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PROPERTIES AND SOLIDIFICATION OF DECONTAMINATION WASTES*

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ABSTRACT

LWRs will require one or more chemical decontaminations to achieve their designed lifetimes. Primary system decontamination is designed to lower radiation fields in areas where plant maintenance personnel must work. Chemical decontamination methods are either "hard" (concentrated chemicals, approximately 5 to 25 weight percent) or "soft" (dilute chemicals less than 1 percent by weight). These methods may have different chemical reagents, some tailor-made to the crud composition and many methods are and will be proprietary. One factor common to most commercially available processes is the presence of organic acids and chelates. These types of organic reagents are known to enhance the migration of radionuclides after disposal in a shallow land burial site. The NRC sponsors two programs** at BNL that are concerned with the management of decontamination wastes which will be generated by the full system decontamination of LWRs. These two programs focus on potential methods for degrading or converting decontamination wastes to more acceptable forms prior to disposal and the impact of disposing of solidified decontamination wastes. The results of the solidification of simulated decontamination resin wastes will be presented. Recent results on combustion of simulated decontamination wastes will be described and procedures for evaluating the release of decontamination reagents from solidified wastes will be summarized.

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INTRODUCTION

The nuclear industry is actively considering the potential advantages of primary system decontamination to ensure the safe operation of light water reactors (LWRs). The Nuclear Regulatory Commission (NRC) is responsible for insuring the public health and safety, and will therefore require a careful evaluation of different decontamination processes and the unique wastes they produce. The major areas of concern for the NRC in evaluating the effectiveness and safety of chemical decontamination processes are: the compatibility of the chemical system with the primary system materials, the long term stability of the primary system following one or more decontaminations, the rate of radioactive contamination buildup after decontamination, and the type, volume and toxicity level (radiotoxicity as well as chemical toxicity) of the radwaste streams generated by the decontamination as well as their subsequent management at the plant and at the disposal site.

There are two generic methods proposed for the chemical decontamination of primary systems: "hard" (concentrated chemicals; approximately 5 to 25 weight percent) or "soft" (dilute chemicals approximately 1 weight percent). These methods may have different chemical reagents, some tailor-made to the crud composition. Many processes are and will be proprietary. Existing work also indicates that the chemical systems needed to decontaminate boiling water reactors (BWRs) are different from those needed to decontaminate pressurized water reactors (PWRs). However, both reactor types require treatments involving fairly complex chemistry.

Two research programs, sponsored by the NRC and being carried out at Brookhaven National Laboratory, are concerned with the management of the decontamination wastes which will be generated by the full system decontamination of LWRs. One program entitled "Decontamination Impacts on Solidification and Waste Disposal" focuses on methods for converting decontamination wastes to more acceptable forms at the reactor site prior to disposal. The other program, "Properties of Solidified Decontamination Wastes," is aimed at providing the technical information needed to evaluate the impact associated with near surface disposal of decontamination wastes. These wastes contain organic acids which if released to the disposal site may enhance the migration of radionuclides through their ability to form soluble complexes with the radionuclides. Highlights of the work in these programs are presented here. Details of these studies can be found elsewhere.⁽¹⁻⁷⁾

PROCESSES FOR THE MANAGEMENT OF DILUTE DECONTAMINATION WASTES

The processes being studied are those that have been proposed for the management of normal reactor resin wastes. These processes include acid or chemical digestion, incineration, pyrolysis and wet-air oxidation. All of these processes are expected to be very aggressive toward resins and also have a good potential for destroying organic complexing reagents. Although

scoping tests on acid digestion have been performed the major effort thus far has been given to the evaluation of a laboratory scale incineration of organic acids and ion exchange resins.

A schematic diagram of the incineration apparatus is shown in Figure 1. Those parts of the unit which are exposed to high temperatures ($>500^{\circ}\text{C}$) [i.e., the main combustion changer, afterburner, and copper oxide (CuO) catalyst chamber] are made of quartz. The quartz afterburner is dimpled, providing a greater surface that should improve heat transfer to the combustion gas mixture. Additional details of the apparatus and procedure have been published.⁽⁵⁾

The gas scrubbing system consists of one gas bubbler containing hydrochloric acid (0.1 N HCl) followed by a bank of six gas bubblers, each containing 100 mL of sodium hydroxide (1.0 N NaOH). The HCl bubbler is intended to trap amines and any organic species in the gas stream, while the NaOH reacts with CO_2 in the off-gas to form a carbonate (CO_3^{2-}) solution. The exit gas passes through three gas-sampling bulbs before being vented to a laboratory hood.

The NaOH trap solutions are removed following an incineration. The amount of CO_2 generated by combustion of the material is determined using ASTM D 513-80 which is a titration method for measuring carbonate in solution.

Table 1 summarizes the titration data for the incineration of EDTA, anion resins and citric acid. The available carbon for EDTA and citric acid monohydrate were derived from the molecular weight and the grams of acid incinerated. The amount of carbon trapped is calculated from the volume of acid required to titrate from $\text{pH} = 8.3$ to $\text{pH} = 4.5$. This represents $>98\%$ of the carbon. The error in the carbon trapped given in Table 1 is based on three titrations.

In the case of anion resins the amount of trapped carbon is based on two assumptions: the water content of the resins is $\sim 45\%$ by weight and the carbon content is $\sim 78\%$ of the dry resin weight.

For EDTA and citric acid the amount of carbon trapped as CO_3^{2-} is ~ 90 to 100% of the available carbon. This indicates that for the present incineration system complete destruction of the acids occurs. For the resins the titration results indicate that 65 to 80% of the estimated available carbon is trapped as CO_3^{2-} .

Only a small amount of gas was collected in the gas sampling bulbs. Analyses of this gas have been reported.⁽⁵⁾ The analyses indicate that the CO_2 present in the gas samples accounts for only a small portion of the CO_2 present and trapped in the NaOH solution.

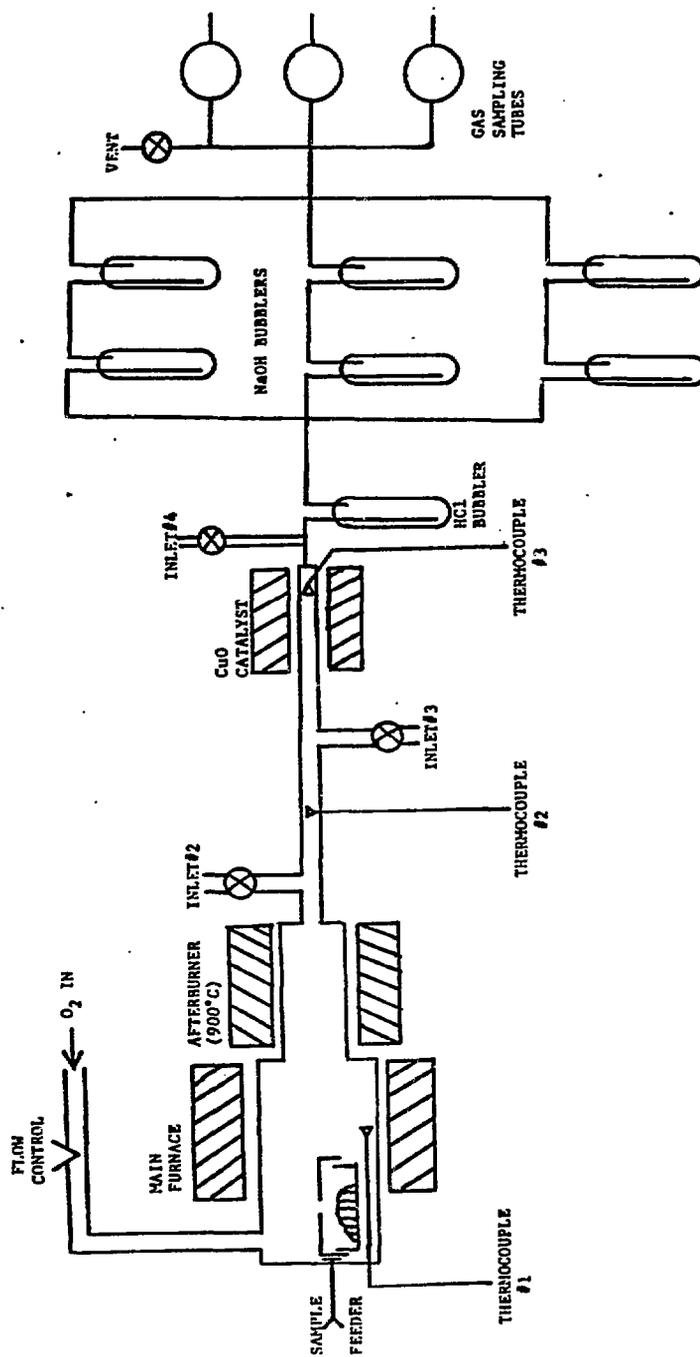


Figure 1. Laboratory scale incinerator.

TABLE 1. INCINERATION TEST - TITRATION RESULTS

Sample	Available Carbon ^a (g)	Trapped Carbon ^b (g)	Percent Trapped
EDTA 1	0.8215	0.717(+0.008)	87.3
2	0.8199	0.821(+0.002)	100.2
3	0.8512	0.861(+0.01)	101.2
4	0.8299	0.839(+0.01)	101.1
5	0.9188	0.858(+0.015)	93.4
Citric Acid 1	0.8569	0.827(+0.016)	96.5
Anion Resin 1	4.5474	2.952(+0.05)	64.9
2	4.4187	3.597(+0.045)	81.4
3	4.3758	3.275(+0.012)	74.8

^aAnion resin samples are assumed to have a water content of 45% by weight and a carbon content of 78% of the dry resin weight. Citric acid is in the monohydrate form.

^bThe amount of trapped carbon is determined from the equivalents of HCO_3^- measured by titration from pH = 8.3 to pH = 4.5.

Based on a carbon mass balance the incineration of EDTA and citric acid appears to result in complete conversion to CO_2 and water. No effort was made thus far to measure nitrogen-containing products from the combustion of EDTA or the resins. Resin samples appeared to be at least 65-80% consumed. The values given for the resin are more uncertain than those for the solid organic acids. The primary sources of uncertainty include the water content of the resins, the carbon content of the resins and the trapping efficiency of the scrubbing solutions.

SOLIDIFICATION OF SIMULATED DECONTAMINATION WASTES

Five simulated decontamination resin waste streams were incorporated in masonry cement and Portland I, II and III cements. The waste forms were cured for 7 and 28 days, examined for physical integrity and immersed in water. If a waste form withstood immersion in water, compressive strength measurements were performed.

The five organic acids used to simulate the decontamination resin wastes were oxalic acid, formic acid, picolinic acid, citric acid and disodium EDTA. The organic ion exchange resins used were a strong acid

cation resin (IRN 77, H⁺ form) and a strong base anion resin (IRN 78, OH⁻ form) manufactured by Rohm and Haas. The amount of acid present in a sample was that required to exhaust 50% of the anion sites. No simulations of radionuclides present in the actual decontamination wastes were considered in this study. The formulations used for the preparation of the cement forms have been reported.(2,6,7)

Table 2 summarizes the results of the water immersion tests using forms allowed to cure for 28 days. The water immersion test data indicate the inability of a single cement binder to satisfactorily maintain a solidified product for all five simulated decontamination wastes. With the exception of citric acid wastes all the waste forms exhibit good physical integrity (i.e. freestanding monoliths) when they were removed from the polyethylene molds. The simulated citric acid resin waste forms had not cured properly after a total of 30 days.

TABLE 2. WASTE FORM IMMERSION RESULTS

Acid	Portland I 28 Day	Portland II ^a 28 Day	Portland III 28 Day	Masonry 28 Day
Control (resin alone)	A (2 days)	H-F (1 day)	A (2 days)	H-F (2 hours)
Oxalic	C ^b (9 days)	D ^c (9 days)	F-S ^c (8 days)	H-F (2 hours)
Picolinic	A ^d (9 days)	C ^e (3 hours)	A ^d (9 days)	S-C (2 hours)
Formic	A ^d (21 days)	A ^d (21 days)	A ^d (9 days)	C (2 hours)
Disodium EDTA	C ^e (9 days)	D (9 days)	C ^c (9 days)	H-F ^f (2 hours)
Citric	Waste form still curing. After 28 days, free liquid still observed.	Still curing. Composite soft and free liquid observed.	Removed from container after 28 days. Composite moist and has poor mechanical stability.	Cured 30 days. Bottom half has harder set. H-F developed at hard set/soft set interface.

Legend: A - Denotes a waste form with physical integrity. D - Denotes disintegration.
H-F - Denotes hairline fractures. C - Denotes fractures of cracking.
S-C - Denotes surface cracking. F-S - Denotes fracturing and separation.
The time given in the parenthesis is the total immersion time or the time to gross failure.

^aDetails of further tests with Portland II cement are reported in Reference 6.

^bCracked from midsection to bottom of form.

^cCrack originates at center of waste form and radiates to the top.

^dCompressive strength data given in Table 4.4. Reference 1.

^eCrack originates at top of waste form and radiates down.

^fCrack originates at bottom and radiates up.

Portland I and III cements appear to be most suitable for solidifying the simulated decontamination wastes but are in no way universal. In addition, there may be some dependence of waste form stability on cure time. The composites cured for seven days maintained their integrity when immersed in water, more often than composites that were cured for 28 days. One potential explanation of this behavior is that in the seven-day cure samples there is more free water available for maintaining the resin-water balance and the cement hydration process.

Portland I and III cements appear to be the most useful for solidifying resin wastes containing picolinic acid or formic acid. However, the difference observed between composites with other acids cured for seven days and those cured for 28 days reduces overall the usefulness of these two cement binders for studying the releases of decontamination reagents from these wastes.

In those samples that failed when immersed in water, the fracture pattern observed seemed to be dependent on the type of cement and the organic acid. The differentiating characteristic is the point at which the fracture initiates. If the waste form is divided into three sections, top, middle and bottom, the crack will normally begin in one section and then radiate up or down. For example, with masonry cement the crack was usually initiated over the bottom third of the waste form and radiated upward. In Portland II cement⁽⁶⁾ the crack normally is initiated at the middle and radiates upward. This trend, however, does appear to be dependent on the acid as well. In Portland I cement containing oxalic acid resin waste, the crack is initiated in the midsection and radiates down, while with EDTA resin wastes the fracture is initiated at the top of the waste form. It has been noted that when simulated resin wastes were incorporated in Portland II cement the forms exhibited signs of segregation. The resin beads tended to concentrate in the top of the waste form.⁽⁷⁾ If the resins do segregate in those binders that have failed, it would appear to depend on the cure time, the cement and the acid. The area in which the resins concentrate may be more susceptible to failure resulting in the asymmetric deterioration of the waste form. The cause of the segregation is not known although it may be due to a delay in set time caused by the acid and the difference in densities of the resin and the cement mixture. In addition, the segregation of the waste leads to a higher local concentration of waste in the cement. This effect may also lead to failure since the integrity of cement solidified resin wastes is sensitive to the waste loading.

Compressive strengths of cement waste forms that withstood immersion in water were generally greater than 1000 psi implying that the mechanical stability of the waste may be acceptable.

In addition to solidification in cement, the five simulated decontamination resin wastes were solidified in a thermosetting resin, vinyl ester-styrene (VES). Details of the solidifications can be found in Reference 5.

All untreated simulated decontamination waste/VES composites were solidified successfully yielding homogeneous waste forms. All oxalic acid waste forms had a uniform surface texture. However, unexplained irregularities were observed on the surfaces of almost all of the samples containing disodium EDTA, picolinic acid and the controls. Waste forms containing formic acid and citric acid also had surface defects but to a lesser degree.

The mechanical strengths at 10% deformation of the VES composites were measured. All of the composites had compressive strengths between 1100-1300 psi with the exception of the controls whose mechanical strength at 10% deformation was ~950 psi.

Determinations of the quantity of free liquid associated with the VES solidified wastes were made using two test procedures. In the first test measurements were made of what is referred to as pourable liquids. If a sufficient quantity of unbound liquid remained in the solidification container following the removal of the composite, the container was inverted and the liquid contents poured off and weighed. A subsequent 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. Results of free liquid measurements on nominal 2 in. diameter x 4 in. high waste forms are given in Table 3.

TABLE 3. DECONTAMINATION WASTE/VES FREE LIQUID MEASUREMENTS^a
NOMINAL 2 IN. x 4 IN. WASTE FORMS

Acid	Pourable Free Water (g)	Tissue Sorbed Water (g)	Total of Pourable and Sorbed (g)
Control	0.08 + 0.04 ^b	0.46 + 0.07	0.50 + 0.08
Oxalic	0.17 + 0.04	0.23 + 0.05	0.40 + 0.07
Picolinic	0.18 + 0.11 ^c	0.41 + 0.11	0.55 + 0.08
Formic	0.11 + 0.05 ^d	0.36 + 0.05	0.40 + 0.05
Na ₂ EDTA	e	0.63 + 0.05	0.63 + 0.05
Citric	0.46 + 0.21	0.35 + 0.04	0.81 + 0.18

^aAverage based on five composite measurements.

^bAverage based on three of the five composites that exhibited pourable liquid.

^cAverage based on four of five composites that exhibited pourable free liquid.

^dAverage based on two of five composites that exhibited pourable free liquid.

^eNo pourable liquid present.

The second free liquid test involved repeated determinations of any moisture released from the form following the initial drying of the container and composite. The free liquid performance of these composites for the single measurement test and for the 35-day repeated measurement test are compiled in Table 4. Based on the single measurement test all the composites may meet the 0.5% limit specified for drainable liquid in the NRC Technical Position on Waste Form. However, with time the associated free liquid can be as great as 1%. At present it is not known whether the results reported here are representative of full-scale waste form behavior.

TABLE 4. PERCENTAGE FREE LIQUID GENERATED FROM
NOMINAL 2-IN. X 4-IN. COMPOSITES.^a

Acid	One Measurement (Pourable)	One Measurement (Total)	Repeated Measurement (Total) ^b
Control	0.05	0.32	0.79
Oxalic	0.11	0.25	0.76
Picolinic	0.11	0.35	0.90
Formic	0.07	0.25	0.78
Citric	0.29	0.51	1.06
Disodium EDTA	----	0.40	0.54

^aCalculations were performed using a composite volume of 158.10 cm³.

^bSum of the 35-day free liquid totals and the initial measurement from Table 3.

METHODS FOR THE ANALYSIS OF LEACHATES FROM DECONTAMINATION WASTE FORMS

Because of the concern about the ability of organic reagents used for decontamination to enhance the migration of radionuclides^(8,9) in shallow land burial sites leach testing of laboratory scale simulated decontamination waste forms is planned. Suitable analytical techniques for detecting low levels of these reagents must be developed. The decontamination reagents released from solidified, simulated decontamination wastes will probably require pre-concentration prior to detection and/or separation and detection. A series of column experiments has been initiated to determine the degree of pre-concentration available with specific column materials and eluants. In general 10⁻⁴ mole of organic acid (e.g., EDTA) was added to a column of anion exchange resins (Amberlite IRN 78) having a 1-cm diameter and a 10-cm length. Several eluants were tested for their ability to release the organic acid from the resins. Thus far 0.1 M CuSO₄ and a

mixture of 0.16 M NaNO_3 with 0.3 M H_3BO_3 have proved most promising giving concentration factors of between three and four. It appears that processing of leachates to pre-concentrate acids for analysis is feasible, however, an optimal system has yet to be developed. These column experiments have demonstrated that organic acids can be eluted from ion exchange resins with solutions containing ions such as sulfates and nitrates.

Based on these findings a scenario may be possible in which chelating organic acids may be released by groundwater from decontamination resin waste in a breached high integrity container.

Sensitive analytical procedures are necessary to measure the release of organic acids or metal complexes of organic acids from solidified waste forms. The utility of some published methods, with or without modifications, has been examined for the detection of the following acids: ethylenediaminetetraacetic acid, oxalic acid, citric acid, formic acid and picolinic acid.

A standard method (ASTM D3113-80) for the determination of tetrasodium ethylenediaminetetraacetic acid, Na_4EDTA , (i.e., a sodium salt of EDTA) in solution has been examined and found to be suitable for the detection of oxalic acid in water as well. A method for the separation of a mixture of aminocarboxylic acid chelates by high performance liquid chromatography⁽¹⁰⁾ was described in which the optical spectrum of the Cu(II) complexes of the chelates was used for detection. In an excess of Cu(II) , changes in the absorption spectrum of a copper complex can be used to determine the concentration of the complexing species. Tests have shown that this method can be used to detect EDTA, oxalic acid, picolinic acid and citric acid in aqueous solution. Ongoing work is directed at establishing the accuracy of these methods.

Scoping tests were performed to demonstrate the utility of the spectrophotometric test methods for the detection of organic acids leached from laboratory scale cement waste forms used in immersion tests. Estimates of the amounts of chelate detected in the aqueous solutions are given in Table 5. The data show agreement within a factor of two between the two techniques. Clearly some of the acid had leached from the forms and was detectable by this analytical procedure.

These data should be viewed cautiously. While the presence of chelates in solution is indicated, the values shown for total moles of acid available is an estimate based on a 50% exhaustion of the anion bed capacity (~1.2 meq/mL). The actual amount of acid on the resins is uncertain. In addition, the solutions tested contained waste forms that had undergone severe degradation, so that the amount released may be an upper limit under static conditions.

TABLE 5. MOLES OF ACID IN IMMERSION TEST SOLUTION

Sample	Organic Acid	Total Moles of Acid in the Waste Form	Moles of Acid Detected	
			ASTM ^a	Cu(II) ^b
ED1	EDTA	2.3×10^{-3}	1.1×10^{-4}	9.0×10^{-5}
ED05	EDTA	1.2×10^{-3}	3.6×10^{-5}	1.3×10^{-5}
OX1	Oxalic Acid	7.8×10^{-3}	1.8×10^{-5}	3.8×10^{-5}

^aSolutions tested after 97 days of immersion.

^bED1 and ED05 solutions tested after 91 days of immersion.

OX1 solutions tested after 99 days of immersion.

SUMMARY

Research aimed at the pretreatment of decontamination wastes has focused on the evaluation of a laboratory scale incineration. Tests with the apparatus resulted in complete combustion of EDTA and citric acid. Anion exchange resins appeared to undergo 65 to 80% conversion to CO₂ when incinerated.

Experiments on the direct solidification of simulated decontamination wastes focused on mixed bed ion exchange resins containing organic acids which are believed representative of decontamination agents. The organic acids tested were: formic acid, picolinic acid, citric acid, oxalic acid and disodium EDTA. Composites of the resin waste with cement and with vinyl ester-styrene were prepared. Although none of the cements tested were effective at solidifying resin containing citric acid, Portland I and III appeared to be most useful for the solidification of the waste. Solidification of the simulated decontamination resin wastes in vinyl ester-styrene binder resulted in freestanding monoliths. The waste appeared to be homogeneously distributed in the form, to have a compressive strength at 10% deformation of greater than 1000 psi and to be able to withstand immersion in water. Tests based on a single measurement showed that all of the composites had less than 0.5% free liquid associated with the form. However, with time the associated free liquid can be as great as 1%.

Two analytical methods were effective for the detection of organic acids in waste form leachates. Additionally as a first step to the analysis of leachates it is believed that pre-concentration of the organic acids may be necessary. Thus far, two elution systems have been reasonably effective; providing concentration factors between three and four. Finally, the analytical methods under investigation were used to determine the concentration of complexing agents in the aqueous solutions from the immersion tests of some laboratory scale cement waste forms.

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