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DECONTAMINATION IMPACTS ON SOLIDIFICATION*

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INTRODUCTION

The increased occupational exposure resulting from the accumulation of activated corrosion products in the primary system of LWRs has led to the development of chemical methods to remove the contamination.

In the past, the problem of enhanced migration of radionuclides away from trenches used to dispose of low-level radioactive waste, has been linked to the presence, at the disposal unit, of chelating or complexing agents such as those used in decontamination processes. These agents have further been found to reduce the normal sorptive capacity of soils for radionuclides. The degree to which these agents inhibit the normal sorptive processes is dependent on the type of complexing agent, the radionuclide of concern, the soil properties and whether the nuclide is present as a complex or is already sorbed to the soil. Since the quantity of reagent employed in a full system decontamination is large (200-25,000 kg), the potential for enhanced migration of radionuclides from a site used to dispose of the decontamination wastes should be addressed and guidelines established for the safe disposal of these wastes.

BACKGROUND

In December, 1982 the NRC rule on the "Land Disposal of Radioactive Waste, 10 CFR Part 61" became final. This rule generally defines those wastes which are acceptable for disposal in a shallow land burial site and establishes a waste classification system and minimum performance objectives for each class of waste. The rule makes provisions also for the disposal of large quantities of decontamination wastes.

> "The Commission has placed on the disposal site license applicant the responsibility for describing the conditions for disposal of waste containing chelating agents. If approved by the Commission, site-specific requirements will be placed on the disposal facility licensee. At this time the waste generator will be required only to identify such wastes in the information contained on the shipping manifest."

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Existing sites' licenses such as that for the disposal site at Barnwell, South Carolina, contain more specific requirements for the disposal of wastes containing more than 0.1% by weight chelating agents. At Barnwell wastes containing between 0.1% and 8% by weight chelates must be solidified in an approved medium and segregated from Class B and C wastes. The Beatty, Nevada, site requires that wastes containing more than 1% by weight chelating agents be segregated from all wastes by ten feet of soil. At the Hanford site in Richland, Washington wastes containing greater than 1% by package volume of these agents must be segregated from other wastes by ten feet of soil.

These requirements, both those of the NRC for the development of site-specific criteria and those in existence at operating sites, have come about as a result of problems encountered in the past with waste containing organic complexing agents.

As early as 1965[1] it was noted that trace quantities of some radionuclides were migrating from radioactive waste disposal trenches at Oak Ridge National Laboratory. These trenches had been used to dispose of both liquid and solid wastes. The form (solid or liquid) in which the complexing agents were disposed of is generally unknown. Cobalt-60 levels were as high as 10^5 dpm/g* in the soil and 10^3 dpm/mℓ in the water at about 100 yards from one disposal pit (Trench 7). Lower concentrations were measured near other disposal areas (Pit 4 and Trench 5). The enhanced migration may have been due to many factors inherent to the site. These include a large annual rainfall, shallow groundwater levels and the presence of numerous fractures in the rock. However, laboratory studies[2] and analyses of actual water taken from the site indicated that organic complexing agents reduced the sorptive capacity of the host media and contributed to the movement of activity from the disposal trenches.

In 1972, monitoring samples collected near burial trenches at Maxey Flats revealed increased levels of radioactivity. While there is uncertainty about how movement occurred, there was extensive movement of ^{238}Pu and ^{239}Pu several hundreds of feet from the original disposal trenches.[3] Work done by various laboratories[4-7] has led to the conclusion that the enhanced migration observed at Maxey Flats was in part due to the presence of organic complexing agents such as EDTA.

In the past, the problem of enhanced migration of radionuclides away from trenches used to dispose of low level radioactive waste, had been linked to the presence of chelating or complexing agents present in the disposal unit. The reagents found to enhance migration or to decrease the sorptive capacity of soils are typical of those that may be employed in processes being developed to decontaminate LWRs. The actual hazard posed to the public will depend on the waste (type and quantity), the disposal site properties and the way the waste is managed prior to disposal.

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*dpm/g = disintegrations per minute/grams of soil.

WASTE CLASSIFICATION AND CHARACTERISTICS

All low-level radioactive waste destined for disposal in a Shallow Land Burial (SLB) site must comply with the minimum criteria given in 10 CFR Part 61 for Class A wastes. In addition, if the waste classification is Class B or Class C the waste must be stabilized and for Class C wastes, intruder protected. One of the first concerns with decontamination wastes is the waste classification. The rule, 10 CFR Part 61, specifies the waste class by means of radionuclide specific concentrations in the waste.* Waste containing only the long-lived radionuclides listed in Table 1(a), in which the concentration does not exceed 10% of the value listed in Table 1(a) are Class A. Wastes whose concentration exceeds 10% of the values listed but does not exceed the maximum values are Class C wastes. If wastes do not contain the long-lived radionuclides listed under Table 1(a), then the waste classification is determined from Table 1(b) in the following manner. Class A waste are those wastes in which the concentration of the short-lived radionuclides does not exceed that given in Column 1. Class B limits are listed in Column 2 and Class C limits in Column 3. Any wastes whose concentration exceeds the concentration limits in Table 1(a) or Column 3 of Table 1(b) are generally not acceptable for near surface disposal.

If the wastes contain mixtures of long-lived and short-lived radionuclides, the classification is determined from Table 1(b), if the concentration of the long-lived radionuclides does not exceed 10% of the value given in Table 1(a). When the concentration of the long-lived radionuclides exceeds 10% of the value given in Table 1(a) but does not exceed the limit given in Column 3, [Table 1(b)] for short-lived nuclides, the waste is Class C.

The minimum requirements that must be met by all wastes (Classes A, B and C) are set forth in Section 61.56(a). These requirements include the stipulation that waste containing liquids must be packaged with enough adsorbent material to absorb twice the volume present. For solid wastes containing liquid, the amount of free liquid should in no case exceed 1% of the volume. Class B waste must meet these requirements and, in addition, must be stabilized. The stability requirement is meant to insure that the waste does not compromise the integrity of "the disposal unit and thereby lead to the infiltration of water"[8] as well as limit exposure to the inadvertent intruder by being recognizable as waste.

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*In all cases when the waste contains mixtures of radionuclides the total concentration is determined by the sum of fraction rules [10 CFR Part 61, Section 61.55(a)7].

Table 1

Concentration Limits for the Classification of Radioactive Waste[8]

(a)

Radionuclide	Concentration (Ci/m^3)
^{14}C	8
^{14}C in activated metal	80
^{59}Ni in activated metal	220
^{94}Nb in activated metal	0.2
^{99}Tc	3
^{129}I	0.08
Alpha emitting transuranic nuclides with half-life greater than five years	100[a]
^{241}Pu	3500[a]
^{242}Cm	20000[a]

[a]Units are nanocuries/gram.

(b)

Radionuclide	Concentration (Ci/m^3)		
	Col. 1	Col. 2	Col. 3
Total of all nuclides with less than five-year half-life	700	*	*
^{3}H	40	*	*
^{60}Co	700	*	*
^{63}Ni	3.5	70	700
^{63}Ni in activated metal	35	700	7000
^{90}Sr	0.04	150	7000
^{137}Cs	1	44	4600

[a]There are no limits established for these radionuclides in Class B or Class C wastes. Practical considerations such as the effects of external radiation and internal heat generation on transportation, handling, and disposal will limit the concentrations for these wastes. These wastes shall be Class B unless the concentrations of other nuclides in Table 1(a) determine the waste to be Class C independent of these nuclides.

At present, the means by which the stability requirements for Classes B and C wastes can be met, are by the waste form itself, by processing the waste to a stable form or placing the waste in a container (high integrity container, HIC) or structure that provides stability. Structurally stable waste should maintain both its physical dimensions and form under disposal conditions (e.g., overburden, microbial action, the presence of water) and under internal stress such as chemical changes and radiation. In addition to the minimum requirements on liquid wastes or solid waste containing liquids, there should be as little free liquid as possible and in no case exceed 1% of the waste volume when the waste is disposed of in a container for stability or 0.5% of the volume of waste for waste processed to a stable form.

In general, for Class B (and C) waste, liquids must be solidified. The waste must present a recognizable form and maintain structural stability. In principle, these requirements can be met by a waste form, a HIC, or both. There are no leach or release requirements in 10 CFR Part 61 although a waste form or package that limits the release of radionuclides offers distinct advantages to insuring the health and safety of the public.

Class C waste must meet all the criteria for Class B waste. In addition, it must be intruder protected either by disposal at a greater depth or by use of engineered barriers (e.g., concrete covers) whose lifetime is 500 years.

In addition to 10 CFR Part 61, the NRC has provided guidance in the form of a Technical Position on Waste Forms.[9] The Technical Position specifically outlines test methods and criteria for waste forms "acceptable to the NRC staff for implementing the 10 CFR Part 61 waste form requirements." The Technical Position specifically suggests a minimum requirement on the mechanical stability of solidified wastes, outlines procedures for determining the sensitivity of solidified wastes to radiation, biodegradation and thermal degradation, limits the amount of free liquid and the leachability of stabilized waste. The Technical Position also addresses the use of HICs for the disposal of Class B and Class C wastes. It is recommended that a HIC should have a design goal of a minimum lifetime of 300 years. It is desirable that a HIC provide containment of the waste for some portion of its design life. Tests are recommended to determine its resistance to corrosion or degradation from chemical effects, resistance to radiation damage and biodegradation, and tests to determine its mechanical stability. Wastes disposed of in a HIC should have closures designed for a positive seal that will last the lifetime of the container and passive vents to release internal pressure. The amount of free liquid present should not exceed 1% of the waste volume, and voids should be eliminated to the extent practicable.

DISPOSAL OF OR LONG-TERM STORAGE OF CHEMICAL DECONTAMINATION WASTES

The amount of information that would be required to demonstrate the acceptability of chemical decontamination wastes for disposal, depends primarily on the waste classification. Cobalt-60 is the radionuclide of principal concern when chemical decontaminations are conducted. While the Class A limit

for wastes containing ^{60}Co is 700 Ci/m^3, the presence of other nuclides (^{137}Cs, ^{90}Sr, ^{63}Ni) which may be present following cleanup of the primary system could alter the waste classification based on ^{60}Co alone. Mieliv[10] recently proposed scaling factors for difficult to measure radionuclides in which the ^{63}Ni activity is based on the ^{60}Co inventory. At the Class A limit for ^{60}Co (700 Ci/m^3), the projected ^{63}Ni concentration for a BWR would be $\approx$14 Ci/m^3 or a factor of three larger than the Class A limit in Part 61 for that nuclide. If, based on the radionuclide concentrations, the waste is Class A waste, then the generator must only comply with the minimum requirements of 10 CFR Section 61.56 and properly document the waste as specified in 10 CFR Section 20.311. This includes an identification of wastes containing more than 0.1% by weight chelating agents for which the weight percentage of the chelating must be estimated.

If the wastes exceed the radionuclide specific limits for Class A wastes, then stability of the waste must be assured. Stability might be achieved by solidification in appropriate media or by placing the waste in a container or structure that provides for stability. Guidance has been given by the NRC in the Technical Position on Waste Forms which outlines numerical goals for waste/container properties and short-term tests or procedures for evaluating material properties.

For dilute process wastes which consist primarily of resin wastes and some filter cartridge wastes, the waste classification will depend on the inventory removed, the amount of resin containing that inventory and how the resins are managed following the decontamination. In a full system decontamination it is anticipated that those beds containing the decontamination reagent (anion or mixed bed resins) will exceed the 0.1% by weight limit on chelates as determined prior to any further management (i.e., solidification).

Various methods for managing the dilute process decontamination resin wastes have been considered. Some include a dilution of the reagents by the addition of other resin wastes, however, the primary concern surrounding disposal of these wastes is the total quantity of complexing agents. Dilution of these wastes with other wastes may not be within the spirit of providing for safe disposal. There are several points to note with each of the management methods beyond the need to establish the waste classification.

For those methods which dewater and containerize the high activity cation resin beds, damage to the resins may occur. The presently recommended maximum loading is that which would not exceed a total dose of 10^8 rad. Methods which employ separate solidification of both resin types offer some advantage in terms of waste classification and structural stability. Combining decontamination wastes with normal spent resin wastes prior to solidification or disposal in a container does not necessarily result in a significant dilution of activity or reagent. This would depend on the volume of such wastes at the reactor. In addition, this method would add complexing agents to normal reactor wastes.

For a resin waste similar to the one proposed by Anstine[11-12] in which anion resins pre-saturated with reagent are used to remove the activity, the pre-processing or pre-solidification stability of the resulting waste stream should be investigated. While cation resins can withstand a total dose of the order of 10^8 rad; anion resins are known to degrade at a lower total dose with the release of gas, loss of their exchange capacity (i.e., ability to retain the activity) and deterioration of their physical properties.[13-14]

For the resin beds containing the reagent that are not processed and are solidified prior to disposal specific areas in need of investigation include:

a. Conditions for solidification and the appropriate media for solidification.

b. The ability of the solidified waste to retain or control the release of complexing agents to the environment. While there are no release criteria in 10 CFR Part 61 this type of information would be valuable in assessing the impact of disposing of solidified decontamination wastes in a SLB site.

c. If resins are stored for some time prior to solidification the long-term effects of the activity on the integrity of the wastes and the ability to solidify should be investigated.

If those beds are added to other normal reactor resin wastes it may be necessary to assess whether the dilution is an effective means for reducing the problem and is in keeping with the intent of 10 CFR Part 61 and future site-specific criteria for these wastes. The possibility exists that the resultant radionuclide concentration in the combined wastes will be greater than that if the reagent containing beds were handled separately. The problems with the long-term stability of the wastes could become more complex.

SOLIDIFICATION OF SIMULATED DECONTAMINATION RESIN WASTES

A laboratory evaluation of methods for solidifying decontamination wastes was performed by Brookhaven National Laboratory (BNL) in order to assess whether the soldified wastes will meet the applicable criteria. The simulated decontamination resin waste composites were examined for the presence of free liquid, tested for mechanical strength and tested for their ability to withstand immersion in water. Further, mechanical strength tests were performed after the water immersion testing.

Simulated dilute decontamination resin wastes were solidified in Portland I cement and vinyl ester-styrene (VES). The following reagents were used in the testing: ethylenediaminetetraacetic acid (EDTA), oxalic acid (OA), citric acid (CA), EOC (an equimolar mixture of EDTA, OA and CA), picolinic acid (PA), formic acid (FA), simulated LOMI reagent (an equimolar mixture of PA and FA was used) and LND 101A (a proprietary reagent supplied by London Nuclear Limited). Two types of anion-exchange resins were used: IRN-78 (Rohm and

Haas), a polystyrene strong base anion exchange resin in the ^{-}OH form and IONAC A-365 (Sybron), a polyacrylic weak based anion exchange resin with exchange groups in the free base and ^{-}OH form. Samples made with mixed bed resin had IRN-77 (Rohm and Haas) as the cation exchange resin used in the H^{+} form. Enough IRN-77 was used to produce a weight ratio of two parts anion exchanger to one part cation exchanger. The anion exchange resins were equilibrated with an amount of acid that would exchange with 50% of the available sites.

Portland I cement was selected for this work based on the results of a series of scoping experiments.[15-16] The resin waste slurry was pre-treated, prior to solidification in cement, with sodium hydroxide to increase the pH to approximately 12.* Anion resin wastes solidified in VES were adjusted to pH ≈9.5 with hydrochloric acid if necessary whereas mixed bed resin samples were solidified without pre-treatment. The laboratory scale waste forms had either a nominal 2-in. diameter by 4-in. height. Details of the solidifications are given in Reference 15 and references therein.

Simulated Resin Wastes Solidified in Cement

In all waste forms except those containing citric acid, the forms cured to free standing monoliths with no free liquid within 28 days. Cement solidified mixed bed resins containing citric acid cured to a hard set after ≈90 days. Citric acid/anion resin composites had not cured after ≈90 days. All waste composites exhibited compressive strengths within a range of 2100 to 3400 psi.[15] This is well in excess of the 50 psi minimum recommended in the NRC Technical Position on Waste Form.

Five waste forms of each waste type were immersed in one liter of deionized water (DIW) to test the ability of the composites to maintain their physical integrity during continued exposure to water. During the 90-day immersion tests of mixed bed resin wastes solidified in cement, three of five forms containing LND-101A disintegrated. Mixed bed resin waste containing Na_2EDTA also exhibited a cracked or scaled surface although no flaking was observed. Cement composites of picolinic acid on polystyrene mixed bed resin showed a cracked pattern on the upper third of the waste form. All citric acid/mixed bed resin/cement composites cracked during 90 days of immersion. All of the forms that were suitable for compression testing had compressive strengths greater than 50 psi after immersion in water.[17]

Following 90 days of immersion, waste composites containing LND-101A on anion resins had cracked. Fractures were also evident on anion resin composites containing EDTA-oxalic acid-citric acid (EOC) and on composites containing Na_2EDTA. All waste composites that maintained integrity after water immersion had compressive strengths greater than 50 psi.[18]

*Anion resins containing LOMI reagent were treated with hydrochloric acid to decrease the pH to about 5.5 in order to slow the set time and allow sufficient mixing of the composite.

Simulated Resin Wastes Solidified in VES

The compressive strengths at 10% deformation of the simulated decontamination mixed bed resin waste/VES composites were well in excess of the 50 psi recommended in the Technical Position on Waste Form.[15] Immersion in DIW caused no sample deterioration or expansion after 90 days.

The compressive strengths at 10% deformation of simulated anion resin/VES composites were also greater than 50 psi. Samples containing simulated wastes in general had lower compressive strengths than the control sample.[7] During the compression tests of the anion resin composites liquid was observed seeping from the surface of specimens containing IRN-78 resins with either picolinic acid, oxalic acid, citric acid, EOC or LND-101A but not the control specimens.[15] Both the IONAC control and LOMI specimens released liquid under compression. The presence of the organic acids and the resin type in the VES forms may influence the behavior of the form. Therefore the presence of decontamination reagents in a waste stream needs to be considered when establishing a solidification process using VES.

Samples of each VES composite containing reagent on anion resins showed no sample deterioration or swelling after 90 days of immersion in DIW.

Free liquid was observed on removal of the VES waste forms from the containers. Two different free liquid generation tests were performed on simulated mixed bed resin wastes/VES composites. In conjunction with these tests, two different measuring techniques were employed. The initial measurement was concerned with what is defined as drainable liquids (ANSI/ANS-55.1-1979), but in this study the term pourable liquids was substituted. If a sufficient quantity of unbound liquid remained in the polyethylene container following removal of the composite, the container was then inverted and the liquid contents poured off and weighed. The second measurement was performed using an absorbent tissue. Any weep water located on the exterior of the form or residual water on the inside container walls was absorbed with a tissue and quantified by weighing.

The second free liquid test involved repeated determinations of any moisture generated following the initial drying of the container and composite. Measurements on one sample from each acid type and the control were determined. The free liquid performance of these composites (based on the ANSI/ANS-55.1-1979 criterion, although pourable liquids are not included) was calculated and is summarized in Table 2.

Free liquid measurements were made on anion resin-VES composites. These data are given in Table 3 and represent a single determination (five replicates) of each waste type of the "pourable" and tissue sorbed liquid. No measurements were made of free liquid generation with time although a separate set of composites were measured approximately one week after the initial determinations. The amount of free liquid (pourable and tissue sorbed) was equivalent to that measured initially within the error given.

Table 2

Percentage Free Liquid
Simulated Mixed Bed Resin Decontamination Wastes in VES.

	Composite Size		
	2.6 in. x 3.1 in.[a]	Nominal 2 in. x 4 in.[b]	
Acid	One Measurement	One Measurement[d]	Repeated Measurement[c]
Control	—	0.32	0.79
Oxalic	0.16	0.25	0.76
Picolinic	0.09	0.35	0.90
Formic	0.07	0.25	0.78
Na_2EDTA	0.44	0.40	0.54
Citric	0.47	0.51	1.06

[a]Calculations were performed using a composite volume of 284.93 cm^3.
[b]Calculations were performed using a composite volume of 158.10 cm^3.
[c]Measurements were made over a period of 35 days.
[d]A total of pourable and sorbed liquid.

Based on single measurements of the free liquid, most waste composites are within the 0.5% limit for solidified waste as recommended in the Technical Position on Waste Form. The potential exceptions are forms containing citric acid/mixed bed resin waste, EOC/polystyrene anion resin waste and simulated LOMI wastes on polyacrylic resins. In the case of the LOMI/polyacrylic resin composites, the percent free liquid by volume approaches the limit for Class A wastes. If the standard had been applied to those mixed bed composite samples measured for recurring free liquid generation, they all would have been in excess of the 0.5% for solidified wastes.

Table 3

Percentage of Free Liquid
Simulated Anion Resin Decontamination Wastes[a] in VES

Acid/Resin	% Pourable[b] Liquid by Volume	% Total[b] Liquid by Volume
EDTA/PS[c]	0.1	0.2
PA/PS	0.3	0.3
EOC/PS	0.4	0.5
OA/PS	0.3	0.4
FA/PS	0.2	0.3
CA/PS	0.2	0.3
LND-101A/PS	0.2	0.3
LOMI/PA[d]	0.9	1.
C-PS[c]	0.2	0.2
C-PA[d]	0.1	0.2

[a]Values based on 5 replicate measurements.
[b]Average volume assumed to be 165 cm^3 ± 2.0 cm^3 from random measurements of diameter and height of several samples.
[c]PS is Amberlite IRN-78 anion exchange resin; C-PS is a control sample containing resin only.
[d]PA is IONAC-365A anion exchange resin; C-PA is a control sample containing resin only.

LEACHABILITY OF DECONTAMINATION REAGENTS FROM CEMENT WASTE FORMS

BNL is also studying the leachability of organic reagents from solidified decontamination wastes. Laboratory scale waste forms previously described were leach-tested, and a leachability index for the organic acid was calculated according to the procedure given in ANS 16.1.[20]

Procedures for determining the concentrations of organic acids in leachate solutions have been described elsewhere.[21,22] The quantity of organic acid in each leachate sample was used to determine the effective diffusivity. In all cases, the fraction leached from the samples was less than 20% of the quantity of organic acid initially present and thus the effective diffusivity, D (cm^2/s), was calculated using the equation given in ANS 16.1. A leachability index was calculated as prescribed for each leach period by the ANS formulation:

$$L = \log (\beta/D)$$

where β is a constant (1 cm^2/s) and D is the effective diffusivity.

Both EDTA and picolinic acid were leached from cement solidified resin wastes. Figure 1 is a plot of CFR vs square root of leach time for release of EDTA and PA. The data for each acid appear to follow a linear relation suggesting that the release of the acids are diffusion controlled.[23] The slopes of the two lines are different indicating different effective diffusivities of each acid. Differences in the diffusivities and corresponding leachability indices are most likely a consequence of the organic acid being leached from the forms since the samples were prepared using the same formulations, cured for about the same time and leach tested by the same procedure.

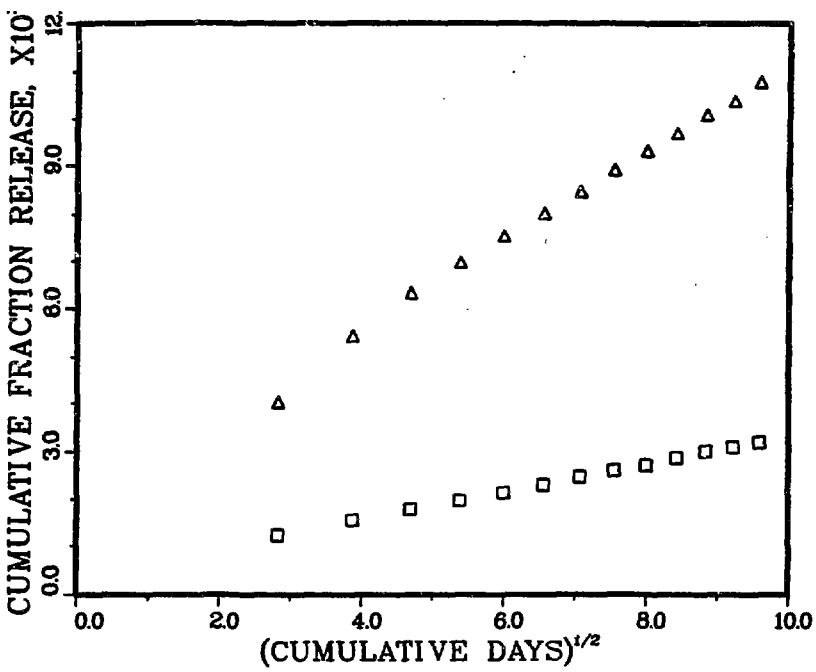

Figure 1. Cumulative fraction release of EDTA and picolinic acid vs the square root of leach time. The samples tested were EDTA/MB (□) and PIC/MB (Δ).

The leachability indices for the release of the organic acids from cement solidified resin samples are summarized in Table 4. The average leach index is specific for the different reagents in the forms. Further, the measured values are reproducible among replicate samples. Only small differences in L and the bias on L are observed for samples having the same reagent but different resin types (or different leach test procedures). The percent bias given in the table indicates that the average of the first four leach indices is that percentage larger (+ sign) or smaller (- sign) than the average of the last four leach indices. The ranges of the leach indices are also given with the range percent in parentheses.

Table 4

Summary of Leach Test Results for Cement Solidified Wastes

Organic Acid	Resins in Forms	Average Leach Index[a]
EDTA	mixed bed	10.1+2%
EDTA	anion	10.3+5%
EDTA (EOC)[b]	mixed bed	10.5+7%
EDTA (EOC)	anion	10.5+5%
Oxalic (EOC)	mixed bed	12.0
Oxalic (EOC)	anion	11.0
Citric (EOC)	mixed bed	10.3
Citric (EOC)	anion	9.9
Picolinic	mixed bed	9.1+3%
Picolinic	anion	9.1+2%
Picolinic (LOMI)[c]	mixed bed	8.8+8%
Picolinic (LOMI)	anion	8.7+1%

[a]No bias is listed for samples having fewer than six leach indices for the average.
[b]EOC indicates that the specimens contained an equal molar mixture of EDTA, oxalic acid and citric acid.
[c]LOMI indicates that the specimens contained an equal molar mixture of picolinic acid and formic acid used to simulate the LOMI reagent.

PROCESSING OF DECONTAMINATION WASTES

Mixed bed or anion resins and perhaps high activity resins may be processed or degraded by in-plant methods before disposal. BNL has investigated the degradation of simulated decontamination wastes by incineration and acid digestion. Results indicate that both processes can, in principle, be very

effective for degrading these wastes. Under the conditions studied incineration appeared to be slightly more effective than acid digestion. However, it should be noted that the work conducted at BNL was limited to a single combustion unit, a single chemical digestion system and three simulated waste streams: reagents alone, anion resins alone, and anion resins equilibrated with candidate chemical reagents. Only small variations in process parameters were considered. While the data indicate the applicability of these processes to these types of wastes, it is recommended that any process being considered for use should be tested with the appropriate waste stream or a simulation of the waste stream to insure that conditions are adequate for processing and degradation of the wastes. A review of this work can be found elsewhere.(15)

SUMMARY

The primary concern surrounding the disposal of chemical decontamination wastes is the potential impact that these wastes may have on the long-term performance of a burial site.

The way in which decontamination wastes are disposed of and the manner in which other wastes are disposed of will determine the impact on the migration of nuclides. Decontamination wastes solidified in a highly leach resistant waste form may have very low releases over long time periods, during which many radionuclides will have decayed. Therefore, in a site that may experience a large annual rainfall or has poor soil sorption properties, it may be desirable to ensure that organic decontamination wastes are released to the site slowly. This may be achieved by a good waste form, a high integrity container with a long lifetime or a combination of these methods. On the other hand, for an arid site or one with extremely good soil properties it may not be necessary to use as careful a packaging of these wastes as for a wet site. One of the problems of disposing of complexing agents is their persistence in time. When the wastes are packaged in a HIC that maintains its integrity during decay of many short-lived nuclides, the eventual release of the organics may still result in the complexation of longer-lived nuclides present in the site or other waste. Thus, segregation of these wastes may be desirable.

Each site, each waste type, and the way it is packaged for disposal will, therefore, impact on the hazard posed by disposal of these wastes. It is desirable then to examine all the technologically feasible methods for safe management of these wastes, and to examine the interplay of site and waste characteristics.

Work has been conducted by BNL on the processing of simulated decontamination waste, the direct solidification of these wastes and magnitude of release that might occur from these wastes following disposal. Tests conducted on direct solidification indicate that there is a need for a waste specific determination of the acceptability of these wastes for disposal, i.e., the ability of the waste composite to meet the applicable NRC criteria and site specific criteria. Wastes containing large amounts of citric acid required a long cure period before forming a hard free-standing monolith;

composites containing polyacrylic resins equilibrated with picolinic acid required a different pre-treatment (i.e., addition of acid) than those wastes containing polystyrene resins; even with pre-treatment certain waste types appeared to degrade and others failed after long periods of immersion in water. All of this work indicates that it may be necessary to institute a process control program to determine what compositions will be acceptable for the waste being solidified and the range of conditions (e.g. waste loading, cement-to-water ratio, additive concentration) under which the waste can be solidified to an acceptable product.

For wastes solidified in VES those areas that may require further investigation are the presence of and development of free liquid and the apparent increase in the surface porosity of some acid/resin waste forms.

Incineration and acid digestion of simulated decontamination resin wastes are processes that can, in principle, be very effective for degrading these wastes. Under the conditions studied incineration appeared to be slightly more effective than acid digestion. While the data indicate the applicability of these processes to these types of wastes, it is recommended that any process being considered for use should be tested with the appropriate waste stream or a simulation of the waste stream to insure that conditions are adequate for processing and degradation of the wastes.

Releases of organic reagents from solidified waste forms appear too low. The apparent diffusivities are normally less than or equal to those observed for Cs releases from cement solidified forms. However, since the quantities of reagents that might be disposed of in a SLB site in the future are large, even with solidification, site limits on total quantities may be desirable. At this time, the data base on releases, and their impact on potential sites, dose not warrant a firm conclusion for or against such a site limit. The interplay of site and waste characteristics need to be examined to determine what, if any, further requirements are necessary.

Areas where further investigation may help define the actual impact of these wastes on the disposal site include the effects of biodegradation, the use of a HIC or other container material and impacts of decontamination during decommissioning. While biodegradation may affect the stability of the waste, it may also mitigate the overall impact of reagents released to the trench/site. Aged resins appear to release organics more slowly. However, long-term effects (radiation damage, development of corrosive liquids) may compromise container integrity if the container is used for stability, or, in the case of Class A wastes, may result in release of organics during the early stages of the site operation. During decommissioning, several different techniques and solutions may be employed. Radionuclide inventories will be different and management of these wastes should be consistent with regulations in place for their disposal.

With the approach of the 1986 deadline for siting of regional SLB sites, significant concern has arisen over the ability to store wastes over extended

periods of time prior to the availability of new sites. The effects of long-term storage on the acceptability of wastes for disopsal will need to be addressed.

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