

WASTE MANAGEMENT EVALUATION FOR PWR FULL SYSTEM DECONTAMINATION

A. Valvasori
Nuclear Services Division
Westinghouse Electric Corporation
Pittsburgh, PA, 15230-0355
S. Hodges and R. Voit
LN Technologies Corporation
1501 Key Rd.
Columbia, S.C., 29201

ABSTRACT

A waste management evaluation has been performed for decontamination of an entire PWR primary circuit. A 5-step AP-CanDerem™ decontamination will generate 86 m³ (3050 ft³) of ion exchange resin waste. Cement solidification and resin dewatering have been used for decontamination waste disposal. The total waste processing and burial cost for solidification is at least twice as expensive as for dewatering. A combination of resin incineration, resin oxidation, and dewatering yield the most practical volume reduction.

INTRODUCTION

Chemical decontamination of nuclear reactor systems is an effective method of dose reduction and the current practice in the United States is the decontamination of reactor subsystems. The current trend is towards decontamination of the entire primary circuit to obtain the full dose reduction benefit. Unlike subsystem decontamination, a large volume of waste is generated by full system decontamination. A review of waste management techniques has been undertaken to identify the more feasible methods. This paper identifies the volume of waste generated by the full system decontamination of a Pressurized Water Reactor (PWR) using the AP-CanDerem process, and presents an evaluation of waste management technologies that may be employed.

DESCRIPTION OF THE DECONTAMINATION PROCESS

The dilute chemical decontamination process considered in this paper is a 5-step AP-CanDerem process. It is a multi-step approach consisting of alternate oxidizing and acidic dissolution cycles, beginning and ending with a dissolution step.

Alkaline permanganate (AP) is an oxidation treatment. It employs a dilute mixture of potassium permanganate and sodium hydroxide which oxidizes trivalent chromium in the oxide film to the soluble hexavalent form. Upon completion of the AP treatment, oxalic acid is added to destroy residual permanganate and the manganese dioxide formed during the AP step. After the AP destruction has been initiated, cation resin is used to provide the protons necessary to complete the reaction. The resin retains the cations from the AP reagents and the small amount of metals and radionuclides released from the oxide. If any residual oxalic acid is present in the system, it is removed by anion resin. It is assumed that all of the carbon dioxide produced during the destruction reaction escapes as a gas

and is not removed on the resin as carbonate. Based upon experience, this is a reasonable assumption.

Film dissolution occurs during the CanDerem step. CanDerem is a dilute, regenerative process which employs weak acids and a chelating agent. A process concentration of 0.1 wt % reagent is used. Regeneration is achieved by a sidestream flow of the system fluid through cation resin. The resin retains metals and radionuclides and releases the chelating agent. When the step is complete the reagent is removed by anion resin.

The waste resulting from the decontamination consists of ion exchange resin loaded with metals and radionuclides from the dissolved oxide film and with the decontamination reagents (which includes a chelating agent).

WASTE CHARACTERISTICS

The volume of ion exchange resin waste generated from a PWR full system decontamination is estimated in this study to be 86 m³ (3050 ft³). The waste is estimated to have an average activity loading of 72.9 uCi/ml. This study considers the full primary system decontamination of a standard four-loop PWR with a system volume of 357.7 m³ (94,500 gallons). The fuel is assumed to be removed, thus oxide contributions from the fuel are neglected. A boron concentration of 650 ppm is assumed to be maintained throughout the decontamination. The presence of boron creates a buffer effect. To attain a pH of 10.5 during the AP step, additional sodium hydroxide must be added to counter the buffer effect. A substantial amount of cation resin is required to remove the extra sodium upon completion of the AP steps. Additional oxalic acid must also be added during the AP destruction step to counter the buffer effect, and additional anion resin must be used to remove the oxalic acid.

The two primary materials of construction, 304SS and I600 are considered. The surface areas of 304SS and I600 in the system are estimated to be 2207 m² and 17,692

m² respectively, and include in-vessel nonfuel surfaces and out-of-vessel surfaces. The oxide film inventory is estimated to be 800 mg/dm² on 304SS surfaces and 80 mg/dm² on I600 surfaces, which corresponds to 319 kg of metal. The oxide film inventory is representative of a plant that is greater than 10 EFPY old. The oxide film on 304SS surfaces is assumed to contain 35% iron and 16% nickel. The oxide film on I600 surfaces is assumed to contain 18% iron and 47% nickel. The average corrosion rates of 304SS and I600 in the AP-CanDerem process are assumed to be 0.02 um/hr and 0.03 um/hr, respectively. A five-step application of the AP-CanDerem process is considered. The application times of each CanDerem and AP step are assumed to be 24 hours and 12 hours, respectively. A change in any of these conditions will change the waste volume estimate.

The waste is assumed to consist of strong acid cation and strong base anion resin, which are currently used in CanDerem applications. A 20% contingency of the resin requirement is included in the calculations. The higher capacity weak base anion resin was also considered in this study and would reduce the total waste volume to 73 m³ (2590 ft³). However, use of weak base anion resin has not yet been tested for this application.

The cation resin retains metals from oxide dissolution and base metal corrosion during the CanDerem step and the AP destruction step and retains cations from the AP reagent. Thus the species retained by the cation resin during an AP-CanDerem decontamination are:

- Fe³⁺ and Ni²⁺ from oxide dissolution
- Fe²⁺ and Ni²⁺ from base metal corrosion
- K⁺, Mn²⁺, and Na⁺ from the AP reagents

The anion resin is used for reagent removal upon completion of both the CanDerem and AP steps. Thus the species retained by the anion resin during an AP-CanDerem decontamination are:

- CanDerem reagent
- Residual oxalate⁻ from oxalic acid used for AP destruction and the oxalic acid used to counter the buffer effect of the boron in the system
- Chromate (CrO²⁻₄) from oxide dissolution and base metal corrosion during the CanDerem steps

The 86 m³ (3050 ft³) of resin estimated in this study consists of 13 m³ (470 ft³) cation resin for CanDerem regeneration, 24 m³ (870 ft³) anion rich resin for CanDerem reagent removal, 39 m³ (1370 ft³) cation resin for AP/per-manganate destruction, and 10 m³ (340 ft³) anion resin for AP reagent removal.

EVALUATION OF WASTE MANAGEMENT TECHNOLOGIES

The factors to be considered in disposal of waste include the volume of waste, the activity loading, the waste classification (Class A Unstable, Class A Stable, or Class B), and the concentration of chelating agents in the waste. In this study, resin oxidation, membrane filtration and resin incineration technologies have been evaluated and compared with the traditional solidification and dewatering methods.

SOLIDIFICATION AND DEWATERING

Two methods of processing decontamination waste resin have been successfully used in the past - solidification and resin dewatering. Solidification has been performed with cement to meet stability requirements of 10CFR61 and dewatering has been performed in high integrity containers (HICs), also to meet stability requirements.

Several waste liner or HIC and shipping cask combinations were evaluated for containing the processed waste and shipping it to disposal sites. To compare the relative costs of solidification and dewatering, price estimates have been prepared for processing of the waste and burial at the three following disposal sites: Barnwell, Richland, and Beatty. The following assumptions were used in evaluating the technical feasibility of and pricing for the feasible combinations.

- Waste volume and radionuclide activity loading.
- Solidification waste loading is 18 percent as recommended by the NRC.
- The waste is processed by a supervisor and a technician.
- The processing rate is 4 days per liner for solidification and 3 days per liner for dewatering.
- The transportation rate is \$1.51 per mile.
- The transportation distance from a plant in the northeastern United States to the burials sites is used.
- The shipping cask is not used as a process shield. It is on site for only 24 hours to load the process liner from storage into the cask.
- Burial pricing is based on 1989 published rates adjusted 6 percent per year to yield the anticipated rates in 1992. Out-of-compact fees of \$40 per ft³ are included in the pricing.
- Pricing is based on the use of polyethylene lined HICs or polyimpregnated concrete HICs.
- The State of Washington has approved the use of concrete barriers around a polyethylene container of Class B waste.

- Dewatered resin loaded with chelating agents cannot be buried at the Barnwell disposal site.

A comparison was made of the pricing at Barnwell, Beatty and Richland for 86 m³ (3050 ft³) of decontamination resin waste that has been solidified and dewatered. The least expensive option is to dewater the resin in a NUHIC-136QBS polyethylene container and bury it at the Richland site in a concrete culvert. The next least expensive option is to dewater the resin in the LN-131HQBS high integrity container and bury it at the Richland or Beatty disposal sites. Solidification options are approximately two times more expensive than the dewatering options.

RESIN INCINERATION

Resin incineration can be performed at an incineration processing facility. The decontamination resin waste would have to be dewatered at the site where it is generated and transported to the processing facility. An incinerator can process 455 kg (1000 lb) of organic resin per hour. The process can reduce the volume of resin by a factor of approximately 150.

The key factor in determining the feasibility of incineration is the radionuclide concentration of the waste following incineration. For this study, it was assumed that the decontamination would remove 6280 Ci (equivalent to 3454 Ci Co-60) of activity from the system. Based on previous PWR decontaminations, the distribution of activity on the resin is:

- CanDerem regeneration resin (cation) - 76%
- CanDerem reagent removal resin (anion rich) - 2%
- AP/permanganate destruction resin (cation) - 22%
- AP reagent removal resin (anion) - 0%

The equivalent Co-60 concentration on the CanDerem regeneration resin would be 5.7 Ci/ft³ before incineration and 855 Ci/ft³ after incineration. For the CanDerem reagent removal resin, the equivalent Co-60 concentration would be 0.08 Ci/ft³ before incineration and 12 Ci/ft³ after incineration. The equivalent Co-60 concentration on the AP/permanganate destruction resin would be 0.55 Ci/ft³ before incineration and 82.5 Ci/ft³ after incineration. Almost no activity would be present on the AP reagent removal resin.

Based upon these radionuclide concentrations, incineration is only practical for the resin from the reagent removal steps. Equivalent Co-60 concentrations greater than 15 Ci/ft³ are very difficult to handle and transport.

Resin incineration could be used to reduce the volume of CanDerem and AP reagent removal resin from 1208 ft³ to 8 ft³. This would reduce the total waste resin volume from 3050 ft³ to 1842 ft³ - a reduction of approximately 40%.

RESIN OXIDATION

Organic ion exchange resin can be destroyed by wet resin oxidation using hydrogen peroxide. While destroying the resin, the oxidation process also destroys the chelating agents loaded on the resin. Currently, test equipment is available that can process 0.14 m³ (5 ft³) of ion exchange resin. During testing, the resin oxidation process has reduced the waste volume by a factor of 10.

In this system, resin and water is added to the reactor vessel and heated to a minimum of 100°C (212°F). In the testing, Fe²⁺ in the form of ferrous sulfate was used as a catalyst. Actual decontamination waste resin contains Fe²⁺ so the addition of a catalyst will not be necessary. The hydrogen peroxide is injected into the reactor vessel at a controlled rate. As the resin dissolves, an off-gas of CO₂ and steam is generated. The off-gas is cooled and dehumidified using a heat exchanger followed by a gas scrubber, condensate tank and demister. The process is monitored using a gas analyzer and function recorder. Completion of the resin oxidation reaction is indicated by a decrease in carbon dioxide generation and an increase in oxygen generation. Excess liquid is evaporated and the remaining slurry is pumped out of the vessel into a waste processing container. The slurry consists of the metals and radionuclides loaded on the resin. The resulting slurry waste must then be stabilized according to 10CFR61 guidelines. Solidification in cement may be used for stabilization.

As with resin incineration, the key factor in determining the feasibility of resin oxidation is the radionuclide concentration of the waste following resin oxidation. Based on the distribution of activity on the resin described above, and a volume reduction of 90%, the equivalent Co-60 concentration on the CanDerem regeneration resin would be 57 Ci/ft³ after oxidation. The equivalent Co-60 concentration on the CanDerem reagent removal resin would be 0.8 Ci/ft³ after oxidation. For the AP/permanganate destruction resin the equivalent Co-60 concentration would be 5.5 Ci/ft³ after oxidation. Almost no activity would be present on the AP reagent removal resin.

Based upon these concentrations, and a handling and transportation limit of 15 Ci/ft³, resin oxidation is feasible for resin from the reagent removal and AP/permanganate destruction steps. Resin oxidation could be used to reduce the volume of this resin from 2580 ft³ to 258 ft³. This would reduce the total waste resin volume from 3050 ft³ to 722 ft³ - a reduction of approximately 75%. A combination of resin oxidation and resin incineration would produce a greater reduction in waste volume. If reagent removal resins are treated by incineration and AP/permanganate resin by oxidation, the overall waste volume could be reduced from 3050 ft³ to 610 ft³ - a reduction of 80%.

The resin oxidation process is still in the testing stage. Equipment for processing large quantities of actual waste have yet to be constructed and tested. Another factor to consider is that resin oxidation is a slower process than resin incineration.

MEMBRANE FILTRATION PROCESSING

Membrane filtration processing is a method for removing ionic species from solution. Unlike the methods which are used to process ion exchange resin, membrane filtration is considered as an alternative to ion exchange. The filtration is performed by continuously recirculating the water to be processed through spiral wound membrane filtration modules. The purified effluent flows from the membrane modules to a drain or a storage tank.

Membrane filtration can, in some cases, be used as a substitute for ion exchange resin processing. In an AP-CanDecon process, ion exchange is used for four operations - CanDerem regeneration, CanDerem reagent removal, AP destruction, and AP reagent removal. Since the mechanism of the ion exchange process is required during the CanDerem regeneration and the AP destruction steps, membrane filtration can only be used during the reagent removal steps.

An analysis of volume reduction, operating parameters, tank requirements, and processing efficiency was performed to evaluate the effectiveness of a membrane filtration system for decontamination reagent removal phases. Membrane filtration can reduce the volume of liquid waste by approximately 75%. This yields a greater volume of waste than does ion exchange of the decontamination solution. The membranes used to filter the metals and radionuclides from the solution must also be disposed of. As membrane filtration yields more waste than ion exchange, it is not feasible for processing decontamination solution.

PROCESSING EXPERIENCE WITH DECONTAMINATION WASTE

Until 1989, cement solidification processing of chemical decontamination waste resin has been the only method used for LOMI and CanDecon applications. Then, in 1989 after the NRC approved a polyethylene lined high integrity container, resin dewatering became a viable option for processing Class B resins. The dewatering method has been used at Commonwealth Edison's LaSalle Station for LOMI waste and at Duquesne Light's Beaver Valley Power Plant for AP-CanDecon type waste.

The dewatering option in approved high integrity containers eliminates the concerns that the NRC has expressed about the stability of chemical decontamination waste resins solidified in cement. The NRC has expressed concern about waste loading and about characterization of waste resin from chemical decontamination processes. Be-

tween June, 1987 and October, 1989, the following abnormalities in cement solidification of decontamination waste were discovered.

- A minor bulge was discovered in a solidified LOMI liner. An increase in diameter of about 2% was observed.
- A larger than expected final product volume was observed in a solidified LOMI liner.
- Early thickening in a LOMI liner occurred during processing. The thickening resulted in a product which could not be certified stable because not all of the required chemicals for stabilization were added.
- Formation of a "gel" product (calcium picolinate) in a LOMI liner. Destructive examination showed the processed waste to be unacceptable because un-solidified pockets of the gel product were found. All of the solidification chemicals were added as the problem was not evident during processing, and the liner displayed normal curing conditions.
- Formation of a "gel" product (calcium picolinate) in LOMI waste was observed during preparation of test solidification samples. This eliminated the use of the intended formulation. The waste had to be stored until a new formula was developed.

These occurrences represented one-half of the chemical decontamination liners processed in the United States in this time period. The problem seems to be specific to LOMI waste resin. No problems have been identified with cement solidification of CanDecon waste resin.

Various tests have been performed by waste vendors and by EPRI to correct problems with cement solidification of LOMI resin. The formulations which had the field problems had passed all of the laboratory certification tests prior to use. Therefore destructive testing of a full scale final product is also indicated. This test has not yet been completed. Since cement solidification has such uncertainties associated with it and it is the more expensive option, the dewatering processing method in NRC approved high integrity containers is likely to be the method used for processing future decontamination waste resin.

SUMMARY AND CONCLUSIONS

The volume of waste generated by the AP-CanDerem decontamination of an entire PWR primary circuit has been identified. The solidification, dewatering, resin incineration, resin oxidation and membrane filtration processes for managing the waste have been evaluated.

The 5-step AP-CanDerem decontamination of a four-loop PWR primary circuit will yield approximately 86 m³ (3050 ft³) of ion exchange resin waste. The ion exchange resin is used in four phases of the decontamination: CanD-

erem reagent regeneration, CanDerem reagent removal, AP/permanganate destruction and AP reagent removal. The thickness and composition of the oxide film, the volume of the system to be decontaminated and the boron concentration are a few of the factors affecting the waste volume.

Solidification and dewatering are two traditional methods that have been used to process decontamination resin waste for disposal. Solidification is approximately two times more expensive than dewatering, and problems have been associated with cement solidification of LOMI decontamination waste. For these reasons, dewatering is the more feasible of the two methods for decontamination waste processing.

Resin incineration, resin oxidation and membrane filtration have not yet been used to process decontamination waste. Membrane filtration, considered as an alternative to ion exchange, is not feasible. It would yield a greater volume of waste than does ion exchange processing. Resin inciner-

ation has a volume reduction efficiency of 99.3%. It may be feasible for processing of the reagent removal resins and would reduce the total waste volume by 40%. Resin oxidation has a volume reduction efficiency of 90%. Oxidation of the AP/permanganate destruction and reagent removal resins may be feasible and would reduce the total waste volume by 76%. However, resin oxidation is not yet available for commercial use.

A combination of the resin incineration and oxidation processes would provide the greatest volume reduction. Incineration of the reagent removal resins and oxidation of the permanganate destruction resins would reduce the total waste volume by 80%. The CanDerem regeneration resin could be dewatered and buried in a high integrity container. A detailed evaluation of the total cost of processing and burial will be necessary to determine the most economic combination of waste management techniques.