

WASTE MANAGEMENT ASPECTS OF ENTIRE PWR LOOP DECONTAMINATION

A. P. Murray
Research and Development Center
Westinghouse Electric Corporation
Pittsburgh, PA 15235-5098

J. Roesmer
System Technology Division
Westinghouse Electric Corporation
Pittsburgh, PA 15230

ABSTRACT

The waste management parameters for decontamination of an entire PWR primary circuit have been determined for dilute alkaline- permanganate/citric acid (APCA), LOMI, ozone and cerium acid process variations. APCA processes generate the largest waste volumes; over 140 m³ (5000 ft³) in some cases. This represents a potential disposal cost of one million dollars. The cation regeneration column makes the greatest contribution to the disposal volume. In contrast, the LOMI process generates approximately half as much waste, but it is expected to contain relatively high metal concentrations (200-800 ppm). The ozone and cerium acid processes produce the least waste, usually under 45 m³.

These waste volume estimates represent considerable fractions of a utility's annual disposal volume. Consequently, improved waste processing technology is required, and several approaches are suggested.

INTRODUCTION

Decontamination of nuclear reactors and equipment is becoming increasingly important as the nuclear industry matures. The present trend is towards decontamination of the entire primary loop, as opposed to isolated components. This approach has the benefits of minimizing the use of nozzle seals, hoses, and temporary piping, but it adds complicating factors such as large fluid volumes, numerous materials/metals, and fuel concerns. The waste management issues and associated costs are frequently overlooked in the planning of a decontamination campaign, but become major concerns for an entire, primary system application. This paper presents analyses on the waste generation and disposal aspects for dilute chemical decontamination of a large Pressurized Water Reactor (PWR), using several different processes.

DESCRIPTION OF THE DECONTAMINATION PROCESSES

There are three categories of dilute chemical decontamination processes for PWR applications:

- dilute APAC variations
- ozone methods
- inorganic acid treatment

APAC represents **A**lkaline **P**ermanganate **A**mmonium **C**itrate (1). This is a multi-treatment approach consisting of alternating cycles of oxidation (for trivalent chromium removal by oxidation to chromates) followed by acidic conditions (for oxide dissolution and contamination removal). The literature presents three- and five-step variations, often with proprietary reagent formulations. For these analyses

and discussions, the paper defines AP to be a mixture of 50% potassium permanganate and 50% sodium hydroxide, and a 50% reconstitution quantity is used to account for permanganate reaction and decomposition. The three-step process analyses assume a .5% concentration for the AP solution, while the five-step variation uses a .1% value. These are based upon process effectiveness results reported in the literature. The AC-like dissolution treatment often contains organic acids and multidentate chelants, such as ethylenediaminetetraacetic acid (EDTA). For this paper, it is defined as a .1% citric acid solution, using cation ion exchange resins to regenerate the reagent by metal and radionuclide removal. The .1% concentration is used for both the three- and five- step variants of the Alkaline Permanganate-Citric Acid ("APCA") process. This type of process has been extensively used for plant applications, and includes commercial processes such as Can-Decon and Citrox (2,3,4).

The LOMI process represents an interesting modification of dilute APAC processes (5). LOMI represents Low Oxidation-state Metal Ion, and uses vanadium (II) to increase the dissolution reaction kinetics. For PWR applications, the LOMI process normally consists of the following steps (1):

- AP- a sodium hydroxide (.05%) and potassium permanganate (.05%) solution
- NP- a nitric acid (.01%) and potassium permanganate (.05%) solution.
- LOMI reagent - a solution of vanadium (II) (.05%), picolinic acid (.1%), and formic acid (.4%)

The NP step preferentially dissolves trivalent chromium on stainless steel oxide surfaces, while the AP step is more specific for films on high nickel alloys. For both permanganate applications, a 50% reconstitution quantity is assumed. A small amount of oxalic acid is added before the LOMI step to destroy the oxidizing agent. Ion exchange resins are only used after the oxalic acid addition and at the conclusion of the LOMI step, as a final cleanup and rinse.

The second group of processes substitute ozone for the AP treatment (6,7). Ozone is produced in a silent-arc generator, and introduced into the coolant via a contactor (usually a packed column). Thus, the radioactive oxide film is predominantly exposed to dissolved ozone at low temperatures. No pH adjustment is necessary. After sufficient time for chromium oxidation, the ozone treatment is discontinued, the temperature is raised, and a dilute acid solution is introduced to dissolve the oxide film. As before, this analysis assumes that citric acid, at .1%, is the dissolution reagent. Therefore, ozone application results in a two-step process, although ozone, by itself, does not contribute to the waste processing.

Inorganic acids constitute the third group of reagents. Sulfuric, nitric, sulfamic, and cerium acids fall into this category (1). These represent true one-step decontamination reagents, and the acids are sufficiently powerful to remove the trivalent chromium in the oxide film without any pretreatments. These reagents tend to be more concentrated than the organic acids in order to overcome passivation effects on stainless steels. For the purposes of this paper, the analyses use a 6% solution of cerium acid as a representative reagent, because of its documented efficacy on PWR samples (8).

BASIS FOR THE WASTE MANAGEMENT ANALYSES

This study considers a standard four-loop PWR design, with a primary coolant volume of 378 m³ (100,000 gallons), and a standard shutdown concentration of 2000 ppm boron. For the present purposes, the fuel is assumed to be removed, and fuel crud contributions to the activity and waste volumes are neglected. The corrosion product oxide film on primary surfaces is estimated to be 5 microns thick. This represents an older plant, and corresponds to some 395 kilograms of oxide (~280 kilograms of metal). Specific activities vary considerably based upon published analyses and no generic estimate can be made. Ion exchange is used for waste treatment for the APCA, LOMI, and ozone processes, while evaporation and direct solidification are the preferred approaches for treating the waste from the cerium acid process.

RESULTS

Table I summarizes the results of the analyses. Figure 1 graphically presents the results, and includes a four-step

LOMI process for comparison. The dilute APCA processes generate 135-150 m³ of waste resin. This is some 40% of the primary loop volume, and it is in agreement with the 30-50% value calculated by assuming a directly proportional scale-up of steam generator channel head decontamination results (1,9). Approximately 50% of the decontamination waste volume accrues from metal removal during the citric acid regeneration and oxide dissolution treatment. Surprisingly, manganese accounts for 20% of the total metal loading.

Manganese dioxide is generated both as a byproduct of the chromium oxidation and as a permanganate

TABLE I

Process Waste Generation Estimates (5 μm film)

Process	Waste Volume, m ³		Waste Volume Percentage	
	With Boron	Prior Boron Removal	With Boron	Prior Boron Removal
APCA, 5 step	148.5	137.4	39	36
APCA, 3 step	138.2	148.6	37	39
LOMI	69.5	79.8	18	21
Ozone	60.3	92.1	16	24
Cerium acid: Direct solidification*	34	65.8**	9	17
Evaporation†	78.7	101.4	21	27

decomposition (reduction) product; the subsequent citric acid step only partially dissolves the manganese precipitate. Reagent removal represents another 25% of the waste resin volume; treatment of the citric acid solution consumes two-thirds of this value. The remaining 25% of the waste volume accrues from boric acid in the coolant. The AP oxidation step requires strongly alkaline conditions (pH > 10) for effectiveness. Each AP application generates additional waste from neutralization if boric acid remains in the coolant. This effect is of a similar magnitude as the resin volume required for boric acid removal. Consequently, boric acid effects cannot be neglected.

The three step LOMI process generates 70-80 m³ of waste resin, or about 40-50% less than the APCA process. Most of this reduction is attributable to the use of mixed bed resins for metal removal at the process' conclusion, instead of a low capacity, regeneration cation bed. Therefore, dissolved metal removal only consumes 15-20% of the resin volume. Formic acid removal occupies approximately 30% of the resin usage, and boric acid effects account for ~40%.

The ozone process produces a waste volume in the 60-90 m³ range, which is 30-50% lower than the dilute APCA processes. The reduced volume occurs because the reactions of the oxidation reagent make a negligible contribution to the dissolved solids concentration, no neutralization is necessary, and no manganese precipitation occurs.

The cerium acid approach uses evaporation or direct solidification technology, and ion exchange is relegated to a minor role (i.e., recycle water polishing). Thus, the waste volumes tend to be lower than the other processes, particularly for the direct solidification approach (as low as 34 m³).

DISCUSSION

The estimates presented in Table I are based on a 5 μ m film thickness, which represents an older plant (≥ 10 EFPY*). Improved coolant chemistry guidelines (12) produce thinner corrosion product oxide films, sometimes as low as a 1 μ m average. Table II presents waste volume estimates for the 1 μ m film thickness condition. A comparison with Table I indicates that most of the estimates decrease because the corrosion product inventory decreases. This effect is greatest for the APCA processes because of the cation regeneration column. Figure 2 graphically summarizes the film thickness effect upon the waste volumes.

The Cation resin volume represents the largest contribution to the APCA process waste. Citric acid regeneration is mandatory for maintaining process kinetics and for avoiding process upsets, such as precipitation. In dilute acid solutions, cation column capacity decreases rapidly with decreasing pH values, and this effect is accelerated by the presence of complexing agents such as citric acid and EDTA. Consequently, the actual resin capacity is a fraction of the theoretical capacity (usually in the 10-20% range (1)). Figure 3 illustrates the effect of cation column efficiency upon the APCA process waste volumes. Clearly, the effect is very pronounced. These estimates assume an efficiency of 20% (6.7 g Fe(III) per liter

of resin), based upon published experimental results (11). It is unlikely that cation resin chemistry can be modified to significantly improve these capacities.

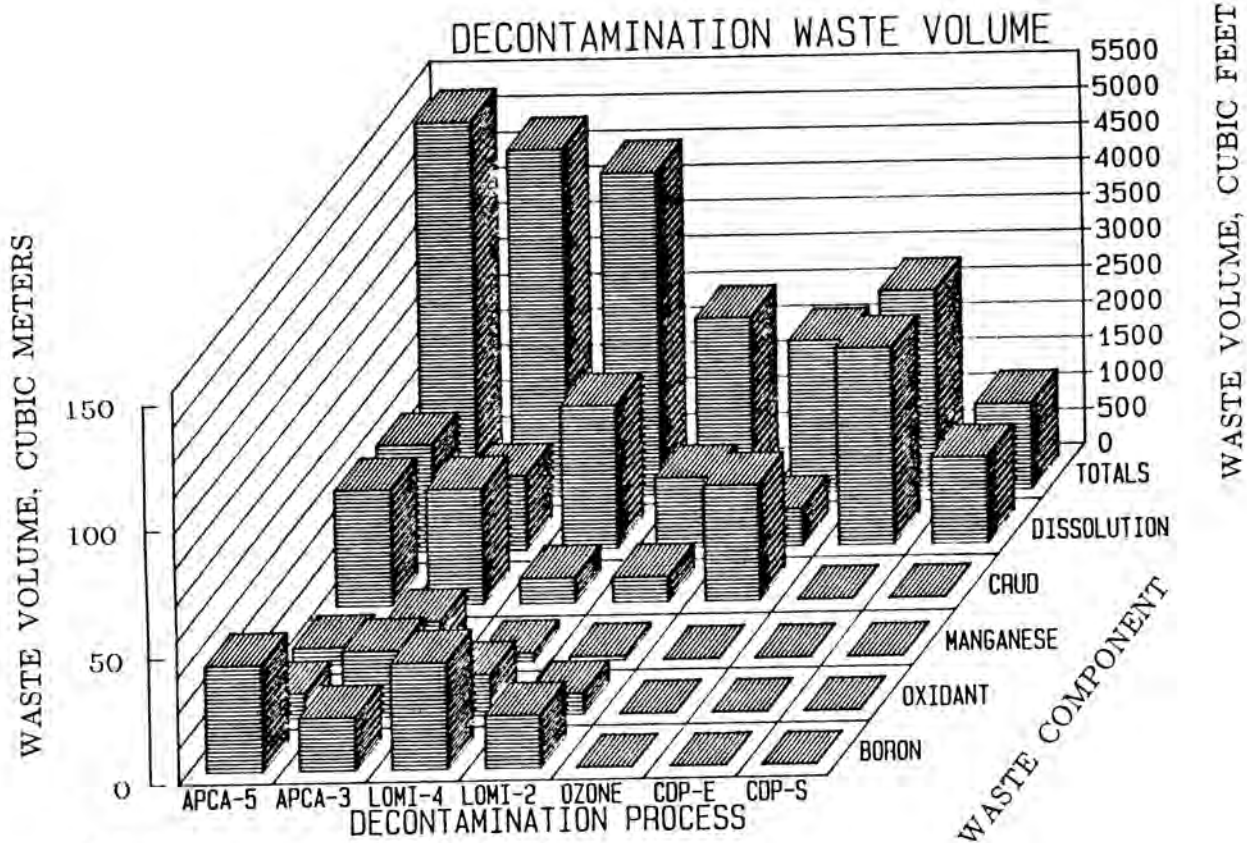
Anion resin regeneration of the acidic solution has been suggested as an improvement over the cation resin approach. Anion regeneration removes the entire metal citrate complex, and releases fresh citric acid to the solution. However, this only increases the iron loading to approximately 7 g/L. This represents a small improvement, but close chemistry control is required.

The anticipated plant application conditions also impose a limit upon solution regeneration. Typical PWR plant ion cleanup systems have flow rates in the 200-500 gpm range. These correspond to time constants of 200-500 minutes for the primary coolant. Therefore, there is a high probability that the decontamination effect will be completed before the solution is completely regenerated, and, hence, a considerable fraction of the dissolution metal cations would be removed as a complex on the citric acid removal resin. Figure 4 illustrates this effect. Note that 100% represents no solution regeneration, while 0% represents complete regeneration. Present day applications of regenerative processes typically contain ~100 ppm of dissolved metals when the reagent removal step begins (13). This corresponds to ~10% and ~50% removal on the anion column for the 5 μ m and 1 μ m film thicknesses, respectively.

The LOMI PWR process waste principally accrues from two factors: the formate content and the boric acid. LOMI formulations containing approximately 50% less formate have been developed, and this would reduce the waste volume by ~15%. Iron and manganese removal use a cation resin within a mixed bed column, and, thus, a small waste volume results (~15% of the total). Significantly, relatively high dissolved metal concentrations will occur during the LOMI treatment: H800 ppm and ~200 ppm for the 5 μ m and 1 μ m film thicknesses, respectively. Consequently, the process would benefit from metals removal/regeneration treatment and intermediate rinsing after the NP/AP treatments. Finally, a LOMI process variation without an AP treatment (such as LOMI-NP-LOMI) would eliminate the need for boric acid neutralization and reduce the waste volume considerably. Fig. 4. Simultaneous metal complex and citric acid removal at the termination of the process.

Permanganate decomposes into manganese during the AP and NP treatments. Figure 5 compares the effects of the AP formulation and total decomposition percentage upon

* EFPY = Effective Full Power Years.



- APCA-5: Five-step APCA process
- APCA-3: Three-step APCA process
- LOMI-4: Four-step LOMI process
- LOMI-2: Two-step LOMI process
- Ozone: Ozone process
- CDP-E: Cerium acid using neutralization/evaporation
- CDP-S: Cerium acid with direct solidification
- Boron: Boron/boric acid contribution
- Oxidant: Contribution from oxidant removal
- Manganese: Manganese effect (from AP or NP steps)
- Crud: PWR oxide film contribution
- Dissolution: Contribution from dissolution reagent removal

Fig. 1. Estimated Waste Volumes from Entire Primary System Decontamination (5 μm Film).

TABLE II

Process Waste Generation Estimates (1 μm film)

Process	Waste Volume, ft^3		Waste Volume Percentage	
	with Boron	Prior Boron Removal	with Boron	Prior Boron Removal
APCA, 5 step	111.7	100.6	30	27
APCA, 3 step	73.1	111.8	27	30
LDMI	61.3	71.6	16	19
Ozone	23.4	55.3	6	15
Cerium acid:				
Direct solidification	33.8	65.7*	9	17
Evaporation**	78.2	100.9*	21	27

* Boric acid removed by ion exchange.

** Neutralize and evaporate to a 40 wt% concentration.

a. EFPY = Effective Full Power Years.

the waste volume, and assumes that any manganese precipitates are subsequently dissolved in citric acid and removed upon a cation column operating with 20% efficiency. The waste volume rapidly increases with the decomposition quantity and permanganate concentration. For APCA-like processes, the AP formulation should be optimized to minimize manganese precipitation. This is an arduous task, and significant permanganate decomposition and precipitation will probably still occur at the optimum condition (14).

Boric acid effects upon the waste volumes are on the order of 28 m^3 . Boric acid is used as chemical shim control in Westinghouse PWR's, with a typical shutdown concentration of 2000 ppm boron ($\sim 1.14\%$ boric acid, the assumed basis). After fuel removal and reflooding of the system with deionized water, some 800-1000 ppm of boron will still remain. Therefore, the effects of boric acid, from either removal or neutralization, are not negligible. There are only three approaches available to decrease the effect:

1. remove and store the boric acid solution
2. use lower boron concentrations
3. design the chemical decontamination processes to avoid large pH changes and neutralizations.

The first approach substitutes critical path time for a lower waste volume. The second approach can be achieved

with the use of boron-10, which results in a 5-10 fold lower boron concentration during all aspects of the fuel cycle. The third approach consists of processes that are effective under acidic conditions, and it is represented by the ozone and cerium acid processes.

The ozone process achieves a lower waste volume than the APCA process for the following reasons:

- no AP reagents are required
- no manganese precipitation occurs
- the oxidation reagent is volatile, and does not contribute to the waste
- no boric acid neutralization is necessary

The regeneration and citric acid removal columns are essentially identical to those of the APCA process, and have been discussed previously. Substitution of ozone for AP appears to be a logical development of the APCA process, and offers a sizable waste volume reduction. With optimization, a 12-15% waste volume percentage appears achievable. Obviously, further developmental work is necessary, particularly relating to the plant engineering aspects of handling gas evolution in the primary system.

The cerium acid route offers the best waste management approach of the three decontamination processes, and the volume estimates are essentially invariant with the plant conditions. It is unlikely that the waste volume can be reduced significantly below these estimates. Cerium and inorganic acids appear to be the best approach for preparing plants for decommissioning purposes. Routine operating plant use requires a complete corrosion evaluation because of the potentially aggressive nature of the reagents.

POTENTIAL IMPROVEMENTS

The estimates from these analyses have to be put into perspective. A typical PWR generates approximately 280 m^3 of low level waste annually, of which some 75 m^3 constitute wet wastes (i.e., ion exchange resins (10)). Consequently, the resin volume estimates of Table I constitute a significant increase in both waste type and quantity, which will affect shipping and burial ground allotment. Furthermore, the waste volume represents a considerable cost by itself (i.e., excluding processing/equipment expenses). Burial ground, shipping, and analysis/certification charges are rapidly approaching $\$3500/\text{m}^3$ ($\$100/\text{ft}^3$). If one adds to this the resin procurement expenses, then a 140 m^3 waste volume represents approximately a million dollars. Federal and burial site regulations also govern the complexing agent content of radioactive waste. Unsolidified waste containing over .1% complexing agents must be segregated from other wastes and a concentration above 8% is prohibited at the Barnwell site. These rules consider citric acid, oxalic acid, and EDTA as complexing agents. Clearly, further process

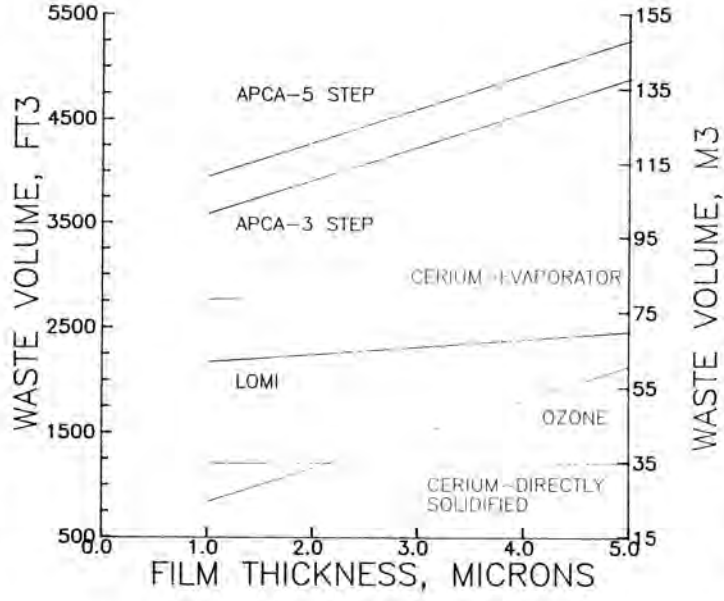


Fig. 2. Crud Inventory and Process Waste Volumes.

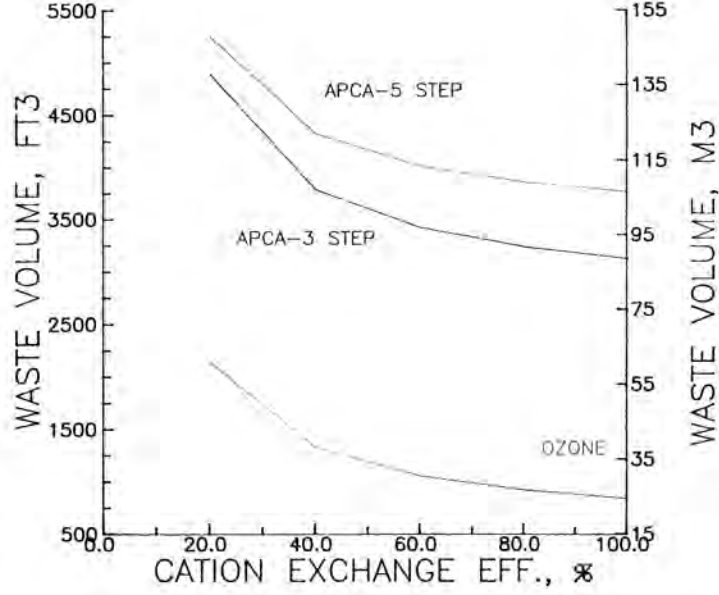


Fig. 3. Effect of Cation Column Efficiency Upon APCA Process Waste Volumes.

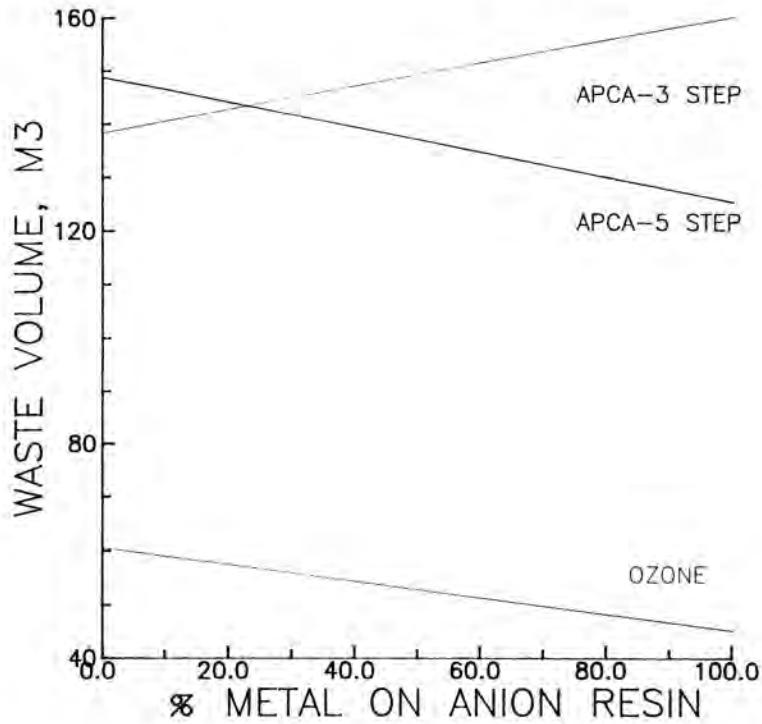


Fig. 4. Simultaneous Metal Complex and Citric Acid Removal at the Termination of the Process.

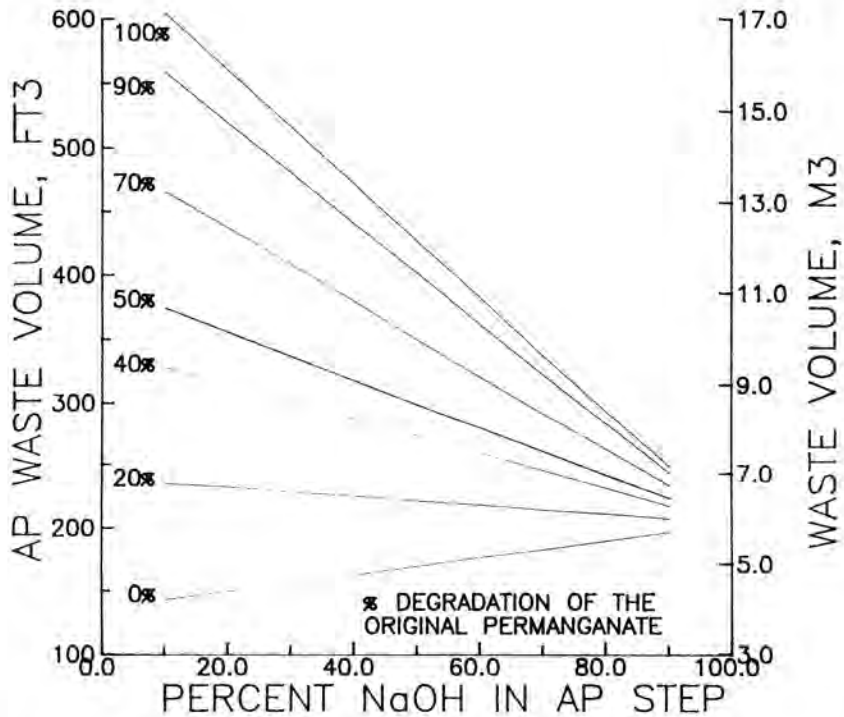


Fig. 5. Resin Waste Volume From Different AP Formulations With Varying Decomposition Quantities.

development and refinement is necessary, and careful planning must be made for the decontamination campaigns.

The estimates are analyzed with this perspective in mind. The APCA processes are the most developed approaches, are supported by extensive corrosion testing and results, and have had the most plant applications and experience. Unfortunately, as Table I indicates, APCA processes also generate the most waste; therefore, waste volume reductions are desirable. Several improvements are capable of achieving this objective. First, feed and bleed operations can be used to transfer reagent containing coolant to a holding tank, where it can be treated in batches. The treatment can be by evaporation (forced recirculation evaporators usually achieve 40% total solids concentration without any problems, versus a 2-5% equivalent concentration for ion exchange resins). Such concentration levels exceed the Barnwell limit, and such wastes must be disposed of at the Western burial sites.

A second approach destroys the organic acid content of APCA processes by oxidation. This removes citric acid as a dissolved solid and a burial site concern. Thus, the removal resins only perform a polishing function on the 10-20% of the reagent that cannot be readily reacted or removed from the system by any other means.

The third approach uses advanced technologies to reduce the waste volume. These technologies are:

- electrolysis/electroplating
- membranes
- direct solidification
- vitrification

Electrolysis substitutes a porous electrode reactor for the ion exchange resins, and has the greatest potential for metal cations and radionuclides. Tests at Westinghouse have achieved the continuous removal of over 40% of the dissolved iron in a cerium acid-like solution. In contrast, cation exchange resins are completely ineffective under the same conditions.

Membrane effectiveness depends strongly upon its selectivity between the different reagents. Hyperfiltration and ultrafiltration membranes are the best choice, but, at the present time, membranes appear to be useful only as a substitute for ion exchange resins during the boric acid removal step (15).

Direct solidification neutralizes and coagulates the solutions. Several tests have achieved volume reductions comparable to evaporation (i.e., 35-45 wt% equivalent). The residue is a white deposit amenable to filtration and dewatering. If the solidification is performed in the presence of boric acid, then the deposit is amenable to vitrification. Vitrification in the 500-1000°C range thermal-

ly decomposes any organic constituents in the waste and achieves the lowest waste volume possible; some 11 m³ for citric acid solutions.

Further developmental work and testing is required on all of these alternate technologies. Significantly, these approaches require innovative approaches to the handling of large, batch volumes of radioactive fluids at the plant site. The net effect of all of these improvements is a waste volume percentage decrease to ~30% for APCA-like processes.

SUMMARY AND CONCLUSIONS

The waste management aspects of decontaminating an entire PWR primary circuit have been determined for the following processes: dilute alkaline permanganate - citric acid (APCA)

- LOMI (AP-NP-LOMI)
- ozone - citric acid
- cerium acid

For large scale, PWR decontamination, the APCA process generates the greatest radwaste volume: some 140 m³ (5,000 ft³). This corresponds to a disposal expense of approximately one million dollars. The cation resin volume accounts for 50% of the waste; the remainder is evenly divided between reagent removal and boric acid effects. Evaporation, reagent destruction, electrolysis and bleed/fill operation are viable alternatives to ion exchange technology for this process. The magnitude of the estimated APCA process waste clearly necessitates further improvements in volume reduction.

The LOMI process generates 70-80 m³ of spent ion exchange resin, almost half of which is associated with the neutralization or removal of boric acid. The LOMI volumes are lower because the metals (iron from the oxide film and manganese from permanganate) are removed on a cation resin under near neutral conditions. However, the LOMI dissolution step is expected to contain large concentrations (200-800 ppm) of dissolved metals.

The ozone and cerium acid processes offer significant waste volume reductions (60 and 35 m³, respectively). Ozone replaces the AP treatment, and eliminates the associated manganese and boric acid neutralization problems. Cerium acid represents a true one-step reagent, and benefits from its direct solidification capability. Both processes should be investigated further. In particular, an ozone process is a logical improvement of the APCA approach.

Finally, this analysis has only considered the waste management issues of entire loop decontamination. Obviously, corrosion, system, and equipment evaluations and analyses are also necessary prior to a plant application.

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