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Decontamination and Recycling of Radioactive Material from Retired Components

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ABSTRACT

There are significant potential benefits, both economic and environmental, in recycling materials from retired nuclear facilities for new controlled uses within the nuclear industry. Provided that materials have first been decontaminated to below unrestricted release levels, there is no objection in principle to using non-radioactive facilities for recycling and manufacturing activities, so long as the materials are properly tracked to prevent their uncontrolled release. The EPRI DFDX Process is an efficient and economic decontamination method for preparing materials for recycle. This technology includes processing of the radioactive solution using electrochemical ion exchange. Recent results from a field-test in Sweden are presented, and the use of this process for recycling activities will be described, including potential applications on retired steam generators.

I. INTRODUCTION

Waste management and disposal of retired nuclear plants and components demands the proper management of the process, both for economic reasons and for retaining public confidence in the continued use of nuclear power for electricity generation. The cost and ease of management of radioactively contaminated components can be greatly assisted by the application of decontamination technology.

EPRI initiated a program of research and development work in collaboration with Bradtec, which has led to the "EPRI DFD" (Decontamination for Decommissioning) Process, that has been patented and licensed to six companies worldwide. The purpose of this process is to achieve efficient removal of radioactivity with minimum waste from retired nuclear components and plant systems. The process uses dilute fluoroboric acid with controlled oxidation potential. By removing all the outer scale and a thin layer of base metal from the surfaces, contamination can in many cases be reduced below the levels required to allow clearance (free-release) or recycle to form new components for the nuclear industry. This reduces the need for on-site storage or burial of large amounts of contaminated material at low level radioactive disposal facilities.

The EPRI DFD process has been applied successfully by EPRI licensees to many different components, in addition to the primary coolant systems of Big Rock Point BWR and Maine Yankee PWR, including pumps and heat exchangers, and material from DOE facilities. A key aspect of the existing technology that required further development for new applications of the DFD process is the management of secondary waste. Essentially, the disposal of the resulting radioactive ion exchange resin is unpopular and expensive, and is therefore the main constraint limiting further applications. For this reason, market penetration has been relatively slow.

II. ELECTROCHEMICAL ION EXCHANGE

A development to overcome this disadvantage has been demonstrated in laboratory tests, and a patent has been awarded. The new process is termed EPRI DFDX. This is the adaptation of the technology of electrochemical ion exchange, in which conventional cation exchange resin is used to take the metallic and radioactive ions out of the decontamination solution. However, instead of the resin being in a self-standing column, it is "sandwiched" between a cathode and anode compartment. The boundaries between the cathode, resin and anion compartments are formed by cation selective ion exchange membrane, which only permits the passage of cations. Electrodes are placed in the cathode and anode compartments, and electric current is passed through the cell while the solution is flowing through the resin compartment. At the anode protons are formed, which travel through the cation membrane. These protons displace metal cations held on the ion exchange resin, and the metal cations then pass through into the cathode compartment, where the metal ions are deposited as metal. The DFDX flow system is shown in figure 1. The development work resulted in a simplified cell design, shown in Figure 2. The central compartment was eliminated, as it proved to be unnecessary for the fluoroboric acid system. This has the advantage of permitting a higher current density, thereby increasing the overall efficiency of the system.

The overall process enables the collection of radioactive contamination from a thin layer of the surface of components and systems and its conversion into metal powder for disposal, driven by electrical energy. The metal powder, consisting primarily of iron, nickel and cobalt (including cobalt-58 and cobalt-60 radioisotopes) is easily collected. No other wastes are generated, and thus the new development represents almost theoretical efficiency of decontamination.

The chemical reactions involved in the electrochemical ion exchange process are shown in Table 1.

III EXPERIMENTAL

In 2004, the DFDX process was demonstrated in a field-test at Studsvik’s facility at Nyköping in Sweden, using a pilot-scale portable equipment skid. It was possible to achieve electrochemical ion exchange with a high degree of efficiency using the fluoroboric acid system.

A number of small radioactive samples were assembled for exposure in the tests. A larger quantity of non-radioactive material (carbon steel plates and stainless steel powder) was also used in the test to simulate operation on a larger scale. This methodology had the benefit of exposing the samples to decontamination under realistic conditions and validating the technical performance of the plant itself, while minimizing the levels of radioactive contamination employed, and hence the cost and hazard of the test.

The main decontamination test was performed without any permanganate cycles to test the decontamination performance in these conditions. Certain specimens were withdrawn and exposed to the permanganate cycles in separate lab scale facilities and then replaced during the test.

One further objective of the test program was to assess the possibility of using the DFDX cell to treat ion exchange regenerant solution. Accordingly it was planned that at the end of the test a simulant regenerant solution would be passed through the DFDX cell to assess the cell's performance in this latter type of application.

One extra feature of the test was the use of cesium selective ion exchange material in the process. Cesium is not susceptible to deposition as a metal in the DFDX process, and unless it is controlled any cesium radionuclides released during the decontamination process will simply build up in concentration in the solution. However, in principle a very small amount of cesium selective ion exchange resin is sufficient to collect any circulating cesium, and can be added to the process filter. This was tested as part of the program.

Three types of radioactive samples were provided for the test program. Two specimens of fuel reprocessing plant origin were provided by UKAEA Dounreay. The EPRI DFD Process has not been used previously to clean fuel reprocessing plant. There are specific issues relating to the use of organic solvents in a high radiation environment in the reprocessing plant which might compromise the decontamination achievable, hence it was essential in advance of the Dounreay test to ensure that good decontamination could be achieved. Also it was important to establish the extent of alpha decontamination achievable for this application. The specimens provided were lengths of stainless steel tube, having a fairly heavy deposit on the inner surface. One sample was placed in the main decontamination flowpath (no permanganate) and one in the sample chamber. In this chamber it was possible to extract the sample during the decontamination for permanganate cycles, as referred to above.

One specimen of Inconel steam generator tube was provided by Studsvik, which was divided into two. The main question here was the possibility that Inconel could be cleaned without the "permanganate cycles" typically employed in the EPRI DFD Process. It has been noticed in previous decontamination work that while stainless steel requires the permanganate cycles for efficient decontamination, Inconel is subject to continuous metal loss throughout the decontamination, even when no permanganate is present. Accordingly the possibility exists of achieving decontamination of Inconel without the use of permanganate, which would significantly simplify commercial application of the

EPRI DFD or DFDX process for this application. The test procedure was designed to establish this. As with the Dounreay specimens, one sample was placed in the main flow path and one in the sample chamber for application of permanganate cycles.

The final sample was a specimen of carbon steel Magnox boiler tube originating from Berkeley Power station in the UK. This sample was typical of the “finned tubes” used to transfer heat from the contaminated gas circuit (outer surface) to the uncontaminated water/steam circuit (inner surface) in the Magnox gas cooled reactor. It has previously been shown that boiler tube specimens can be decontaminated to free-release conditions by a two-stage process of which EPRI DFD is the second stage. The purpose in this test was to find out if good decontamination could be achieved in a single process step employing the EPRI DFDX Process. It has been established in previous work that spray-rinsing the surface during decontamination is beneficial, since chemical decontamination can be hindered by the presence of insoluble deposit on the tube surface. However, if some dissolution of the base metal occurs first, this insoluble deposit can easily be dislodged by the action of spraying, thereby exposing the surfaces for the decontamination to be completed. Accordingly, the specimen was suspended in the process tank in the main circuit, in such a way that it could be withdrawn for spray rinsing during the decontamination.

Additional to the radioactive samples Studsvik provided some (uncontaminated) carbon steel plates having several square metres of surface area. These plates could be exposed in the solution and would corrode rapidly in the hot decontamination to provide a source of iron in solution simulating the presence of up to 100 square metres of stainless steel surface. Finally a concentrated solution was prepared by dissolving stainless steel powder in fluoroboric acid. This procedure has been used in earlier work to provide a source of material for decontamination treatment testing. In this case the purpose of generating this solution was to test the use of the DFDX cell to treat a simulant ion exchange regenerant solution.

IV RESULTS

The decontamination of the samples in the Studsvik loop were as shown in Table 2, readings after deduction of background. More detailed nuclide specific measurements of the samples are provided in Table 3. These results show that all the samples were effectively decontaminated. The alpha decontamination results are significant – the lack of a full number of permanganate cycles might have been expected to lead to a lower DF on the Dounreay stainless steel specimens, but the results show that alpha activity is nevertheless effectively removed. The Magnox specimen showed a rather high percentage weight loss, but that was due to the specimen being left in the solution for an unnecessarily long time. This parameter can easily be optimized in future work to reduce the weight loss. The results for the steam generator specimen confirmed the earlier results could be achieved on Inconel-600, but it was also found that permanganate was not necessary. The final results from the samples subjected to the permanganate treatment are not available yet, but the decontamination of these specimens was not as effective as those in Table 3-1. The conclusions to be drawn from these results are that permanganate steps are not necessary for treatment of any of the particular samples used in this test, and that the effect of temperature (higher for the samples in the Studsvik loop than in the specimens exposed to permanganate) is more important than permanganate for achieving good results.

V. DISCUSSION

The DFDX electrochemical cell performed effectively, indicating that application of the electrochemical technology with DFD is possible with much smaller equipment, and the economics are favorable. This development can reduce the volume of waste arising from the DFD Process, by a factor of 10. Waste volume reduction achieved by electrochemical ion exchange permits collection of the radioactive residue as metal particles, which can conveniently be fluidized into a small container for storage or disposal as radioactive waste. The volume of the metallic waste is sufficiently small that storage, for example, in a nuclear facility’s fuel pool, to take advantage of radioactive decay, is technically feasible.

Potential applications for the process include replaced components from operating nuclear power plants (such as retired steam generators), and material from DOE facilities and decommissioned power plants to allow disposal or storage with minimal LLW generation.

In the longer term the new process may have an important role in allowing new reactor plants to adopt a "zero-waste" approach, in which the plant does not require off-site radioactive waste disposal facilities during its operational life.

VI. CONTROLLED REUSE OF MATERIAL

There are significant potential benefits, both economic and environmental, in recycling materials from retired nuclear facilities for new uses rather than disposing of them as radioactive waste. Although it is technically possible to decontaminate many retired nuclear components to reduce contamination levels to below those appropriate for free release into the public domain, there is public unease at the prospect of formerly contaminated materials passing into unrestricted public use. As a result, the Nuclear Energy Institute’s policy in USA is not to encourage unrestricted release. Greater support for recycle can be achieved by converting decontaminated materials into products for new controlled uses, particularly within the nuclear industry.

Good economics can be achieved by decontaminating the materials and then using existing non-radioactive facilities for fabrication of new components. Provided that materials have first been decontaminated to below unrestricted release levels, there is no objection in principle to using non-radioactive facilities for recycling and manufacturing activities, so long as the materials are properly tracked to prevent their uncontrolled release.

Many of the reservations about recycling nuclear materials are removed if the material is recycled into a restricted use in the nuclear industry. Whether or not new nuclear power plants are built, the industry will require large quantities of materials for various facilities in the future (e.g., waste containers, structural steel, plant and building materials). The idea that these components should, where possible, be built out of recycled materials appears to command widespread support. The industry would also be likely to accept this practice if it permits a significant proportion of its waste materials to be treated in an economic manner.

This practice is well established already for certain types of product (shielding blocks, etc.). However, the practice has so far been limited because it involves using specific manufacturing processes set up within the nuclear industry. In most cases the facilities are radiologically controlled and thus are inevitably expensive, small scale and rather inflexible. It would never be possible to manufacture the full range of products the industry needs in facilities of this kind.

An alternative approach is to clean materials to unrestricted release standards and then pass them through the normal (non-radioactive) manufacturing chain to form products for the nuclear industry. The material is “tracked” through the manufacturing chain to ensure compliance with the restriction to end-use in the nuclear industry. There are several advantages to this approach. Because existing manufacturing facilities are used there is no need for extensive investment, and there is the flexibility to convert a wide variety of cleaned material to recycle into almost any nuclear industry product (pipes, valves, fasteners, waste containers, etc).

Clearly the greatest benefit will be obtained when the material in question has high value (e.g., nickel, platinum). Successful completion of this initiative will open up a new disposal option that will result in the cleanup of radioactive materials that are a concern to the public, and provide high quality alloys at reduced cost for reuse in the industry, thereby reducing some of the roadblocks to deployment of new nuclear power plants.

REFERENCES

1. C. J. WOOD, D. BRADBURY AND G. ELDER, The EPRI DFD Process – Decontamination for Decommissioning: *Proceedings of Spectrum 2002*, (2002).

2. D. BRADBURY, G. ELDER AND C. J. WOOD, The EPRI DFD Process – Decontaminating Retired Components and Reactor Coolant Systems Following Plant Shutdown, *Radwaste Solutions*, September/October 2001 pp16-23 (2001).

Table 1: Chemical Reactions in the DFDX Process

Metal Dissolution

$$Fe + 2\,HBF_4 \longrightarrow Fe(BF_4)_2 + H_2$$

DFDX Cathode Process

$$Fe(BF_4)_2 + 2e^- \longrightarrow Fe + 2BF_4^-$$

Anode Process

$$H_2O \longrightarrow 2H^+ + 2e^- + \tfrac{1}{2}\,O_2$$

Recombination after membrane transfer

$$2H^+ + 2BF_4^- \longrightarrow 2HBF_4$$

Table 2: Decontamination Results from Field Test at the Studsvik Facility in Sweden

Sample i.d.	Before Cps	After Cps	DF	Weight loss g	weight loss %
Dounreay 1					
Surface	25	2	12.5	2	0.25
End shine	695	5	139		
Steam Generator 1	>5000	Back Ground	>> 5000	1.97	3.8
Magnox Boiler Tube	390	Back Ground	>390	164	9.8

Table 3: Decontamination and Weight Losses on Samples in Studsvik Loop

SAMPLE	BEFORE (Bq g^{-1})	AFTER (Bq g^{-1})	DF
Magnox Boiler Tube			
Cs-137	476	0.02	23,800
Co-60	370	0.18	2,055
S.G. Tube			
Co-60	10,000	0.4	25,000
Sb-125	76	Not Detected	>76
Dounreay Pipe			
Cs-137	30	1.4	21
C0-60	Not Determined	0.16	-
Alpha (Pu-238)	0.6	0.12	50

Figure 1: Schematic diagram of the Flow Path for the DFDX Equipment

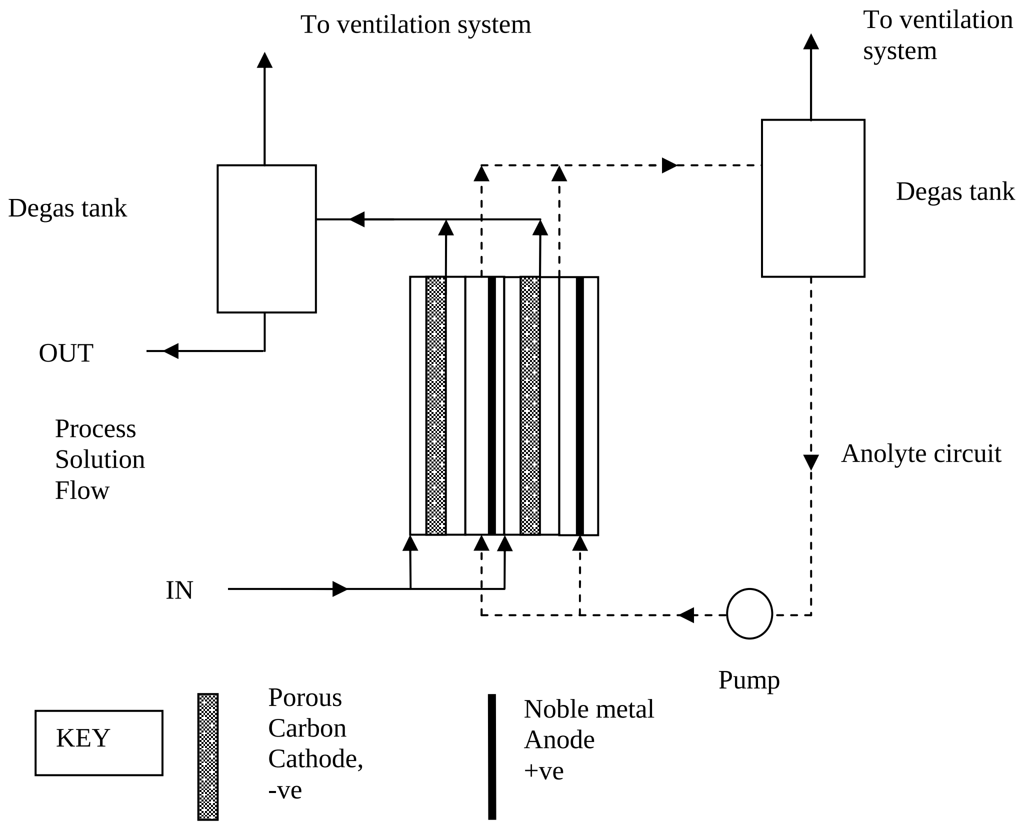

Figure 2: Schematic block diagram of the DFDX Electrochemical Cell