RECENT DEVELOPMENTS IN CHEMICAL DECONTAMINATION TECHNOLOGY

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INTRODUCTION

Chemical decontamination of parts of reactor coolant systems is a mature technology, used routinely in many BWR plants, but less frequently in PWRs. This paper reviews recent developments in the technology - corrosion minimization, waste processing and full system decontamination, including the fuel. Earlier work was described in an extensive review published in 1990 (ref. 1).

Part System Chemical Decontamination Experience

In the 30 months up to March 1994, over forty part-system decontamination applications were carried out by U.S. vendors, primarily at operating nuclear power plants in USA. A similar number of applications were carried out by vendors in other countries. Table 1 summarizes the decontamination applications carried out in the United States between September 1991 and March 1994. Clearly, chemical decontamination is a mature technology that is playing a major role in the worldwide drive to reduce occupational exposures. For example, applications of the LOMI (low oxidation-state metal ion) process have saved over 13,000 person-rem (cSv.) between 1986 and 1992, equivalent to $132 million using typical exposure costs.

Most applications have been carried out on BWR reactor water cleanup systems and recirculation piping systems, but several applications on PWR channel heads and heat exchangers have been reported, also. Typically, stainless steel or carbon steel components are decontaminated, although low alloy steels and nickel-based alloys, such as Inconel 182 and 600, are included frequently in the flow path for the decontamination solvents.

Most proprietary decontamination reagents consist of mixtures of organic acids and/or chelating agents, such as citric acid, oxalic acid and EDTA (ethylene diamine tetra acetic acid). These mildly reducing agents are often used in multi-step processes with oxidizing steps, such as alkaline potassium permanganate (AP), nitric acid/permanganate (NP) or permanganic acid. The LOMI process uses a mixture of vanadous formate and picolinic acid, which is more strongly reducing than the purely organic processes. LOMI is also used in combination with AP or NP steps, particularly for removing chromium-rich oxide films formed in the reducing coolant chemistry of PWRs and in some cases in BWRs operating with hydrogen addition (ref 1).

Examination of Table 1 indicates that different processes are favored for different applications. LOMI is the process of choice for BWR recirculation piping (where intergranular stress corrosion cracking is a major concern), while the regenerable CANDECON and CITROX processes are favored for systems with high surface/volume ratios, such as heat exchangers.

All the above reagents are currently used in relatively dilute formulations which give decontamination factors of 5 - 15, adequate for operating plants. However, changes in water chemistry can make the radioactive oxide films more tenacious and difficult to dissolve. The use of hydrogen water chemistry combined with zinc injection in BWRs has the potential to produce an oxide containing more chromium and zinc than typical; such oxides have proved to be difficult to dissolve in the past.

These dilute reagents have the advantage of not completely removing the inner, high-chromium, protective film on stainless steel surfaces. As a result, recontamination rates are not excessive, and in fact chemical passivation is not so effective on decontaminated surfaces as on fresh surfaces found on newly replaced components. For this reason, passivation techniques are not applied after chemical decontamination. In contrast, the strong chemical processes used 15-20 years ago resulted in a rough oxide-free surface that recontaminated more quickly than even newly-installed components, often resulting in higher radiation fields after one cycle of subsequent operation than measured before the decontamination.

As discussed above, these dilute reagents are not able to completely remove all the radioactivity in the oxide film, as required for free release of decommissioned components. For decommissioning applications, stronger oxidizing reagents (such as cerium compounds) or electrochemical processes are required. Typically these processes remove some of the base metal, which is acceptable for replaced components but obviously not for components to be returned to service.

Corrosion Issues

Concerns about intergranular stress corrosion cracking, particularly of sensitized Type 304 stainless steel in BWRs and of mill-annealed alloy 600 in PWRs, have lead to comprehensive corrosion testing with decontamination reagents. These tests included measurements of general corrosion, galvanic corrosion and crack growth measurements with stressed specimens.

For BWRs, accelerated corrosion is generally observed only when oxalic acid is present, and even then only in isolated cases (ref 2). Tests on irradiated materials, subject to irradiation-assisted stress corrosion cracking, showed no adverse effects. A detailed evaluation of all corrosion data by General Electric concluded that the LOMI process was qualified for use throughout the entire reactor system (ref 3). Insufficient data (particularly crack growth measurements) were available for other processes, and the same conclusion was reached for the alkaline permanganate oxidizing step. Thus, while no adverse effects had been reported, unrestricted endorsement of AP for complete reactor coolant system use has not been obtained. Nitric permanganate (NP) is not recommended, as a result of accelerated cracking with low alloy steels. There is a need for improved oxidizing pretreatment processes, such as permanganic acid used in the CORD process (ref 4), to be qualified for BWR use.

As part of the qualification program for PWR full system decontamination, corrosion characteristics of 40 materials in AP/LOMI and AP/CANDEREM have been established. These tests covered three cycles of normal decontaminations and one cycle of decontamination under fault conditions, corresponding to the most aggressive situation that could result from loss of process control. Typically, the one fault cycle gave as much corrosion as three normal cycles. Both processes were deemed acceptable for at least one application (ref 5).

Waste Processing

Radioactive waste processing and disposal has become the main impediment to more extensive use of decontamination technology. Improvements in the formulation and application of decontamination processes have been made to reduce waste volumes. For example, improved ion exchange resins, such as ion-specific resins are being developed. For LOMI, two changes have already been implemented: the use of "low formate" reagent and a reduction in the amount of picolinic acid used to maintain the dissolved metals in solution. With all such improvements the gains achieved are economically worthwhile but limited.

Several more radical technical developments in this area are providing alternatives to the current practices of disposing of ion exchange resins in high-integrity containers, or solidified in cement. Low temperature resin oxidation (ref 6) and Vitrification techniques are methods currently under development that have the objective of substituting a compact quantity of chemically-inert residue for the relatively large volume of ion exchange resin that results from current practice. Vitrification converts ion exchange resin into a glass matrix, suitable for long-term storage or disposal. Wet oxidation processes use hydrogen peroxide to oxidize organic material, leaving a residue which is readily incorporated in cement.

Electrochemical processes, such as the ELOMIX (electrochemical LOMI ion exchange) process, hold the promise of revolutionizing decontamination waste processing (ref 7). The objective of the ELOMIX technique is to reduce the volume of waste arising from the LOMI process by continuously removing the radioactive elements from solution using an electrochemical cell.

Ion exchange resin is used as an intermediate, rather than a final, waste form, and is continuously regenerated by the passage of electric current. The radioactivity is converted to a particulate metallic deposit which can be transported hydraulically to a vessel for encapsulation.

There are three main benefits of the process: smaller waste volume, inorganic waste form and regeneration of the chemical reagents; the latter reduces chemical costs, while the other two facilitate long-term storage, allowing most of the radioactivity to decay before disposal. Small scale field-tests during routine decontaminations at Dresden and

River Bend BWR power plants have demonstrated the feasibility of the concept, and provided parametric data required for the design of full-scale electrochemical cell modules.

PWR Full System Decontamination

Complete reactor coolant system decontamination has long been used in pressure tube reactors (CANDU and SGHWR) but has not been applied to large commercial reactors in the United States. However, full-system decontamination offers several important advantages: lower background fields, more effective decontaminations, and reduced recontamination rates (ref 8).

Significant strides in the area of PWR full-system decontamination have been made recently, with a plant demonstration planned at Con Edison's Indian Point 2 (IP2) station in 1995. Radiation fields at the plant have increased to a point where they are above the industry average. Numerous efforts to address the radiation exposure have not yielded the desired results.

In 1988 a qualification program for the chemical decontamination of the entire RCS of a Westinghouse PWR began. This qualification program was successfully completed in 1991. The LOMI and CAN-DEREM processes, with an alkaline permanganate (AP) conditioning step, were qualified for use as long as the fuel was removed.

An estimation of recontamination rates based on industry experience and computer analysis indicated a full-system decontamination would achieve a DF of 5 and that the benefit would last for 5 operating cycles, or at IP2, about 10 years. Potential exposure savings were then calculated for a range of plants. The exposure that could be avoided over 5 operating cycles ranged from 1000 rem to 3500 rem.

The measured recontamination rates of previously decontaminated subsystems at IP2 are well below what had been projected in the full-system decontamination report. Two factors could be that IP2 has maintained the higher pH values recommended for the RCS and has worked to replace cobalt sources in the equipment. If the recontamination rates were to continue at the low levels, the radiation levels may never return to the original levels and the exposure saved could be even greater than originally estimated.

Development of the procedures and equipment for the decontamination are well advanced. A 6-day schedule for implementation of the decontamination process has been established. CAN-DEREM and AP will be alternated during the process.

The IP2 full-system decontamination will be done with the fuel removed. A separate program started in 1989 to qualify nuclear fuel for full-RCS decon application. This program involves the chemical decontamination of actual fuel assemblies in a specialized canister at the V. C. Summer PWR plant, using the same dilute chemical solvent parameters as were employed in the full-RCS qualification program.

To take account of current generation fuel and future generation fuel designs, one assembly of Westinghouse Vantage 5 and one assembly of Vantage-Plus type fuel were exposed to CAN-DEREM solvents and one assembly each was exposed to LOMI solvents.

The qualification program necessitated the design and fabrication of a specialized decon test loop at the same conditions of flow, temperature, pressure, and chemical environment as would exist for the fuel in the reactor vessel during full-RCS decontamination. The specialized loop was designed, fabricated, tested, and installed in 1991. Extensive TV visual and eddy current cladding oxide thickness inspections were performed before and after exposure to solvents with the same inspections planned after one full cycle of operation. That operating cycle was completed in March 1993 and inspections were performed on the non decontaminated control assemblies and the fuel assemblies subjected to decontamination treatment. Preliminary evaluation of the cladding oxide thickness data shows no significant cladding corrosion performance differences between any of the assemblies. High-magnification TV visual examination of the grids, grid springs and assembly nozzles, and hold downsprings show no adverse effects.

A number of decontamination process application anomalies were observed. These anomalies resulted in recommendations for further study of boron control, ion exchange resin utilization, carbon dioxide generation, EDTA chemical analysis and decomposition, picolinic acid analysis and decomposition, vanadous formate oxidation, and reassessment of metals and radioisotopes removed. Other general recommendations included revisiting each facet of

the study to extend the evaluations to include the "fuel-in" full-RCS decontamination scenario and submittal of a second Topical Report to the NRC for its approval.

BWR Full System Decontamination

Full-system decontamination applied to BWRs is less complex than for PWRs. Thus, the BWR programs have been smaller. In a collaborative CECO/EPRI project, the LOMI process was qualified and a safety review prepared. That work, which used Quad Cities as the reference plant, has now been extended to more modern BWR5 designs, such as LaSalle. In another project an engineering design study based on the Brunswick plant has been completed.

Full-system decontamination for BWRs could be economically attractive for removing deposits in the lower parts of the BWR cores to aid inspection/repair or to remove radioactive material that could be redistributed to out-of-core areas on switching to hydrogen water chemistry. It is interesting to note that, whereas originally the main concern with BWR decontamination was the potential for increased corrosion resulting from attack by the decontamination chemicals, full-system decontamination is now seen as potentially helpful in overcoming corrosion problems with core internals.

The LOMI process has already been tested successfully on BWR fuel in a test at Quad Cities BWR in 1986. This project was similar in many ways to the PWR fuel test described above. However, far more radioactive material was removed than anticipated, thus reducing the probability of future applications. Development of the ELOMIX electrochemical ion exchange process is continuing and this could well change the economics of all decontamination applications in the future.

Conclusions

This paper has identified a number of challenges that have been overcome, such as corrosion qualification, others where significant progress has been made (waste processing) and the future challenges of full system decontamination. Chemical decontamination has been one of the most significant causes of the reduction in radiation fields (and hence exposures) that U.S. plants have achieved in recent years. Looking ahead, further advances in decontamination technology will provide enhanced options as the industry faces the challenge of controlling radiation exposures during major repair/replacement work.

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