher redeposition than most other processes (primarily associated with carbon steel surfaces), but acceptable. Effectiveness enhanced somewhat by borate addition.
AP-ACE	ACE: diammonium citrate, EDTA, diethylthiourea	Lowest DF for stainless steel tube specimens of all solvents tested. The process was detrimentally affected by borate addition. Fairly high redeposition rate in the presence of borates.
OPG-AP-CITROX	OPG: oxalic acid, sodium oxalate, gluconic acid, sodium gluconate, hydrogen peroxide, 8-hydroxy quinoline, (boric acid)	Adding the OPG step to the AP-CITROX process greatly enhanced uranium oxide dissolution performance and DF. Redeposition was acceptable in the presence of borates, but marginally high without borate. Performance was enhanced by borate addition and was overall the most effective of the seven processes tested.
PBC-AP-CITROX	PCB: sodium carbonate, sodium bicarbonate, hydrogen peroxide, 8-hydroxy quinoline, boric acid	Uranium dissolution good and DF for stainless steel superior to all other processes tested. However, DF for Inconel is low and redeposition rates are high if borates are not added. High redeposition and rapid decomposition of the PBC solvent which caused foaming and off-gassing problems during application.
CAN-DECON	LND-101A, boric acid	Low uranium oxide dissolution performance. Good DFs at least in the presence of borates. Low redeposition.
LOMI-NP-LOMI	see section 0	Low uranium oxide dissolution. Moderate DFs. Low redeposition.
NS1-AP-NS1	DOW NS-1: chelant, inhibitor, boric acid	Process was affective and produced acceptable redeposition. However, the process is slow and requires high application temperature (124°C)

Three of these seven chemical decontamination processes performed particularly well and were selected for further evaluation: The most effective method, OPG-AP-CITROX, combined two of the processes tested – an alkaline permanganate-citric acid/oxalic acid (AP-CITROX) process and an oxalic acid, hydrogen peroxide, and gluconic acid (OPG) solvent. The addition of the OPG solvent greatly enhanced uranium oxide dissolution and increased the effectiveness of decontamination. Redeposition of radioactive material on cleaned surfaces remained at acceptable levels in the presence of borates but was marginally too high without borates.

The CAN-DECON™ three-step process resulted in poor uranium oxide dissolution, effective decontamination in the presence of borates, and low redeposition of radioactive materials.

The third “acceptable” process, LOMI-NP-LOMI, produced poor uranium oxide dissolution, moderately effective decontamination, and low redeposition of radioactive materials. None of the solvents, with or without borates, produced any detrimental corrosion in the construction materials tested.

4.1.9 Other chemical decontamination processes

Except for the techniques presented above also some other chemical decontamination techniques exists. Their commercial impact is, however, low and they have not been as widely applied as LOMI, CAN-DECON™ or HP/CORD UV.

4.1.9.1 Dilute concentrate decontamination (DCD)

Dilute chemical decontamination techniques use dilute solvents (i.e. concentrations of solvents <1 wt%). They were extensively studied by Battelle, Pacific Northwest Laboratories in the late 1970’s and the early 1980’s [54-56]. The above mentioned commercially more important decontamination techniques can be included in the DCD techniques but they are usually treated separately even though several similarities between techniques exist.

There have been mainly two reasons to develop the DCD techniques: (1) The dilute processes could be used frequently and they do not necessarily claim for so many preparatory measures (reactor modifications) as “hard” decontamination with concentrated solvents. (2) The waste disposal after the dilute process is less expensive and easier to take care of than when using concentrated solvents. Since many chelants are composed of carbon, hydrogen and oxygen, they can be destroyed by oxidation to produce carbon dioxide and water.

However, it was recognised that dilute techniques are not to be used for fuel crud removal and they do not remove oxides totally but leave behind to some extent passivated surfaces. Decontamination factors will be much lower, decontamination times longer and process temperatures higher with dilute techniques in comparison to concentrated ones.

In a dilute chemical decontamination process that is operated in the regenerative mode, the ion-exchange resin is used for regenerating the exhausted formulation. Hence, the amount of decontaminating chemicals required in a DCD process operated in regenerative mode is several times lower than that stoichiometrically required for the dissolution of the oxide inventory present in the system. Dilute chemical decontamination methods are preferred over other techniques because of their effectiveness in removing the undesirable radioactivity at a minimum corrosion loss to the structural materials. Also, the process generates only solid radioactive wastes, mostly in the form of ion-exchange resins that are used to collect the radioactive and inactive metal ions released from the surfaces and to collect the injected chemicals. [57]

Battelle laboratories developed dilute techniques mainly for Canadian reactors and therefore the techniques have not been so widely applied as such in LWRs. They made separate studies for both BWRs [55] and PWRs [56] using both laboratory and plant samples. For BWRs the dilute processes consisted of either pure chelants (EDTA, HEDTA, NTA) or of chelants with ammonium citrates and oxalates. In case of PWRs chelating agents have been used with or without organic acids, chromous iron, reducing agents (e.g. vanadonous ion and hydrazine) or PWR coolant additives (lithium, boron). In BWR environments acceptable decontamination rates were obtained with almost all used solvents. The main disadvantages, however, were that some of the solvents turned out to be too corrosive or strong complexing agents. Furthermore, the reaction mechanisms are poorly known and only little experience on in-reactor use of these chemicals exists. In PWR conditions some solvents gave slow dissolution rates of Cr-rich PWR oxides and some solvents resulted in formations of particulates. The latter point is essential to be taken into account when using these techniques as the particulates may redeposit on surfaces and their removal from the used decontamination solutions claim for effective filtration. This consequently increases the cost of the decontamination.

EDTA is the most often used of all organic chelating agents used in decontamination. EDTA is well known for its efficiency in dissolving the corrosion product oxides and removing the radionuclides from the metal surfaces in comparison to other reagents. However, it suffers from some disadvantages when it is used in dilute chemical decontamination processes operated in regenerative mode. Its removal on a strong-acid cation exchange resin, especially in the heavy water medium, results in large variation in its concentration during the regeneration stage of the process. In addition, corrosion product metal ions other than Fe^{2+} form relatively strong complexes with EDTA, thereby disfavoring their transfer to and retention on the cation exchange resin. Thus, regenerability of EDTA is poor when metal ions such as Ni^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} are expected to be released in significant concentrations. EDTA is also known to suffer from the disadvantage that it requires relatively large volumes of anion exchange resin for its removal from the solution. One positive aspect of EDTA is that as positively charged complexes its complexes formed with Co^{2+} and other metal ions are not removed by cation exchange resin. [57]

As another example of organic chelants studied, HEPDA (1-hydroxyethane-1,1-diphosphonic acid) combined with a strong reducing agent such as sodium formaldehyde sulfoxylate (SFS) can be mentioned [58]. This specific chemical combination was studied because for many other chemicals the attack of the chemical on the substrate metal is known to increase waste volume, reduce solvent utilization, and compromise the integrity of the equipment and facilities. HEDTA was found to be effective in rapidly dissolving goethite, hematite, and magnetite-based scales. Dissolution of spinel oxides is more difficult and requires longer contact times and, perhaps, single-electron reductants. Dissolution of surface oxides from actual steels was demonstrated for both carbon steel and Type 347 stainless steel. The carbon steel was easily cleaned in a few minutes by using dilute HEDPA at 50°C. With a decontaminant of 1.0 M HEDPA and 0.005 M SFS, only the matte finish of the Type 347 stainless steel could be removed; the associated decontamination factors are 1 to 28, depending on the radionuclide. Increasing both the HEDPA and SFS concentrations not only removed the surface film but also surmounted the passive range of the stainless steel, resulting also in significant base metal dissolution.

NTA (nitrilo-tri-aceticacid) has been applied for example in India, where an experimental system (consisting of AISI 316 and partly carbon steel) simulating the reactor coolant system had been decontaminated after Mg-contamination [59]. NTA was applied with hydrazine at different pHs at 170°C. It was found out that carbon steel corrodes quite strongly in this decontamination solution when pH<8 whereas on stainless steel the corrosion was negligible. The oxides on both steels dissolved rapidly in a couple of hours during the decontamination and in that sense the NTA + hydrazine solution was concluded to be effective decontamination reagent.

All in all, the dilute techniques presented in references 54-59 contain very many parameters, the dependencies of which on process conditions are not properly known. It was found that almost in all cases the decontamination effectiveness of the used solvent is dependent on pH, temperature, surface roughness, etc. Therefore, no far reaching conclusions of the applicability of different dilute solvents on decontamination was made in these studies. Especially in PWRs the usage of several chemicals together at the same time seemed difficult to control (e.g. the formation of particulates in some solvents) and would indicate that more detailed investigations are required

4.1.9.2 EMMAC process

This solvent is a proprietary French process that includes oxidizing and reducing solutions. It is applied at approximately 80°C. The oxidant is NP, and the reductant is a mixture of nitric and ascorbic acids. The dissolution of Cr(III) is the same as that shown for NP above. [17]

The EMMAC process has been developed by EdF. [60] A cycle of hot treatment (80°C) includes the use of an oxidizing solution, which ensures the solubilization of the chromium then a reducing solution dissolves the residual oxide. It is nowadays used during the Replacement of Steam Generators (RSG) for decontamination of the primary system pipes end as well as for the hydraulic parts of the reactor coolant pumps. The results in terms of dose rate reduction factor have been during RSG operations as follows:

- Hot leg dose rate reduction factor from 50 to 70,
- Cold leg dose rate reduction factor around 60.

This process is specifically adjusted for stainless steel casing in the primary cooling system. When it is used to decontaminate the steam generator channel heads, the dose rate reduction factor obtained is around 5. In this case, the stainless steel surfaces account for only 5% of the total surface to be decontaminated, the rest (95%) consists mainly in nickel alloy (Inconel 600). The qualification tests have shown that the efficiency of the EMMAC process on nickel alloys is reduced. The EMMAC process is widely used in France because it is efficient with regards to the type of contamination encountered (hot fixed contamination) and the materials concerned. The chemical products used and the effluents generated are also compatible with the waste treatment systems of the nuclear plants. Westinghouse has used this process during artefact testing.

Electrochemical decontamination [15,61]

4.1.10 General considerations

Electrochemical decontamination or electropolishing may be considered in principle to be a chemical decontamination assisted by an electrical field. Electropolishing is a process widely used in non-nuclear industrial applications to produce a smooth polished surface on metals and alloys. It may be considered the opposite of electroplating as metal layers are removed from a surface rather than added as a coating. Electrochemical decontamination uses direct electric current, which results in the anodic dissolution and removal of metal and oxide layers from the component. The dissolution may be conducted by immersing items to be decontaminated in an electrolyte bath as anode or fitted with anodes. This method is useful for decontaminating items with easily-accessible surfaces. Current may also be delivered to a submerged component by moving a pad over the surface to be decontaminated, as an efficient method for regular surfaces. The electrolyte is continuously regenerated by recirculation.

Electrochemical decontamination processes may only be applied for removing radionuclide contamination from conducting surfaces, such as iron-based alloys (including stainless steel), copper, aluminium, lead and molybdenum. They are highly effective and give a high decontamination factor. Important operating parameters for electrochemical decontamination are electrolyte concentration, operating temperature, electrode potential and current density.

The effectiveness of the decontamination may be limited by the presence of adhering materials on the surface of the items to be decontaminated. Materials such as oil, grease, oxides (rust) and paint or other coatings should be removed before decontamination. The use of electrochemical decontamination is limited, when immersion is used, by the size of the bath, and when a pad is used, by the geometry of the surfaces and the available free space around the part being treated. This makes the method almost inapplicable for industrial decontamination of complex geometries (e.g. small-diameter pipes).

4.1.11 Chemical reagents

Phosphoric acid is normally used as electrolyte in electropolishing because of its stability, safety and applicability to a variety of alloy systems. Moreover, the non-drying nature of phosphoric acid helps minimise airborne contamination, and the good complexing characteristics of phosphoric acid for metal ions is a significant factor in minimising recontamination from the electrolyte. E.g. in Paks NPP in Hungary, a mixture of phosphoric acid, sulphuric acid and oxalic acid with a current density of 0.25 A/cm^2 has been used to decontaminate main circulation pumps in the 1980’s [62].

Other electrolytes, such as nitric acid and sodium sulphate have been investigated and proposed as alternatives to phosphoric and sulphuric acid. The need for new electrolytes was initially motivated by the incompatibility of phosphoric and sulphuric acids with the existing treatment facilities and the possibility of producing secondary liquid waste which is easier to process or regenerate. Today, problems associated with the treatment of secondary liquid waste have only partly been resolved. Using nitric acid (strong mineral acid) one can obtain good results on welded surfaces but is likely to generate hydrogen and nitrogen gases. It cannot be used on carbon steel and can cause fires and explosions when combined with incompatible materials.

Decontamination processes based on application of organic acids have a good pH stability resulting from hydroxide formation. Also, the destruction of organic acid component yields non-acid waste. Although organic acids are more expensive than some strong mineral acids and have slower reaction time, they are ideal for non-destructive cleaning. They do require neutralization of the pH before treating as radioactive waste.

Also totally neutral decontamination solutions (alkali metal sulphates) have been used in electrochemical decontamination as in the ELDECON process [63]. In this process the metal ions produced during dissolution of oxide and base metal precipitate as hydroxides which form sludge when the electrolyte is settled. However, Cr is dissolved in hexavalent state as chromate ions and it needs to be reduced to trivalent state before it can produce hydroxide. The reaction products from the process are oxygen gas, hydrogen gas and metal hydroxides containing the radioactive nuclides. ELDECON process has been applied at least in Sweden (in Barsebäck and Ringhals NPPs) and Finland (Olkiluoto NPP).

Electrochemical polarisation techniques are also applicable to remove selectively active isotopes from the coolant before they adsorb on unfavourable positions in the reactor. For example, Varga et al. [64] have demonstrated a laboratory test in which Co isotopes were removed from the PWR coolant by anodic polarisation that resulted in formation of Co-oxide. With this method up to 80% of the active Co could be removed within a period of 60 hours by continuous cycling in the potential range of 1.10 to 1.60 V_{RHE}.

In general, electrochemical polarisation can be also combined with almost any chemical decontamination technique. The main point to take into account is that the decontamination products are not too reactive and the waste management does not become a problem. Typically in the applications presented in literature the parameters for electrochemical decontamination have been: current density ~0.25 – 0.6 A/cm^2, DC voltage ~3- 8 V, temperature 20…90^{o}C and obtained DFs ranging from ca. 10 to several hundreds depending material and shape of the decontaminated component as well as on the decontamination electrolytes and flow rates applied. [62,65,66]

4.1.12 Secondary-waste generation

Electrochemical decontamination by electropolishing causes a steady increase of dissolved iron in the phosphoric acid. If the iron content exceeds 100 g/dm^3, precipitation of iron phosphate occurs and deteriorates the efficiency of the decontamination process. Therefore, the acid has to be exchanged or regenerated periodically. In doing so, the volume of effluents is limited; however, handling the parts to be immersed or the pad, may lead to additional exposure to workers.

4.1.13 Advantages and disadvantages of electrochemical decontamination techniques

When selecting a suitable electrochemical decontamination process, criteria must be considered in a detailed analysis based on site-specific conditions. These are similar to the general criteria for decontamination, but taking into account that electrochemical decontamination processes require conducting surfaces. Some main advantages and disadvantages of this technique may be indicated to allow selection of the most appropriate technique.

Advantages

- Electropolishing is commercially available. Major equipment is relatively inexpensive and process and processing procedures fairly simple. It is capable of decontaminating to background levels for decommissioning purposes, removing practically all radionuclides covering the surface, including plutonium, uranium, radium, cobalt, strontium, cesium and americium, giving typically decontamination factors of more than 100.
- Electropolishing may decontaminate flat areas, corners, recessed geometries, tanks, etc., where measurement up to release levels do not cause any problem. It produces a smooth polished surface with a low inherent ability to be recontaminated. The thickness of metal removed during decontamination is generally less than 25 µm.
- When compared to the volume of liquids required for chemical decontamination, electrolyte volumes for electrochemical decontamination are relatively low.

Disadvantages

- For the most widely used process (i.e. in-tank), the item to be decontaminated must be removed from the plant and immersed in the tank with electrolyte. For the in-situ process, access or entry for the device into the item to be decontaminated is required. Therefore, the use of electrochemical decontamination is limited by the size of the bath, when immersion is used, and by the geometry of the surfaces and the available free space around the part being treated, when a pad is used. This makes the method less applicable for industrial decontamination of complex geometries (e.g. small diameter pipes).
- The treatment of the electrolyte for disposal (if not recyclable) requires neutralisation and processing in a treatment system for liquid radioactive waste.
- Electropolishing does not remove (or removes with difficulty) fuel fines, sludge or any insulating material from the surfaces.
- Hidden parts as the inside of tubes are treated poorly.
- Handling of components may lead to additional exposure to workers.

5 Summary

In this literature survey the most used chemical, electrochemical and mechanical decontamination techniques have been briefly introduced. The goal has not been to rank the techniques but to get a general idea of the types of various techniques that have been used to remove radioactivity from material surfaces in nuclear power plants.

The need for decontaminating will exist as long as nuclear power is used. Even though several very extensive studies on different decontamination techniques have been done in the past (e.g. EPRI and IAEA reports), also in the future there will be an even increasing interest towards these techniques. Also the increasing decommissioning of the power plants will increase the need for effective ways to decontaminate components and systems.

From the purely mechanical techniques different water jet and ultrasonic applications are the most used techniques in nuclear power plants. Still, also the techniques that used plenty of hand tools are used especially for components that have complex geometries. The main advantages of mechanical techniques are that they are rather easy to use, easily available, inexpensive and effective. The main disadvantage is that they usually remove also the protective oxide layers and wear the material surfaces exposing them to different corrosion phenomena. Many of the techniques also claim for the presence of a person to operate the device within a close distance to contaminated surfaces and therefore increase the radiation dose.

The chemical and electrochemical techniques are more used on a system decontamination level. However, in many power plants chemical decontamination is used in separate pools for components.

The water chemistry history and the type of oxide on material surface are the determining factors for selection of a suitable chemical decontamination technique. The basic steps in chemical and electrochemical decontamination are:

(1) dissolution of Cr-rich oxide layers,
(2) dissolution of Fe- and Ni- rich oxide layers.

After repeating some cycles of these basic steps, a final repassivation of the surface may be necessary. In BWRs the removal of Cr is usually rather easy but in PWRs the Cr –rich layer may be difficult to dissolve. From a historic perspective, different oxidation-reduction techniques, based on several combinations of chemicals (e.g. LOMI, CANDECON™, HP/CORD) had been used in various modifications. Currently, the AREVA's HP/CORD process is the most often used technique worldwide (except in the U.S.). However, being a proprietary process and to some extent rather expensive, many modifications to this process have been presented in order to avoid IPR problems. Also, new decontamination processes are actively developed all the time. In general, chemical and electrochemical decontamination techniques have so many adjustable parameters (e.g. pH, temperature, concentration, flow rate) that the comparison of different techniques is rather difficult and in many cases the selection of the proper technique is based on extensive laboratory testing.

The main advantages of chemical and electrochemical decontamination are: (1) lots of information exists for different processes and the processes are commercially available, (2) processes are effective resulting to high decontamination factors and (3) chemical decontamination is applicable for complex geometries. The main disadvantages are related to high waste volumes and possible corrosion problems caused by the chemicals. In addition to these, for electrochemical decontamination one of the main advantages is that the electrolyte volumes needed are relatively low. On the other hand, the additional radiation exposure to workers is a risk during the component handling and electrolyte disposal.

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APPENDIX 1

Table 7. Advantages and disadvantages of different nonchemical decontamination methods [1-9].

TECHNIQUE	ADVANTAGES	DISADVANTAGES
Mechanical methods		
• **brushes**	• proven industrial effectiveness • readily available in a wide range of sizes, materials, and bristle stiffness • relatively inexpensive and easy to use • remove light deposits of loosely held material and scale easily and quickly • low volume of waste material • flexible enough to conform to pipe I.D. irregularities • pass through smooth bends • air- and water-driven motors are commercially available to rotate brushes on flexible shafts to clean tube and pipe I.D.'s • low labor cost	• heavy duty rotating brushes may smear the surface and, perhaps, trap some of the radioactive contamination in pits or grooves in the pipe • excessive contact time and bristle pressure can result in striation of the surface • some types of brush cleaning can be labour intensive
• **drill bits**	• clean out crud and hard scale • low volume of waste material • are commercially available	• have a fixed O.D. and thus would have only limited application in cleaning a seamless pipe • effective only for preliminary, rough cleaning of pipes or tubes that were plugged or heavily encrusted on the I.D.
• **scrapers**	• widely used for cleaning condenser and heat exchanger tubes • remove crud and hard scale as well as local growths such as tubercles • can be blown through tubes by air or water pressure at speeds on the order of 20 ft/sec • can be used to clean curved tubes • barrel-shaped scrapers will remove hard scale and corrosion from the insides of pipes • can be made to provide complete coverage of a pipe I.D • pipesavers can be used to clean long lengths (2 miles and more) of pipe in situ • most scrapers permit remote cleaning	• blown-through scrapers would be of only limited value in cleaning the inside of a pipe due to the variation of the pipe I.D. • most scrapers are not effective in removing thin, tightly adherent layers such as corrosion
• **pigs**	• pass through sharp 90° bends, e.g. crosses, and tees • pass through gate and ball valves	• require access to both ends of section to be decontaminated

	• permit remote cleaning operation • adapt to local discontinuities in pipe • can scrape or abrade pipe I.D. • provide complete coverage of pipe I.D. • low in capital and operating costs	
• **vibrators**	• remove hard scale	• of little use in removing films, crud or corrosion layers
• **cutters**	• remove dirt and hard scale • clean curved lengths of pipe • clean irregular surfaces	• would probably leave a striated surface
High-pressure water *The force of the water jet impinging on the surface of the object at velocities in excess of 400 ft/sec provides the cleaning action. Water pressure ranges from 1,000 to 20,000 psi. Chemical additives and/or an abrasive can be used to enhance the decontamination action.*	• commercially available process • adaptable to remote operation for reduced exposure • no effect on dimensional tolerances • no effect on corrosion of stainless steel unless additives are used • decontamination factors up to several hundred • adaptable for decontamination of a wide variety of pipe sizes, tanks, equipment and large planar surfaces • water can be filtered and recycled to minimize radwaste volume	• for the internal surfaces of closed systems, with no access by design, holes must be cut to permit entry of the nozzle and lance • without recycling, a large amount of contaminated water is generated • the direction of the stream of high pressure water must be carefully controlled to avoid injury to personnel • high-pressure water cleaning may not remove well-bonded or tightly adherent contaminated surface films • structural or equipment items in close proximity to a high-pressure water cleaning activity must be shielded from back-splash of contaminated water • an additional rinsing operation may be required to remove residue of chemicals that were added to enhance decontamination action
Ultrahigh-pressure water *Ultrahigh-pressure water systems are those capable of producing a water jet at a minimum of 20,000 psi and ranging upward to 60,000 psi.*	• basic equipment is commercially available • similar process applications have already been developed • adaptable to remote operation • no effect on surface of metals at usual operating pressures • good decontamination factors • able to decontaminate concrete or other materials with impregnated and tightly adhering contaminants • waste generation can be kept at a minimum by recycling waste water • can be adapted to decontaminate pipes and accessible tanks as well as planar or curved surfaces (floors, walls, etc.)	• for internal surfaces of pipes or tanks significant access must be available • care in design and operation must be taken to capture all the particulate matter removed • capital investment in this type of equipment is quite high

Abrasive cleaning		
• **air abrasive blasting** • **swirling air flow dry abrasive cleaning** *A high velocity jet of compressed air, about 1,100 ft/sec, into which is fed a stream of particles of an abrasive material .In dry abrasive cleaning a swirling flow of air propels abrasives along an inside surface of a pipe.*	• proven effectiveness • equipment is well developed and is commercially available • gives good decontamination factors • remove tightly adherent material including corrosion • equipment is available for remote cleaning • can be used to clean the insides of tanks and pipes • dry methods decrease the amount of waste	• difficult to control the amount of base metal removed • other than dry methods produce a large amount of waste • resulting rough surface is conducive to recontamination • requires careful control to prevent spread of contamination
• **vacuum blasting** *A modification of air abrasive blasting for in place use, wherein the discharge nozzle is surrounded by a concentric hood.*	• method is well developed and equipment is commercially available • produces only a small amount of uncontrolled dust • good method for in situ decontamination of concrete surfaces • permits recycling of abrasive	• equipment is bulky and awkward to handle • produces some atmospheric pollution • generates a large amount of waste • primarily applicable to flat surfaces
• **water abrasive blasting** *Water is used at a high pressure, asmuch as 5,000 to 10,000 psi. The water issues from a jet and is mixed with particles of the abrasive material.*	• permits close control of amount of surface material removed • removes tightly-adhering material and corrosion layers • produces no atmospheric pollution • relatively small amount of solid waste produced compared with air abrasive cleaning • equipment is available for remote cleaning applications • more effective in cleaning out cracks and restricted areas than air abrasive cleaning • effectiveness has been proven in practice	• required equipment for remote or special cleaning situations may not be readily available • adherent fine dust must be cleaned off surfaces after decontamination • water slurry must be cleaned up and disposed of
• **air slurry blasting** *Slurry, formed of a liquid (usually water) and as much as 30% abrasive by volume,*	• effectiveness has been proved in practice • permits close control of amount of material removed • much less air pollution than air abrasive blasting • equipment has been developed and is available	• more complicated operation with greater equipment requirement than air abrasive blasting or water abrasive blasting • fine, adherent dust must be removed from decontaminated surfaces • water slurry must be cleaned up and disposed of • some air pollution

is added to a stream of air.		• limited application to inside surfaces of pipes and tanks
• **abrasive slurry cleaning** *Slurry of abrasive particles suspended in a liquid carrier is circulated through a system. The velocity of the mixture should be relatively low, in the range of 5-20 ft/sec.*	• can clean complex piping systems in situ, including fittings and valves • no air pollution • remote operation capability • no spreading of contamination • very little alteration of piping system required • very little removal of metal from the system	• method has not been proven for decontamination • composition of slurry would have to be developed • requires a pump, connecting lines, and a reservoir • would generate a large volume of waste • would require extensive cleanup of system after decontamination
• **surface grinding** *i.e. honing*	• good for removing localized spots of tightly adherent contamination • amount of metal removal can be closely controlled • small amount of waste generated • can be used to decontaminate the inside of a straight length of pipe in situ	• labour intensive • slow process • limited application • could cause spread of contamination if used on outside surface
Vibratory finishing *An item to be cleaned is placed in a tub full of small pieces of metal or ceramic, The tub is vibrated by a system of eccentric weights and the small pieces of the cleaning media rub against the surface to be cleaned.*	• low waste volume • no harm to component during decontamination • smoother surface produced on decontaminated item • low manpower requirements for operating equipment • no hands-on requirement during vibratory finishing operation • decontamination factors of 100 and more • method is effective with metal, hard and soft plastic, and rubber items • removes paint, rust, and other adherent material • can clean different materials, sizes, and shapes at the same time	• component to be decontaminated must be removed from the system and sectioned to size if necessary • definite work-piece size limitation with annular-type vibratory finishing machines • limited ability to clean out cracks and fine grooves
Ultrasonics *Ultrasonic cleaning combines the effects of cavitation of a liquid at the surface to be cleaned with the chemical action of the liquid..*	• relatively low volume of radioactive waste • radioactive waste is easily collected and handled • decontamination factors of 100 or more can be achieved • no damage to decontaminated item • cleans cracks, crevices, and surface irregularities • decontaminates internal, inaccessible surfaces • decontaminates parts of any configuration • low labor requirement • decontaminates components that cannot be disassembled	• the size of the item which can be cleaned is limited • the item must be small enough to fit into the tank • a number of system variables, and all must be properly adjusted for the most effective cleaning action • items being cleaned in a group must be rotated in the bath to expose each surface to maximum cavitation • the cleaning system must be designed for the specific use for which it is intended • of limited effectiveness in removing tightly adherent material • may not remove thick, gummy deposits

High-pressure freon cleaning *Particles of smearable contaminants can be dislodged from surfaces to which they adhere by the impingement of a high-velocity jet of liquid. Radioactive material which dissolves in the liquid can be removed by distillation with FREON 113 that has a low boiling point and a small heat of vaporization.*	• can be used to clean electrical equipment, even operating electrical equipment • the high-density liquid displaces and floats many contaminant materials • the fluid is not harmful to most materials of construction • the liquid can easily be distilled, permitting removal of any dissolved contamination with resulting low volume of radwaste • maximum removal of loose surface contamination as a result of • low surface tension and low viscosity of freon solution enable it to penetrate small clearances and cracks. • no liquid radwaste (except for distillates) • excellent volume reduction of radwaste materials, up to 100:1 • can be used to clean protective clothing, respirators, tools, glove boxes, walls and floors • relatively low labor requirement • good protection for personnel, glove box operation, very little atmospheric pollution and low toxicity • can use a mobile, self-contained, decontamination unit • low power and equipment requirements	• of limited value in removing fixed, non-smearable contaminants • in situ cleaning could result in residual traces of freon which, under special circumstances, could cause stress corrosion cracking • primarily a method for decontaminating components which can be fitted into a glove box
Reflux decontamination *The solvent in the reservoir is boiled to generate hot solvent vapor. This vapor fills the tank up to the cooling zone level, where the solvent condenses and returns by gravity to the reservoir. An item to be cleaned is located in the vapour zone, the solvent condenses on the cooler surface and continuously flushes the surface with pure solution.*	• simple process with minimal equipment requirements • can decontaminate the internal surfaces of large systems with small volumes of decontamination solution • the resultant waste represents only the material removed from the contaminated surfaces and can be readily solidified for storage and disposal • the process can be operated remotely to minimize exposure • system access requirements are minimal • labour and other costs should be low	• it may be difficult to identify decontamination agents that are effective for the contaminants of interest, noncorrosive to system materials, and have suitable boiling point characteristics • the solutions cannot be easily modified to provide the desired combination of characteristics • the process only removes specific soluble contaminants and is ineffective for insoluble particulate contamination • the process is not developed or demonstrated

Dry ice blasting *Contaminated surface is blasted with a dry ice made of liquid CO_2. As a result a mixture of abrasive particles and contaminated materials is produced. At ambient conditions, the dry ice will sublime into gaseous CO_2, leaving behind only the contaminated material.*	• small amount of clean-up required after decontamination • no added residual grit remains after decontamination • very low volume of waste for disposal • minimal atmospheric pollution (no silicon dust) • removes smearable contamination and lightly adhering material • does not abrade metal surfaces • commercially available	• still an experimental process, not proven in use • requires handling of cold, pressurized, liquid CO_2 • requires an insulated, pressurized storage reservoir and a pelletizer • process is not feasible for removing tightly adhering material or corrosion layers
Thermal erosion *Use of heat (e.g. a plasma arc) to remove, or erode, a surface layer of metal a few thousandths of an inch thick. The removed metal and contaminants are prevented from adhering to the decontaminated surfaces by maintaining a water film over the surface being treated.*	• considerable volume reduction of waste • potentially high decontamination factor	• labour intensive process • energy intensive process • increased potential for recontamination • slow process for treating large surface areas • destroys surface films or treatments
Laser cleaning *Laser (e.g. XeCl, Nd:YAG, excimer) surface irradiation induces the adsorption of the photon energy by the first nanometers of material that can lead to the ablation of a thin material layer and loosening of the decontaminated surface layer.*	• ease of minimisation of a decontamination area, which reduces the waste generation • well adaptable for large area surface treatment • dry process • remote control reduces occupational dose to workers • can remove oxides, paintings, polymers or particles • decontamination factors 15…100	• mainly suitable for decommissioning purposes as the surface oxide is totally removed in treatment • radionuclides trapped inside cracks are difficult to remove

THESE FOLLOWING TECHNIQUES ARE IN SOME REFERENCES INCLUDED IN MECHANICAL DECONTAMINATION TECHNIQUES AS THEY ARE NOT CONVENTIONAL CHEMICAL OR ELECTROCHEMICAL PROCESSES		
Electropolishing with acidic electrolytes *The object to be decontaminated is immersed in a tank of electrolyte and serves as the anode in an electrolytic cell.*	• commercially available process with major equipment items being relatively inexpensive • capable of decontaminating to background level • removes a variety of radionuclides • decontamination factors of 100 to 500 or more are routinely achieved • process and processing procedures are relatively simple • can decontaminate complex components and shapes in many instances without prior dissassembly: • produces a smooth polished surface that has a low recontaminability and is easily decontaminated • metal removed during decontamination is generally less than 0.001 in. • electrolyte volumes for decontamination are relatively low compared to requirements for chemical decontamination	• for the immersion process, the item being decontaminated must be removed from the RCS and immersed in the tank of electrolyte • for the in situ process, access or entry of in situ device into item being decontaminated is required • provision for containment of electrolyte must be made • disposal of electrolyte requires neutralization and processing in a liquid radwaste system or solidification in concrete and burial • does not remove fuel fines, sludge, or any insulating material • the electrolyte must be completely rinsed from the component before use
Electropolishing with basic electrolytes *The object to be decontaminated is immersed in a tank of electrolyte and serves as the anode in an electrolytic cell.*	• forms hydroxides that precipitate in the basic electrolyte, permitting removal of most of the dissolved metal and contaminants using simple filtration techniques • the radioactive waste (precipitate) can be readily solidified by drying to facilitate handling, storage and disposal • the amount of secondary waste is held to a minimum • can contain additives to promote criticality safety when decontaminating systems containing fissile material	• requires relatively high current densities and operating temperatures • potential for airborne contamination resulting in contamination containment problems • poor throwing power and incomplete decontamination of welds • possible corrosion problems and fire hazard • not developed or demonstrated for in situ decontamination applications
Steam/hot water cleaning and two-phase mixtures *Steam is supplied by a portable boiler, or an existing steam line, at a pressure of 90 to 100 psig. Chemicals or detergents can be used to remove tight contamination.*	• steam cleaning methods have been well developed and are used extensively for nonradioactive surface cleaning. • the equipment is readily available • very good for cleaning large surfaces such as walls, ceilings, and tanks • steam ejector cleaning produces a relatively small amount of contaminated liquid • removes high levels of contamination • decontamination factors as high as 50 have been obtained. • with an acid additive it can be used to remove scale and corrosion • the high temperature amplifies the cleaning effect of detergent, acid, or solvent additive	• condensing steam can produce fog to reduce visibility • a relatively large amount of contaminated liquid can result from cleaning with a steam injector (hot water cleaning) • the ejector nozzle must be held within a few inches of the surface to be cleaned • potential for contamination spread because of reflected steam and radioactive debris

Decontamination		
• **foams** *Liquid foam usually generated from an acid or acid mixture, using air, nitrogen or an inert gas. Foam solutions also contain various chemical additives e.g. inhibitors, foam stabilizers, and surfactants.*	• relatively small volumes of active chemicals used • use of inert gas for foaming can exclude oxygen • simple operation with few equipment requirements • can decontaminate internal and external surfaces with relatively small volumes of solution • process can be operated remotely • may be inhibited to prevent extensive corrosion • waste involves primarily only active chemicals and material removed from contaminated surfaces	• temperature control is difficult • removal, collapse, and collection of foam may be a problem • decontamination depends entirely on chemical action of agents in foam--no mechanical action • pumping, handling and removal of foams requires some special equipment and handling techniques
• **gels** *Either organic based or inorganic based systems and contain in the gel formulation decontaminating chemicals which are usually acids such as phosphoric, sulfuric, or nitric.*	• small quantities of chemicals will be used • can be applied in thin layers by spraying techniques • easily removed by water rinsing or spraying • effective decontamination is possible • system may be inhibited to remove minimal amounts of base metal	• cannot be easily applied to small diameter internal surfaces • does not lend itself readily to remote operation • requires specialized equipment for effective application • very little process or development work has been done
• **pastes** *Usually consist of filler, a carrier, and an acid or mixture of acids as the active agent.*	• can be applied in thin layers • small quantities of chemical required • small volumes of waste produced • readily removable by water washing • very effective single stage decontamination	• requires manual application until further development work is done • cannot be easily applied to small diameter internal surfaces • very little data or work on process • fillers and carriers added to paste increase waste volume and are not active decontaminants
Strippable decontamination coatings *Usually consist of high molecular weight, film forming, synthetic polymers dispersed as an emulsion in an aqueous base. Coatings contain an active agent, usually an acid or mixture of acids, which attacks the*	• small amount of secondary waste produced • no liquid wastes to be treated, filtered, or processed • no formation of active aerosols or secondary contamination due to splash or flow • contaminants contained in a film which simplifies handling • decontamination of surfaces can be carried out on site without removal of components • easy compaction and disposal of secondary waste • very good decontamination factors obtained • coatings can be readily formulated to specific types of surfaces to be treated	• internal surfaces (pipes, vessels, etc.) cannot be treated readily with current techniques • fairly labor intensive technique • presently requires manual handling of stripped contaminated material • remote operation has not been developed--although some remote techniques appear feasible • decontamination depends almost entirely on chemical action of coating formulation--no mechanical action

contaminants and the surface to which the coatings are applied.	• avoids problems of airborne contaminants and redistribution of contamination • large areas can be treated and decontaminated quickly • thin layers of surface fines may be completely removed in one operation	
Electrochemically activated decontamination solutions *A modification of conventional high-concentration chemical decontamination methods that uses an electrochemically-activated constituent to enhance the surface dissolution and decontamination of metallic components.*	• the activated solution can be applied using simple flow-through or spray-type in situ decontamination methods • more suitable than electropolishing for components with irregular shapes and shielded interior areas • no pretreatment is required, and the decontamination solution will remove contaminated surface organic material • the process appears effective in removing surface contamination and oxide films, and in dissolving fuel-related oxides • the process potentially can be designed to dissolve specific films or oxides that are difficult to treat using conventional chemical agents • secondary waste volumes can be minimized by using lower concentration recycled solutions that are equivalent in effectiveness to high concentration chemical reagents	• relatively high solution temperatures and contact times are required for maximum process effectiveness • significant corrosion problems may exist • special materials of construction are required to contain and transfer the activated solution because of its reactive nature • the process is not developed or demonstrated for large-scale applications
Molten salt methods *Molten salt can be used as oxidizing, reducing, or electrolytic processes to descale or decontaminate metallic surfaces. After salt treatment, complete contaminant removal may require not only a water flush or quench, but also an acid dip or spray as a final step.*	• provides very efficient removal of contaminants from a variety of surfaces and materials • can be a rapid process for decontamination, possibly requiring only a few minutes • generally removes only contaminants and scale and has little effect on the base metal • hot-spraying technique using relatively thin layers of molten salts can reduce waste volumes significantly • salts required are inexpensive • removes wide range of contaminants, both soluble and particulate	• molten salt requires special equipment and care in handling--many safety precautions • can cause distortion of thin-gage metals • may be difficult to operate remotely • operating temperatures may be too high for some metals and alloys • probably costly to set up and maintain

APPENDIX 2

USE OF CHEMICAL DECONTAMINATION TECHNIQUES ON DIFFERENT SURFACES

SS = stainless steel, CS = carbon steel [14, 16]

CHEMICAL TECHNIQUE	DESCRIPTION	APPLICATION MATERIAL/SURFACE	REMARKS/ADVANTAGES/DISADVANTAGES
Strong mineral acids	A strong acid is an acid that ionizes completely or nearly completely in aqueous solution; the concept of strength here does not refer to concentration in aqueous solution. The strong mineral acids can be used either by themselves as dilute solutions, in chemical formulations with other materials, or in combination with each other, such as HCl/HNO_3 (aqua regia). They are flexible, being used as sprays, in dipping processes, or in flushing processes. Their main mode of action is to react with and dissolve metal oxide films that contain contamination. If used in higher concentrations or at higher temperatures for extended time periods, they can work by dissolving the base metal that underlies a contaminant film.	With appropriate care and precautions, they can be used on all metal surfaces except the more reactive metals such as zinc.	Advantages are: • They are relatively cheap. • They are quick and effective. • Their properties are well understood. • They are readily available from chemical suppliers. Disadvantages include: • Safety and handling problems; • The need to neutralize the waste products; • The risk of overly aggressive reaction and the difficulty of controlling the reaction so that only the contamination is removed; • The potential for the creation of explosive (hydrogen) or poisonous (NO_x) gases.
Nitric acid	Nitric acid is widely used for dissolving metallic oxide films and layers on stainless steel and Inconel systems. However, difficulties may still arise in specific applications. For example, it was used on one section of a heat exchanger at the UK's Windscale advanced gas cooled reactor (WAGR) and while very good decontamination of the boiler tubes was achieved, residual activity in the internal insulation of the structure has proved to be a more difficult problem. Successful industrial tests have been carried out in the Russian Federation (at radiochemical combines in Cheljabinsk and Krasnojarsk) and other investigations at the Savannah River site in the USA.	SS, Inconel	Nitric acid cannot be used on carbon steel and may cause fires and explosions when combined with incompatible materials.

Sulphuric acid	Sulphuric acid is an oxidizing agent used to a limited extent for removing deposits that do not contain calcium compounds. It is not as widely used as other strong mineral acids since it is highly corrosive without giving particularly high decontamination factors. It has been used successfully at the JPDR in Japan and sulphonitric acid has been tested successfully at the Rapsodie reactor, France. Cerium (IV) ions were added to improve the oxidativeness of the reagents in order to balance the temperature decrease (Ce^{4+} is a strong oxidising agent). This technique has also been used at the Capenhurst facility in the UK.	CS, SS	
Phosphoric acid	From a purely chemical perspective, phosphoric acid is not really a strong acid since its first ionization constant is 7.5×10^{-3}. However, since this still makes it stronger than most other acids used in decontamination, such as organic acids or acid salts, it is usually considered along with hydrochloric, nitric and sulphuric acids. Phosphoric acid is generally used for the decontamination of carbon steel because it rapidly de-films and decontaminates carbon steel surfaces.	CS	The resulting wastes may create a difficult treatment problem.
Hydrocloric acid	Hydrochloric acid has been widely used as a cleaning agent in the chemical processing industry and in utility boilers. For radiological decontamination operations, it is typically used to remove radiological contaminants and metal oxide films from metal surfaces to depths of up to 90 micrometers. The depth to which the technology is effective in reducing contaminant levels is a function of the base material, the acid strength, and contact time of the decontaminating agent.	Metals and metallic oxides	Generally used for inorganic deposits such as metal oxides but is not effective on organic deposits.
Fluoroboric acid	Fluoroboric acid attacks nearly every metal surface and metallic oxide. It has been described as an excellent decontamination reagent with extremely high decontamination factors. Decontamination for decommissioning (DfD) process was tested in the	Metals and metallic oxides	The main disadvantage of fluoroboric acid is the large amount of waste its use generates, but a process for regenerating and recycling the acid, the DECOHA process, has been developed by a Swiss company Recytec. It is reported that thin layers of the contaminated metal can be removed from the surface with

	mid-1990s with an aim of gaining the unrestricted release of major components. It uses low concentrations of fluoroboric acid, at temperatures ranging from ambient to 90°C, permanganate to vary the oxidizing potential; continual 'rinsing' to give the required decontamination factor, and ion exchange resin cleanup. A major achievement was the release of the reactor water cleanup heat exchangers of Quad Cities NPP for recycling in April 1997.		minimal damage to the object, therefore creating a minimum volume of waste. A process similar to DECOHA has also been developed in the Russian Federation and an experimental facility at Chernobyl NPP has been operating since 1997.
Fluoronitric acid	A process using fluoronitric acid (a 50:50 mixture of hydrofluoric and nitric acids) has been developed for the rapid decontamination of stainless steel. It has been tested at the Belgian reactor no. 3 (BR3).	Metals and metallic oxides	
Acid salts	The salts of various weak and strong acids can be used in place of the acids themselves or, more effectively, in combination with various acids to decontaminate metal surfaces. Possible salts include: sodium phosphates and polyphosphates, sodium bisulphate, sodium sulphate, ammonium oxalate, ammonium citrate, sodium fluoride and ammonium bifluoride.	Metal surfaces	
Organic acids	The use of organic acids is widespread in the nuclear industry for decontamination, mainly during plant operation, and to a lesser extent for decommissioning activities. Examples include formic acid, oxalic acid, oxalic peroxide and citric acid.	Used not only on metal surfaces, but also on plastics and other polymeric compounds.	
Formic acid	A process developed for Slovakia's A1 NPP decommissioning project is based on the treatment of material with formic acid, complexing agent and corrosion inhibitor, and simultaneous agitation by ultrasound in a purpose-built bath. It is reported that this process allowed the fast and effective removal of surface contamination from levels of 10^3–10^4 Bq/cm^2 to below release levels	Metals and metallic oxides	
Oxalic acid	Oxalic acid is effective for removing rust from iron and is an excellent complexing agent for niobium	CS, Al	During cleaning, however, secondary deposits of ferric oxalate containing radionuclides may be formed on the decontaminated

	and fission products. Oxalic acid is a basic component of circuit decontamination technology used for RBMK reactors.		surfaces.
Oxalic peroxide	Oxalic peroxide is used for the simultaneous dissolution of UO_2 and for the de-filming and decontamination of metals.	SS, Al	
Citric acid	Citric acid is used as a reducing agent and it is very effective for decontaminating stainless steel in a two step process following alkaline permanganate treatment (see the CITROX process). It has been used at Capenhurst in the UK and solutions containing citric acid and Na_2-chromotropic acid have been used in the Kola NPP in the Russian Federation.	SS	
Bases and alkaline salts	Caustic compounds are used both by themselves and in solution with other compounds to remove grease and oil films, to neutralize acids, to act as surface passivators, to remove paint and other coatings, to remove rust from mild steel, to act as a solvent for species that are soluble at high pH, and as a means of providing the right chemical environment for other agents, mainly oxidizing ones. Examples include: potassium hydroxide, sodium hydroxide, sodium carbonate, trisodium phosphate, and ammonium carbonate. Experience in the use of sodium hydroxide baths at Gundremmingen-A NPP (KRB-A) and Versuchsatomkraftwerk Kahl (VAK) reactors in Germany proves that its use is often enough to reach free release limits in the case of materials with low levels of contamination.	CS	Facilitate degreasing and passivation. Caution should be exercised when applying high pH solutions to aluminium.
Complexing agents	Complexing agents form stable complexes with metal ions, solubilise them, and prevent their redeposition out of solution. Common applications include use of the following agents: • Oxyethylidenediphosphonic acid (OEDPA) • Diethylenetriaminepentaacetic acid (DTPA) • Ethylenediaminetetraacetic acid (EDTA)	Metals	Prevent redeposition. Problems may occur with the conditioning if the secondary waste contains complexing agents, i.e. solidification of concrete and stability of resins

	• Hydroxyethylenediaminetriacetic acid (HEDTA) • Organic acids • Sodium or ammonium salts of organic acids • Nitrilotriacetic acid • Picolinic acid.		
Bleaching	Bleaching is the most effective in removing chemical agents from surfaces. Traditionally, calcium hypochlorite has been used as the bleaching agent, although recently sodium based bleaching formulations have found some applications.	Organic materials from metals	Used to remove chemical agents
Detergents and surfactants	Detergents are effective, mild, all-purpose cleaners for treating all facility surfaces, equipment, clothes and glassware. They are ineffective in dealing with metal corrosion and long-standing contamination. Surfactants are used as wetting agents, detergents and emulsifiers.	Organic materials from metals, plastics, concrete, glassware	Mild, all-purpose cleaners
Organic solvents	Solvents are used in decontamination for removing organic materials, for example grease, wax, oil and paint from surfaces and for cleaning clothes. Possible solvents include: kerosene, 1,1,1-trichloroethane, tetrachloroethane, trichloroethylene, perchloroethylene, xylene, petroleum ethers and alcohols.	Organic materials from metals, plastics, concrete	
Multiphase treatment processes	Multiphase treatment processes combine a variety of chemicals and processes to achieve a more effective decontamination and are widely used.		
Reducing-oxidizing (REDOX) agents	REDOX agents increase or reduce the oxidation state of the superficial metallic oxide layer on the contaminated metal thereby making it more soluble. Verification tests on REDOX type decontamination techniques have been conducted in Japan and China. Most of these REDOX decontamination processes are multi-step applications. An initial oxidation step (commonly alkaline or acidic permanganate) is used to increase the oxidation state of the metal ions. This is followed by a reduction step aimed at dissolving	CS, SS	Facilitates solubility

	the metal cations.		
Low oxidation state of metal ions (LOMI)	The LOMI process was primarily developed for the Winfrith steam generating heavy water reactor (SGHWR) in the UK. It can be applied to structural materials such as different types of carbon and stainless steels, Inconels and Zircaloys. In PWRs it is normally followed by an oxidizing stage. The LOMI process is described more thoroughly in Chapter 0.	CS, SS, Inconel, Zircaloy	
Alkalaine permanganate	Alkaline permanganate is used to oxidize Cr(III) oxides (which are insoluble in acids and alkalis) present in the corrosion films to Cr(VI) in the form of $HCrO_4^-$ anions which are soluble over a wide range of pH values. The alkaline permanganate–LOMI process has been successfully used to decontaminate stainless steel surfaces of the BWRs at the Tarapur Atomic Power Station in India and a version of the process has also been used at the Paks NPP in Hungary. Alkaline permanganate enhanced with ultrasound has been used at the Junta Energia reactor no. 1 (JEN-1) in Spain.	SS	
Chemical oxidizing/reducing decontamination (CORD) and PWR oxidizing decontamination (POD) multistep processes	In the CORD process, permanganic acid is added to the system to oxidize Cr(III) and dicarboxylic acid is then added directly. Dissolved metals may be removed by ion exchange using on-line systems or by subsequent evaporation of the solvent. The idea of POD method is similar to the CORD and is based on the reduction of an oxidizing solution using organic acids (e.g. oxalic acid).	SS, Inconel	CORD not qualified in the U.S.
Alkalaine permanganate followed by ammonium citrate	Ammonium citrate has been successfully used after alkaline permanganate pretreatment and water rinsing to decontaminate stainless steel and carbon steel.	CS, SS	
Alkalaine permanganate followed by ammonium citrate with EDTA	EDTA can be added to the former process, i.e. alkaline permanganate followed by ammonium citrate, to keep the iron in solution and inhibit its redeposition. One example of its application is at the nuclear submarine prototype reactor, UK.	CS, SS	EDTA added to keep iron oxide in solution

Alkalaine permanganate followed by citric acid	A mixture of oxalic acid, citric acid and an inhibitor is an effective decontaminant of stainless steel as the second step after alkaline permanganate pretreatment.	SS (300 series only), Inconel	
Alkalaine permanganate followed by sulphamic acid	This technique is effective in removing the contaminated film from stainless steel piping without causing redeposition of a precipitate.	CS, SS	No redeposition
Alkalaine permanganate followed by oxalic acid	This process has been successful in removing aged films on high temperature stainless steel water piping, but it has the disadvantage of causing redeposition in the form of a tenacious oxalate film on the metal. This can be avoided by using an acidic permanganate solution. Alkaline permanganate — oxalic acid solutions have been used in the Russian Federation for the circuit decontamination of Novovoronezh NPP (WWER-440), Belojarsk NPP (AMB-100 BWR type) and others. To prevent the formation of secondary oxalate deposits, hydrogen peroxide was used in the final stage.	CS, SS	The main disadvantage of this process (as also for other multistep technologies) is the large volume of spent solution and flushing water generated. This can exceed the original circuit volume by up to a factor of ten.
Nitric acid, permanganate and hydrofluoric acid	The nitric acid, permanganate and hydrofluoric acid process has been investigated and proved successful in China.	CS, SS	
Strong oxidizing decontamination process	The strong oxidizing decontamination process is based on the use of ozone and Ce(IV) in an acid solution. It was applied during the decontamination of the steam generator of the Ågesta reactor in Sweden. A solution of nitric acid, Ce(IV) and ozone was used successfully in the decontamination of Inconel 600 tube bundles at several steam generators in Europe, including the Dampierre PWR, France. The strong oxidizing decontamination method was later tested on stainless steel material from the Greifswald WWER, Germany. It proved capable of reaching clearance levels. The Ce(IV) decontamination process has been applied at the Pacific Northwest National Laboratory (PNNL) and the West Valley demonstration project in the USA.	Inconel 600, CS, SS	
CAN-DECON	The key factor is the decontamination chemical	CS, SS	Used on piping systems, IGA sensitivity if no ferric ions

	LND-101A (EDTA + citric acid + oxalic acid). AP preoxidation used but not advanced.		present in the solution , waste problems due to preoxidation
EMMAC	A proprietary French process that includes oxidizing and reducing solutions. The oxidant is NP, and the reductant is a mixture of nitric and ascorbic acids.	CS, SS, Inconel (to some extent)	Designed specifically for the decontamination of atainless steel components of the primary cooling system. The efficiency of the EMMAC process on nickel alloys is reduced.
CORPEX		CS, SS, Al, Cu, rubber, plastic	
TechXtract		Concrete, Pb	
DECOFOR		CS, SS	
DECOPAINT		CS, SS	
DECONCRETE		concrete	