

THE IMPACT OF LWR DECONTAMINATIONS ON SOLIDIFICATION, WASTE DISPOSAL AND ASSOCIATED OCCUPATIONAL EXPOSURE

ANNUAL REPORT
FISCAL YEAR 1985

P.L. Piciulo, J.W. Adams, and M.S. Davis

January 1986

DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, NEW YORK 11973



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ABSTRACT

Test results are reported for the degradation of simulated decontamination wastes by wet-air oxidation. The data indicate that wet-air oxidation can effectively degrade organic complexing agents typically used in chemical decontaminations. Although less than 90% of the available organic carbon was oxidized, more than 95% of the organic reagent was degraded. Results are given on the solidification test of NS-1 decontamination reagent in cement.

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The IMPACT OF LWR DECONTAMINATIONS ON SOLIDIFICATION,
WASTE DISPOSAL AND ASSOCIATED OCCUPATIONAL EXPOSURE

EXECUTIVE SUMMARY

The Nuclear Regulatory Commission (NRC) is concerned with evaluating the effectiveness and safety of chemical decontamination processes which are being proposed for light-water reactor (LWR) primary systems as a means of reducing occupational exposure and ensuring continued safe operation. The areas of concern being addressed are: the type, volume and toxicity level of the rad-waste streams generated by decontamination and their subsequent management at the plant and at the disposal site.

Because of the large amounts of chelates or complexing agents required for a full system decontamination, it is desirable to determine if there are methods which would convert these reagents to more innocuous forms. The objectives of the program at Brookhaven National Laboratory (BNL) are to identify the information and conduct the tests necessary to aid the NRC in making regulatory decisions on the solidification and waste disposal aspects of chemical decontamination processes. In particular, this program focuses on in-plant methods for converting decontamination wastes to more acceptable forms prior to disposal.

The BNL program has provided an evaluation of potential decontamination processes, the wastes generated and potential waste management practices (NUREG/CR-3444, Vol. 1). Subsequent laboratory studies have confirmed that incineration and acid digestion are capable of destroying selected decontamination reagents. Further, this work has assessed the solidification of simulated decontamination resin wastes in cement and vinyl ester-styrene (NUREG/CR-3444, Vol. 2).

The work discussed in this report covers a continuation of the laboratory evaluation of processes for destroying decontamination reagents. The data indicate that wet-air oxidation can effectively degrade the organic complexing agents typically used for chemical decontaminations. However, the resulting waste stream may need to be evaluated before it can be effectively managed prior to disposal. Further, the solidification studies have been extended to include treatment of a liquid decontamination waste stream. In a limited study, the NS-1 reagent was solidified in cement. A free standing monolith was obtained having no associated free liquid and good mechanical strength.

Based on the efforts to date, areas which should be researched in the future include an evaluation of bitumen as a solidification medium for decontamination wastes and the impacts of decontamination wastes on standard containers. The objective of the work is to generate data that will aid NRC in assessing problems that may be encountered with the long-term storage or disposal of decontamination wastes and to evaluate the acceptability of

on-site decontamination waste handling and solidification processes. These experiments would investigate the corrosion or degradation of container materials in contact with decontamination resin wastes and include examination of the effects of irradiation on decontamination wastes which may result in gas generation or the release of liquids. It is believed that the biodegradation of decontamination wastes should be studied, as well as the effects of thermal cycling on solidified wastes. The tests planned are consistent with those recommended in the Technical Position on Waste Form to demonstrate waste form stability.

1. INTRODUCTION

The chemical decontamination of power reactor subsystems continues to grow as a cost-effective method for reducing radiation fields and subsequent occupational exposure during maintenance operations. The U.S. Nuclear Regulatory Commission (NRC) is concerned with evaluating the effectiveness and safety of chemical decontamination processes. The type, volume and toxicity level of the decontamination waste streams are among the areas of concern, as well as the waste management practices both in the plant and at the disposal site.

In the past, 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. The reagents found to enhance migration or to decrease the sorptive capacity of soils are typical of those that may be employed in processes used to decontaminate light-water reactors (LWR).

The NRC sponsors a program at Brookhaven National Laboratory (BNL) to determine if chemical decontamination wastes can be treated at the plant in a manner that will mitigate the potential hazards associated with disposal of these wastes. The first annual report (NUREG/CR-3444, Vol. 1), evaluated potential decontamination processes, the wastes generated and potential waste management practices. Following this review, a test program was initiated to evaluate the effectiveness of certain processes for degrading decontamination wastes. In addition, the program set out to assess the acceptability of solidified decontamination wastes for disposal in shallow land burial (NUREG/CR-3444, Vol. 2). BNL also evaluated the potential for increased occupational exposure during waste management operations (Davis, M. S., 1985). It was concluded that the increase in occupational exposure during such operations was far outweighed by the estimated exposure reductions following chemical decontaminations.

This program and work conducted in another BNL program (Properties of Solidified Decontamination Wastes) are developing information pertinent to the safe disposal of decontamination wastes and providing basic information for the development of site licensing conditions. Technologies presently available or proposed for the management of hazardous and radioactive wastes are being tested for their ability to degrade the organics to more innocuous forms prior to disposal. Direct solidification of decontamination wastes is being investigated to determine if the solidified waste would meet the minimum requirements established by NRC in the regulation, "Licensing Requirements for Land Disposal of Radioactive Waste" (10 CFR Part 61).

Some of the technologies or methods that may be useful for processing decontamination wastes prior to disposal include incineration, pyrolysis, acid

or chemical digestion, wet air or aqueous-pressurized oxidation and uv-oxyphotolysis. Other procedures such as elution of the reagents from the resins, concentration of reagent solutions and drying of resin wastes are all considered precursors to the more destructive processes.

During Fiscal Year 1984, BNL conducted a laboratory study (NUREG/CR-3444, Vol. 2) of the effectiveness of incineration and acid digestion for destroying simulated decontamination wastes. Additionally, the program has included a laboratory evaluation of the solidification of dilute process decontamination wastes. Simulated decontamination resin wastes have been solidified in cement and vinyl ester-styrene. Waste forms were examined for the presence of free liquid and were tested for mechanical durability and the ability to withstand immersion in water. Work is planned to examine the use of bitumen for solidification of decontamination wastes.

This report describes the research performed during Fiscal Year 1985. The results of tests on the wet-air oxidation of simulated decontamination wastes are given in Section 2. Work on the solidification of simulated decontamination wastes is discussed in Section 3. Particular attention is given to the results of a focused study on the solidification in cement of a liquid decontamination waste stream.

The report concludes with a discussion in Section 4 of the implications of BNL's work on degradation and solidification of simulated decontamination wastes as a means of effectively managing wastes containing organic complexing agents.

2. WET-AIR OXIDATION OF DECONTAMINATION REAGENTS

The program at BNL has addressed methods for converting decontamination reagents into more innocuous forms prior to disposal. Of the destructive methods available, incineration, acid digestion, and wet-air oxidation are being evaluated by laboratory-scale testing. Previously, BNL has concluded that, in principle, both incineration and acid digestion can be very effective for degrading decontamination resin wastes. Incineration appeared to be slightly more effective than acid digestion. However, 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. Details of the testing are given in the report NUREG/CR-3444, Vol. 2. Work has shifted to the evaluation of wet-air oxidation as a method for treating decontamination wastes. In this section, the results of laboratory tests on the wet-air oxidation of simulated decontamination resin wastes are discussed.

2.1 Introduction

Wet-air oxidation has been applied to the treatment of several industrial streams (Ontario Research Foundation). It was claimed that any combustible material that can be maintained in the liquid phase can be oxidized by this process. Wet-air oxidation has also been proposed for management of low-level combustible wastes and alpha-contaminated low-level wastes (Clark, W. E., 1970 and 1973). A limited experimental program (Bonnici, P. J.) was conducted to determine the feasibility of using wet-air oxidation for volume-reducing spent ion-exchange resins prior to disposal.

Wet-air oxidation or pressurized aqueous combustion is a process that involves the oxidation of combustible materials in the presence of liquid. High pressures are employed to maintain the liquid phase. While some work has been reported on batch-type processes (Clark, W. E., 1970 and 1973; Williams, P. E.), the industrial units normally operate with a continuous feed. Recycling the residue and liquid effluent through the process may be advantageous to more complete degradation. Factors affecting wet-air oxidation are temperature, pressure, oxygen availability, agitation, and the amount of material being processed.

Testing of the wet-air oxidation process for destruction of decontamination reagents was carried out in the present study using a batch mode reactor. The types of samples processed by wet-air oxidation include organic reagents, organic anion exchange resins and organic anion exchange resins equilibrated with an organic reagent. The organic acids, combination of acids and actual decontamination reagent, are those which are candidate reagents for use in decontamination processes (Anstine, L. D., 1981; Bradbury, D., 1980; Choppin, G. R., 1979; Pettit, P. E., 1980; and Swan, T., 1982). The resins are those which have been suggested for use with the dilute chemical processes. The efficiency of the process was monitored by measuring the amount of organic carbon oxidized. Further, measurements were made of the quantity of

organic acid remaining in solution at the end of the process. Some efforts were made to examine the effects of variations in process parameters on the oxidation of the samples.

2.2 Experimental

2.2.1 Apparatus

The autoclave used to evaluate the wet-air oxidation of decontamination reagents and ion-exchange resins was a 2-L Zipperclave supplied by Autoclave Engineers, Inc. The assembly, made of 316 stainless steel, was used with a glass insert to isolate the solution from the steel body. There is a cooling coil for quenching a reaction. For high speed stirring of the reaction solution the Zipperclave was equipped with a Magnedrive II assembly and a tachometer. Two 1000-watt ceramic band heaters were used to heat the autoclave.

A thermocouple well affixed to the head assembly allowed monitoring of the solution temperature during the process. Thermocouples were also installed to monitor the heater temperatures and the temperature of the autoclave head assembly. Monitoring the head temperature provided some idea of the temperature in the region of the O-ring used to seal the autoclave. A Kelrez O-ring, lubricated with Dow Corning high vacuum grease was used to seal the Zipperclave.

Several openings were available on the head assembly for accessing the autoclave. One port was equipped with a dip tube and valve for sampling the liquid phase in the autoclave. A gas inlet port equipped with a 1000-psig pressure gauge and a valve was used to pressurize the system with an oxygen containing gas (i.e., air or oxygen). Pure oxygen was used in this work and was supplied from a regulated tank. Another port and valve were connected to a gas sampling assembly. The gas sampling assembly consisted of a small manifold fitted with a 3-psi check valve, a 100-mL gas sample bulb and a vacuum pump. Gases passing through the check valve were exhausted to the atmosphere. Finally, one port was equipped with a pressure release plug and a 3000-psig pressure gauge.

2.2.2 Materials Tested

Table 2.1 gives a list of materials processed and the sample abbreviations used in this report. The reagents and ion-exchange resins were used as supplied.

Samples of resins equilibrated with organic acids were prepared by mixing a measured quantity of ion-exchange resins with a solution of organic acid (or reagent) such that there was an excess of acid to exchange with the theoretical exchange capacity of resins. IONAC A-365 (Sybron) anion exchange resins were equilibrated with picolinic acid. This resin has a polyacrylic matrix with weak base exchange groups and was used because it is the resin of choice for the LOMI decontamination process reagent which uses picolinic acid. Small quantities of the strong base anion exchange resin, IRN-78 (Rohm

& Haas), were equilibrated with an excess of ethylenediaminetetraacetic acid (EDTA), citric acid, oxalic acid and LND-101A reagent. The amount of organic acid (reagent) on the resin/acid samples was determined by measuring the amount of acid in the solution after filtration. The carbon content of the samples was calculated based on the carbon contents of the resins and the acids. Changes in the moisture content of the resins were determined by measuring the quantity of resin and water before and after equilibration. Details of a similar analysis were reported previously (Piciulo, P. L., August 1984b).

Table 2.1

Materials Processed by Wet-Air Oxidation

Na ₂ EDTA	Disodium ethylenediaminetetraacetic acid
CA	Citric acid
PA	Picolinic acid
EOC	Equimolar mixture of EDTA, oxalic acid and citric acid
IRN-78	Strong base organic anion exchange resins used in the OH ⁻ form. Resin has a polystyrene divinylbenzene matrix. Manufactured by Rohm and Haas.
IONAC A-365	Organic anion exchange resins having weak base and free base (NH ₂) functional groups. Resin has a polyacrylic matrix. Manufactured by Sybron.
EOC/IRN-78	Mixture of IRN-78 resins equilibrated with Na ₂ EDTA, oxalic acid and citric acid.
LND-101A/IRN-78	IRN-78 resins equilibrated with LND-101A reagent which is a proprietary decontamination reagent supplied by London-Nuclear Limited.
PA/IONAC A-365	IONAC A-365 resins equilibrated with picolinic acid.

2.2.3 Process Procedure

The samples processed consisted of either organic acids, organic ion-exchange resins or acid/resin mixtures, in one (1) liter of deionized water. Solutions contained either 0.5 or 1.0 percent by weight of material to be processed. The sample was poured into the glass liner inside the autoclave and the autoclave was assembled. The system was then pressurized with oxygen and power was applied to the heaters. Temperatures and pressures were recorded throughout the run.

A summary of the test conditions is given in Table 2.2. The run time reported is defined as the time from turning the heater on to when the heaters were turned off. The autoclave was cooled to room temperature before opening either by quenching with cold water or simply air cooling. During part of the run time, the system was at the maximum temperature and pressure listed.

Table 2.2

WAD Test Conditions

Sample	Quantity (g)	Run Time (h)	Maximum Temp. (°C)	Initial Pressure (psig)	Maximum Pressure (psig)	Stirrer Speed (rpm)	pH Final*	Observations
Na ₂ EDTA	5.0033	30.75	240	110	590	800	6.9	Final solution was colorless and had fine particulates.
Citric Acid	4.9995	28.2	229	110	570	800	3.4	Final solution was colorless.
CA/Fe(NO ₃) ₃	4.9984 ^a	7	212	104	445	800	N.D. ^b	Solution contains red suspensions
EOC	15.052 ^c	6.75	210		625	800	6.70	Yellow effervescent solution
Picolinic Acid	5.0003	6.7	210	202	625	840	6.31	Colorless solution
IRN-78	10.024	23.0	221	110	480	1200	4.4	Final amber solution had no visible resin beads, but some fine particulates.
IRN-78	5.0171	6.5	211	200	545	810	4.37	Solution slightly clouded and yellow in color.
IONAC-365	4.9966	6.5	210	202	545	800	7.48	Yellow effervescent solution.
PA/IONAC A-365 (1) ^d	5.0024	6	231	203	720	840	7.04	Pale yellow solution
(2)	5.0028	5.5	211	203	570	810	6.71	Pale yellow solution
(3)	4.9990	6	211	203	550	810	6.50	Pale yellow solution
EOC/IRN-78 (1)	5.0486 ^e	5.7	220	201	610	810	4.51	Pale yellow/cloudy
(2)	4.9974	6.0	217	250	693	810	4.42	Pale yellow/cloudy
(3)	4.9968	5.75	215	250	653	800	4.44	Pale yellow/cloudy
LND 101A/IRN-78 (1)	4.9955	6	226	202	660	860	4.35	Pale yellow solution
(2)	4.9975	6	220	202	640	830	4.33	Yellow solution/particulate
(3)	5.0002	6	225	202	650	820	4.28	Yellow solution/particulate
Blank	0	6.3	214	200	635	830	6.15	Colorless solution

^aWeight of CA in solution. The process solution also contained 3.4766 g of Fe(NO₃)₃.

^bN.D. = not determined.

^cThe sample consisted of 8.562 g Na₂EDTA, 4.419 g CA and 2.071 g OA.

^dValues in parentheses are used to distinguish replicate runs.

^eSamples contained 1.55×10^{-3} moles each of EDTA, oxalic acid and citric acid.

Aliquots of the processed solutions were collected at the end of the run and, in some cases, at different times during the run. Liquid samples were analyzed for carbon content and, if applicable, the presence of organic acid. A gas sample was collected at the end of the process after the system was cooled to room temperature.

2.2.4 Analytical Methods

2.2.4.1 Carbon Content

The carbon content of the samples was measured using a Beckman Model 915 Total Organic Carbon Analyzer. The instrument can determine either inorganic carbon or total carbon content of a sample. Organic carbon content of the solutions was determined by difference.

2.2.4.2 Organic Acids

Liquid samples collected at the end of the process run were analyzed by ion chromatography for any residual organic acid remaining in the solution. A Dionex 21101 Ion Chromatograph equipped with an AS-7 column eluted with ≈ 16 mM nitric acid was used for the separation. A post column reactor containing iron nitrate and an ISCO V4 UV spectrophotometer were used for detection. Details of the procedures have been reported elsewhere (Picciolo, P. L., August 1984a).

2.2.4.3 Gas Analysis

Gas samples were analyzed with a Perkin Elmer Model 3920 Gas Chromatograph equipped with a column specific for the analysis of permanent gases. Gases detectable with this system include: H_2 , N_2 , O_2 , CO_2 , CO , and CH_4 . Water vapor and other gases in the sample were not measured and residual O_2 (the reaction gas) was not quantified.

2.3 Results

A summary of the process results is given in Table 2.3. The amount of carbon initially present in the sample is based on the mass of the sample processed and the carbon content. Samples of resins and acid/resin mixtures have errors associated with the initial carbon which result from the determination of the carbon content of the samples (BNL-NUREG-33873).

Values of percent organic carbon oxidized are used to monitor the efficiency of the process. These values are based on the amount of organic carbon measured in the process solution as compared with the initial amount of carbon present. All of the carbon in the resins or reagents was considered as organic carbon. Organic carbon remaining in solution after wet-air oxidation may be associated with a fraction of the original organic complexing agent which was not degraded by processing or with other hydrocarbons which were degradation products. If there is insufficient oxygen then hydrolysis can predominate oxidation (Williams, P. E.; Ontario Research Foundation) during

the wet-oxidation process. The products formed (low molecular weight carboxylic acids such as formic, acetic, propionic, etc.) may resist further oxidation (Clark, W. E., 1970 and 1973; Williams, P. E.). Williams (1975) and others have indicated that steady concentrations of formic and propionic acids are produced during the oxidation of butyric acid, and that acetic acid concentrations increase. The work done by Clark (1970; 1973) and by Bonnici (1981) indicates the production of acetic acid which was somewhat resistant to further oxidation. No detailed analyses were made of the organic chemicals remaining in the process solutions. However, when possible the post wet-air oxidation samples were analyzed for the presence of the initial acid being processed. Based on the quantity of reagent remaining in solution, the percent reagent destroyed was calculated and the results are also listed in Table 2.3.

Table 2.3
WAO Carbon Analyses of Post Run Liquid Samples

Sample	Initial Carbon (mg)	Carbon Remaining ^a			Percent of Organic Carbon Oxidized ^b	Percent of Reagent Degraded ^c
		Total (mg)	Inorganic (mg)	Organic (mg)		
Na ₂ EDTA	1616	440	280	160	90	>99
Citric Acid(CA)	1875	360	20	340	82	>99
CA/Fe(NO ₃) ₃	1875	496	220	276	85	N.O.
IRN-78	3360±20	1400	N.D.	N.D.	58 ^d	N.D.
IRN-78	1781±25	722	185	537	70	N.D.
IONAC A-365	1569±40	743	299	444	71	N.D.
EOC	4968	1972	674	1298	56 ^f	99,97,65 ^e
Picolinic Acid(PA)	2570	1800	100	1700	34	>99
PA/IONAC A-365(1)	2190±30	1230	402	828	62±2	>99
(2)	2190±30	1227	303	924	58±2	97
(3)	2190±30	1160	325	835	62±2	95
EOC/IRN-78 ^f (1)	2360±30	1388	210	1178	50±1	>99,99,94 ^e
(2)	2340±30	1011	90	921	61±1	>99,99,92
(3)	2340±30	523	92	831	64±2	>99,99,93
LND-101A/IRN-78(1)	2030±30	733	132	601	70±2	N.R,R
(2)	2030±30	901	90	811	60±2	N.R.
(3)	2030±30	938	103	835	59±2	N.R.
Blank	0	10	0	10	N.D.	N.D.

^aOrganic carbon is determined from the difference between total carbon and inorganic carbon. N.D. means not determined.

^bPercent carbon oxidized is based on organic carbon remaining and the carbon initially present.

^cPercent degradation is based on the amount of organic acid left in solution compared with that initially present.

^dValue reported is based on total carbon and carbon available.

^eValues given are percent destruction of EDTA, OA, and CA, respectively.

^fSamples contained equimolar amounts (1.55×10^{-3} moles) of EDTA, OA, and CA.

^RBecause the composition of LND-101A reagent is proprietary, percent degradation of the component(s) is not reported.

Organic Acids

In initial testing, samples of Na_2EDTA and citric acid were processed for about 30 h. These runs were sampled after various times during processing and the data (although limited) suggest that oxidation of the organic carbon occurs relatively quickly and extended processing time does not result in a large increase in the amount of carbon oxidized. Figure 2.1 is a plot of reaction time vs fraction of organic carbon oxidized for the wet-air oxidation of EDTA and citric acid. After 6.5 h, about 80% of the organic carbon in the EDTA sample was oxidized. An additional 10% of the organic carbon was oxidized after 30 h of processing. Oxidation of organic carbon in citric acid had essentially proceeded to a limiting value after 20 h. The heat was turned off at 28 h and no significant increase in carbon oxidized was observed. The sample collected at 45 h, after the system had returned to room temperature, showed <1% of additional carbon oxidized.

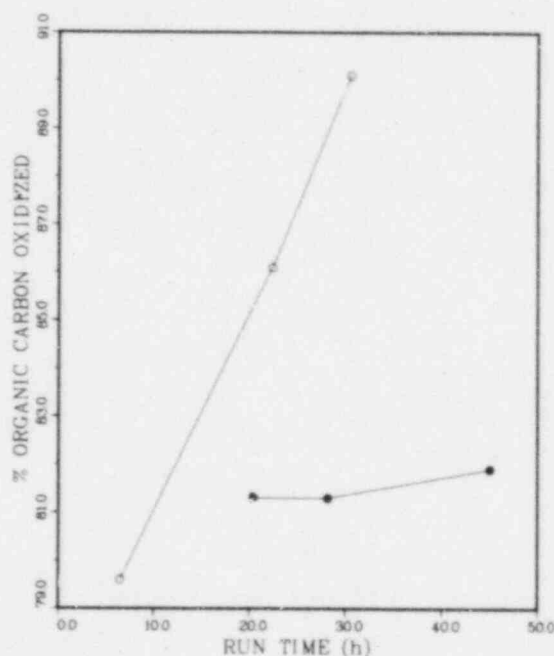


Figure 2.1. Percent organic carbon oxidized vs run time for the wet-air oxidation of EDTA (o) and citric acid (•).

A striking difference between the results for EDTA and citric acid is the amount of inorganic carbon detected in the processed solutions (Table 2.3). Since the disodium salt of EDTA was processed, carbonates and bicarbonates are likely counterions for the remaining sodium present in solution. On the other hand, citric acid contains only C, O, and H, and dissolved CO_2 as carbonic acid may be the likely species to account for the inorganic carbon. The initial amount of Na_2EDTA contains 0.027 moles of sodium which would require an equal number of moles of HCO_3^- or half as many moles of CO_3^{2-} for charge neutrality. Such quantities from the wet-air oxidation would result in ≈ 320 mg

and ≈160 mg of inorganic carbon in solution from bicarbonate and carbonate, respectively. The 280 mg of inorganic carbon may be the result of having approximately 75% of the sodium as NaHCO_3 and the remaining sodium as Na_2CO_3 .

The pH of the solutions changed after wet-air oxidation (Table 2.2). Initial pH values are caused by the acid or resin in solution. The final pH is indicative of chemicals consumed or produced during processing. For Na_2EDTA the increase in pH from ≈5 to ≈7 may be attributed to dissolved sodium carbonate (and bicarbonate) and perhaps quantities of unoxidized carboxylic acids. The pH of the citric acid process sample increased slightly. This may simply be due to a more dilute acid solution, since more than 80% of organic carbon was oxidized and therefore less acid must be present in solution.

After processing the solutions containing EDTA and citric acid, the samples were analyzed for EDTA and citric acid remaining in solution. The results indicated that >99.9% of the EDTA and 99.8% of the citric acid were destroyed by processing. Since the amount of organic carbon oxidized was less than 90% for both acids, other organic carbon containing species must remain in solution. These can include low molecular weight carboxylic acids such as formic, acetic, propionic, etc. (Williams, P. E.; Bonnici, P. J.).

A 1-liter solution of 0.026M citric acid was oxidized for seven hours. The solution also contained 9×10^{-3} M ferric nitrate to determine if the presence of iron ions would enhance the amount of citric acid that is degraded. After processing, the final solution was an opaque red and there appeared to be about 85% oxidation of the acid, based on the amount of organic carbon remaining in solution. The presence of the metallic ion (Fe^{+3}) or perhaps decomposition of nitrate appeared to affect the oxidation. Ion chromatography data are not available for the $\text{CA}/\text{Fe}(\text{NO}_3)_3$ system to compare the amounts of CA left in solution with that determined previously; however, the amount of organic carbon remaining is smaller, indicating some increase in the oxidation of organic carbon.

Wet-air oxidation of the equimolar mixture of EDTA, citric acid and oxalic acid (1.5 weight percent in the simulated waste stream) appears to result in 56% oxidation of the mixture. This result is based on the amount of organic carbon left in solution. Ion chromatography data, however, indicate that more than 95% of the EDTA and OA were oxidized compared to ≈65% of the citric acid. The lower percent oxidation of citric acid in the EOC mixture from that observed for CA alone or in $\text{CA}/\text{Fe}(\text{NO}_3)_3$ may be due to the shorter reaction time, the absence of $\text{Fe}(\text{NO}_3)_3$ or because the sample was a mixture. It is possible that an unidentified product in the wet-air oxidation process solution may interfere with the ion chromatography analysis for citric acid. A chemical having a retention time similar to that for citric acid would be quantified as citric acid. A high estimate of the amount of citric acid in solution would give a corresponding low estimate of the amount of acid degraded. A complete analysis of the products in the process solution was beyond the scope of this work.

A 5.003-g sample of picolinic acid was processed for more than 6 h. The colorless solution recovered at the end of the run was slightly acidic (pH = 6.3). Analysis indicated that only 34% of the organic carbon in the sample was oxidized but more than 99% of the PA was destroyed.

Ion-Exchange Resin

Based on the amount of organic carbon left in solution (Table 2.3), ion-exchange resins present at 0.5 percent by weight were oxidized ≈70%. No resin beads were observed in the post run solution although some "cloudiness" was noted in the solution. Comparing the two oxidations reported for IRN-78, the amount of resins used varied by a factor of two. If the percent oxidation is estimated from the total carbon remaining, there is no significant change (58% vs 60%). However, based on organic carbon in solution, run 2 showed 70% oxidation of the resins. In this run, a larger amount of oxygen was used. The oxidation of the IONAC A-365 resins was comparable to that of IRN-78 resins when processed using similar conditions.

The post run solutions were yellow in color. The pH of the solutions after processing were ≈4.4 for IRN-78 resins and ≈7.5 for IONAC resins. The oxidation products of the two resin types present different water chemistries after processing. These solutions may have different requirements for successful solidification of the process liquids prior to burial.

Acid/Resin Mixtures

Replicate samples of PA/IONAC A-365 processed under similar conditions showed comparable percentages of carbon oxidized. The solutions recovered were pale yellow and neutral to slightly acidic. Small quantities of picolinic acid that were measured in the process solution indicated more than 95% destruction of the acid. Run 1 showed >99% destruction of PA which was the largest of the three runs. The major differences in process parameters were a higher temperature, higher pressure, and higher stirring speed.

Oxygen pressure was varied when processing samples of EOC/IRN-78. An increase of 40 psig in oxygen pressure resulted in an increase in the amount of organic carbon oxidized from 50% to more than 60%. Further, there was ≈50% less inorganic carbon remaining in the process solutions of runs with the higher pressure compared with inorganic carbon in EOC/IRN-78 (Run 1). Analysis of the process solutions indicated that in all cases, >99% of EDTA, 99% of oxalic acid and about 93% of citric acid initially present in the samples was destroyed.

Three samples of LND-101A/IRN-78 were processed at similar temperatures and pressures but with different stirrer speeds. The resulting process solutions differed in that a pale yellow liquid was recovered from run 1 whereas the other process liquids were darker and contained a fine particulate. The carbon content of the process liquids showed that a greater percentage of organic carbon (70%) was oxidized in the first run than in subsequent runs (≈60%). The last two samples were processed under similar conditions and had

similar data for carbon in solution. The major difference among the three runs was the higher stirrer speed of run one. Increased agitation will cause an increase in oxygen transport into the aqueous phase thus promoting oxidation.

Blank

A blank run was performed by processing 1-liter of deionized water under typical conditions used to process other samples (Table 2.2). The results of the carbon analysis show that ≈ 10 mg of organic carbon were present at the end of the run. It is possible that the carbon was removed from parts of the apparatus that are difficult to clean between runs (e.g., pressure gauges, tubing), or was admitted to the system as contamination from the O-ring grease (Dow Corning high vacuum grease, which is a silicone lubricant, was used) or from the oxygen feed line. The 10 mg of carbon observed in the total carbon analysis of the solution is equal to between $\approx 0.5\%$ and 2.8% of the total carbon observed in the wet-air oxidation runs of reagent samples (Table 2.2). This small amount of carbon is not likely to affect either the test being performed or the conclusions drawn.

Gas Samples

Analyses of gas samples provide data on the various gas phase species produced during wet-air oxidation of the simulated decontamination wastes. It was not intended in this work to correlate the carbon in the gas samples with the amount of organic acid destroyed. Table 2.4 gives a summary of the species measured in gas samples collected at the end of the wet-air oxidation process. The analysis was limited to permanent gases (H_2 , O_2 , N_2 , CO , CO_2 and C_1 and C_2 hydrocarbons) by the choice of column. Thus, there are no data on the presence of nitrogen containing compounds like ammonia, volatile amines, and NO_x species which might be produced on the degradation of anion exchange resins and nitrogen containing organic acids (i.e., EDTA, picolinic acid).

Carbon dioxide was observed, as anticipated, in all samples since it is the expected oxidation product for carbon. The presence of CO , however, indicates that oxidation was not complete. Additionally, the presence of methane and hydrogen suggests that oxidation was not complete. These gases were observed in samples containing IRN-78 anion exchange resins and samples containing citric acid.

Table 2.4

Summary of Gas Sample Analyses
(% by volume)

Sample	N ₂	CO ₂	CO	CH ₄	H ₂
CA	8.6	27	1.6	0.1	0.7
CA/Fe(NO ₃) ₃	42	6.5	0.54	-- ^a	--
IRN-78	16	35	3.4	0.2	0.3
IRN-78	7.0	7.4	0.88	--	--
IONAC A-365	3.1	9.2	0.44	--	--
EOC	3.0	27	0.51	--	--
PA	2.7	4.1	0.03	--	--
PA/IONAC A-365 (1)	2.1	11	0.50	--	--
(2)	2.5	11	0.55	--	--
(3)	2.5	11	0.59	--	--
EOC/IRN-78 (1)	2.3	12	0.96	--	0.3
(2)	2.4	8.7	0.65	--	0.1
(3)	1.8	9.6	0.69	--	0.2
LND101A/IRN-78 (1)	2.9	12	1.0	0.1	0.2
(2)	1.3	10	1.0	0.1	0.2
(3)	4.3	10	0.9	--	0.2
Blank	1.5	0.3	0.04	0.1	--

^a-- means not detected.

2.4 Discussion

Based on the wet-air oxidation process data, the percent oxidation of organic carbon in samples of ion-exchange resins equilibrated with reagents ranged between 50% and 70%. Samples of acids alone showed as much as 90% organic carbon oxidized. Analyses of the process solutions for residual organic acid indicated that nearly all of the original acid present was degraded. Citric acid appeared to be the most difficult acid to degrade of the four tested (EDTA, oxalic acid, citric acid, and picolinic acid).

The limited testing reported here indicates that oxidation is sensitive to the amount of oxygen present (initial pressure) and agitation. Process temperature and operating pressure also had some affect on the efficiency of degrading the materials. Extended processing times did not result in significant increases in the amount of carbon oxidized. The quantity of sample being processed also limits the effectiveness of the treatment. These operating parameters should be considered in the design of a large-scale wet-air oxidation system.

Complete oxidation of organic carbon was not achieved under the process conditions used here. In particular, samples containing ion-exchange resins showed less than 70% oxidation of organic carbon. Even though the simulated wastes tested were not completely oxidized, wet-air oxidation was effective at degrading the decontamination reagents. Further processing of the waste may not be necessary if degradation of the organic complexing agents is the desired goal. However, the composition of the process solutions may need to be considered when planning the management of these wastes. For example, the presence of organic compounds may cause difficulties in direct solidification of the process liquids.

Based on the organic carbon analysis, process solutions contained organic species other than the original acid. Characterization of the process solutions was beyond the scope of this study, but it is likely that the composition may vary depending on the materials treated and the final degree of oxidation. Other workers (Bonnici, P. J.) have reported that the products of oxidation of ion-exchange resins contained $\approx 15\%$ low molecular weight carboxylic acid and that acetic acid, a major constituent, was somewhat resistant to further oxidation.

Consideration should be given to the organic acids remaining after wet-air oxidation regarding their potential to enhance radionuclide migration if released to the disposal environment. If the wet-air oxidation process were optimized, it is assumed acetic acid would be the major organic acid remaining. In general, acetate complexes are less stable than metal complexes of EDTA or picolinic acid, which are used in decontamination reagents. Thus, the presence of acetic acid in the final waste form would be of less significance to the enhancement of radionuclide migration compared with the complexing agents used for decontamination (assuming comparable release of the acids from the waste form). If the decontamination waste was oxidized to an intermediate degree such that the decontamination reagents were degraded but acetic acid was not the only organic acid that remained, then the composition of the process waste should be evaluated to determine whether the treatment was of value.

3. SOLIDIFICATION OF SIMULATED DECONTAMINATION WASTES

3.1 Introduction

The waste generated by the chemical decontamination of a light-water reactor will be disposed of in a shallow land burial site. Disposal of these wastes will be governed by the requirements established in the rule "Land Disposal of Radioactive Waste," 10 CFR Part 61, and future guidance given by the NRC and through site-specific criteria. The regulation establishes a waste classification system for shallow land burial and a set of minimum performance objectives. NRC in the Technical Position on Waste Form provides guidance to waste generators on waste form test methods and results acceptable for demonstrating compliance with the waste stability criteria.

A laboratory evaluation of the capability of methods for solidifying decontamination resin wastes has been performed in order to assess whether they will meet applicable stability criteria. The primary objective of the solidification tests was to determine if cement and vinyl ester-styrene binders are viable agents for immobilizing simulated decontamination resin wastes. Based on current information, both mixed bed resins and anion exchange resins were selected for solidification testing. An acceptable waste form was one that met the requirements in 10 CFR Part 61 and the guidelines given in the Technical Position on Waste Form. Tests for acceptability included a visual inspection for the formation of a free standing monolith, the presence of free liquid, testing of the mechanical stability of the waste form and immersion in water. The details of this work and a discussion of the results can be found in Reference 2.

Work on the solidification of simulated decontamination wastes has been extended to include solidification of a selected liquid waste stream from a concentrated decontamination process. The results of the laboratory-scale tests that were performed are discussed in this section.

3.2 Solidification of NS-1 Reagent in Cement

The NS-1 solvent, developed by Dow Chemical Company, is used for decontamination of BWRs. Although designed for use as a "concentrated" reagent, the NS-1 solvent has been used in a diluted form of 10% the original design concentration. Subsystems of various reactors have been treated with either dilute or concentrated NS-1 (Harmer, D. E.).

The waste stream expected from the use of NS-1 as a "concentrated" reagent was to be concentrated by evaporation of the process solvent. It was planned that the concentrated liquid would be solidified in vinyl ester-styrene. This was successfully demonstrated, and BNL reported (NUREG/CR-3165) results of physical tests of the waste product.

Alternate methods of waste management can be used for handling the dilute NS-1 solvent. The reagents can be concentrated to a liquid stream, or removed from solution by ion-exchange. Both the concentrated liquid and resin wastes

from an NS-1 process have been solidified in cement (Soto, R.). Work in the present study was intended to evaluate the direct solidification of dilute NS-1 solvent in cement. Waste composites were prepared and examined for the presence of free liquid, tested for mechanical strength and tested for their ability to withstand immersion in water as recommended in the Technical Position on Waste Form.

A sample of NS-1 solvent was obtained from IT Nuclear Services which is licensed by Dow Chemical Company to apply NS-1. The composition of NS-1 is proprietary. NS-1 is an aqueous solution which in the 100% form contains about 7.5% dissolved solids and has a pH of 3.6. The solvent contains chelates, complexing agents and inorganic salts plus a corrosion inhibitor. BNL received "spent" NS-1 (100%) which had three metallic compounds added to it: 1200 ppm ferric sulfate (or ferric citrate), 600 ppm nickel ammonium sulfate and 30 ppm copper sulfate. It was claimed that this approximates what would be treated following an actual decontamination process.*

It was believed that a probable waste stream from an NS-1 treatment would have a concentration approximately that of the 100% NS-1. This was based on knowledge that 100% NS-1 solvent can be used at the 10% dilution and then concentrated back to 100% prior to solidification. Further, BNL had a limited quantity of the material available for testing. It was anticipated, based on the results of the resin solidification tests, that pre-treatment by pH adjustment of the waste stream prior to solidification would be advantageous. Portland I cement was chosen for the solidification of NS-1.

3.2.1 Experimental

Pre-treatment of the NS-1 was as follows: 24.4 g of NaOH were added to 780 g of 100% NS-1 to adjust the pH of the waste to 12.0. A waste to cement ratio of 0.4 was chosen for the forms based on a preliminary test using a small portion of the pre-treated sample (≈ 30 g). The composites were prepared by a batch method, continuously hand-mixing cement into the liquid waste stream. Before all of the cement had been added, however, the mix became hot, dry, and unworkable. Also a strong ammonia smell was evident. Water was added to the batch until a workable mix was obtained. The resulting formulation consisted of 753 g NS-1, 23.6 g NaOH, 323-g water, and 1850+30 g cement which gives a waste (NS-1, NaOH, and water) to cement ratio of ≈ 0.6 . However, the NS-1 waste stream was diluted to $\approx 68\%$ the original concentration which may be less than the desired amount in a field solidification. The mix had a mud-like consistency and was poured into nominal 2.0-in. diam. by 4.0-in.-high cylindrical polyethylene forms. The eight forms obtained were capped and taped to prevent moisture loss. Within 24 hours, the forms were solid with no free liquid.

*Private communications between Dr. D. E. Harmer (IT Nuclear Services) and Dr. P. L. Picciolo (BNL) on April 18, 1984 and June 15, 1984.

Control forms were also prepared using water adjusted with NaOH to pH=12.0 in place of the waste and a waste-to-cement ratio of 0.6. Six forms were prepared and after 15 days of curing, the samples were solid with no free liquid.

3.2.2 Results and Discussion

The compressive strengths of the cement forms were measured according to the ASTM C39-80 test method. The average compressive strengths of four NS-1 samples and their controls are given in Table 3.1. The mechanical strengths of the controls were smaller than those of the forms containing NS-1. All forms had compressive strengths larger than the 50 psi recommended in the TP on Waste Form.

Table 3.1

Compressive Strengths of Cement Composites

Sample	Cure Period (days)	Compressive Strength	
		psi	MPa
NS-1	34	5840+240	40+2
Control	31	4370+240	30+2

Four NS-1 composites and three controls were immersed in 1-L of water after a 28-day cure period. After the 90-day immersion test, there was no visible sample deterioration.

These limited tests demonstrate that NS-1 can be solidified in cement to at least meet the Class A waste form requirements. However, assuming that half of the 7.5% solids in NS-1 are chelating agents, then the waste (NS-1 plus water) solidified in these tests contained less than 3% chelating agents. In the field, it may be desirable to concentrate the solvent to a waste stream containing a higher concentration of dissolved solids and thus a higher concentration of organic reagents. Solidification of such waste may not proceed as it did in the tests reported here. As with the work done on resin wastes, it is expected that variations in the composition of the liquid decontamination waste stream must be taken into account when establishing formulations for solidification.

4. SUMMARY

Wet-air oxidation appears to be an effective method for degrading simulated decontamination wastes. The process data given in this report show that even though the amount of oxidation of total organic carbon in the acid/resin mixtures ranged between 50 and 70%, there was greater than 92% degradation of the organic reagents. The percent degradation of the organic reagents is based on the quantity of reagent present after processing compared with the initial amount in the sample. It is believed, based on data collected in the ongoing BNL study, that wet-air oxidation can be comparable to incineration and acid digestion for degrading decontamination wastes. Testing in this program was limited to three simulated waste streams: reagents alone, anion exchange resins and anion exchange resins equilibrated with reagents. For each of the processes evaluated in this study, only limited efforts were made to optimize the process apparatus or operating parameters. It is recommended that waste-specific operating parameters be established if any of these processes are to be used commercially.

The acid/resin mixtures tested in this program were intended to simulate dilute process decontamination wastes. Resin wastes from actual reactor system treatments can include cation exchange resins, metal ions and radionuclides. The presence of these materials in the waste stream may affect the efficiency of degradation by wet-air oxidation. Although it was indicated in earlier studies that transition metal ions may catalyze the oxidation of organic materials (Ca^{+2} , Fe^{+2} , and Mn^{+2} nitrates were used as a catalyst by Clark, W. E., 1970), the presence of iron in processing citric acid had a limited effect. It would be necessary to determine whether a catalyst will increase oxidation of the resins at lower operating temperatures.

The present data suggest that the degradation of each acid can be affected by process parameters such as temperature, pressure, and agitation. Agitation (stirring) and oxygen overpressure did increase the amount of organic carbon oxidized in tests of EOC/IRN-78 and LND-101A/IRN-78. An increase in process temperature resulted in an increase in the degradation of picolinic acid in samples of PA/IONAC A-365. However, the temperature increase had a corresponding increase in operating pressure which promotes the rate of oxygen transfer into solution. It is not known if an increase in pressure alone would have given a similar result. Analyses of process solutions showed $\approx 99\%$ degradation of EDTA and oxalic acid, but a somewhat lower percentage degradation was observed for picolinic acid ($>95\%$) and citric acid ($\approx 93\%$) when processed under similar conditions. Thus, the composition of the waste stream to be processed should be considered when establishing process parameters.

The size of the batch-type processor used in the BNL study limited the sample size that could be treated. Additionally, the initial oxygen pressure in the system was limited to 200 psig (<1 mole O_2). Thus, only samples of 0.5 weight percent of waste-to-water were processed which is below the 2 to 20 weight percent organic matter expected to be treated by wet-air oxidation. Recycling the process solution or use of a flow system may increase the total degradation of the waste. The design of the wet-air oxidation reactor must

consider the concentration of waste to be processed; in turn, this will affect the effluent streams (off-gas and liquids).

Management of the effluent streams from the wet-air oxidation process will need to be considered. The process solutions will contain suspended solids, inorganic salts, and can include various inorganic and organic carbon-containing species. Further, the data show that the pH of the liquid stream is dependent upon the material processed. It is anticipated that the volume of the liquid stream would be reduced prior to any further treatment. If this waste stream were to be solidified prior to disposal in shallow land burial, then it should be demonstrated that the subsequent product meets the appropriate requirements of 10 CFR Part 61.

The off-gas stream from the wet-air oxidation of decontamination wastes will contain CO_2 , CO, and water vapor. However, methane and hydrogen have been observed and nitrogen-containing gases such as volatile amines and NO_x gases may also be present. Thus, off-gas treatment may be necessary.

Limited tests have demonstrated that a liquid waste stream from a decontamination using NS-1 reagent can be solidified in cement after pre-treatment by pH adjustment. The test reported here was for a single concentration of NS-1 in the waste stream. It is anticipated that the concentration used in this test is low compared to what may be used in full-scale solidifications under field conditions. As with the work done on resin wastes, it is expected that variations in the composition of the liquid decontamination waste stream must be considered when establishing process parameters for solidification.

Based on the efforts to date, areas which should be researched in the future include an evaluation of bitumen as a solidification medium for decontamination wastes and the impacts of decontamination wastes on standard containers. The objective of the work is to generate data that will aid NRC in assessing problems that may be encountered with the long-term storage or disposal of decontamination wastes and to evaluate the acceptability of on-site decontamination waste handling and solidification processes. These experiments would investigate the corrosion or degradation of container materials in contact with decontamination resin wastes and include examination of the effects of irradiation on decontamination wastes which may result in gas generation or the release of liquids. It is believed that the biodegradation of decontamination wastes should be studied, as well as the effects of thermal cycling on solidified wastes. The tests planned are consistent with those recommended by NRC to demonstrate waste form stability.

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Test results are reported for the degradation of simulated decontamination wastes by wet-air oxidation. The data indicate that wet-air oxidation can effectively degrade organic complexing agents typically used in chemical decontaminations. Although less than 90% of the available organic carbon was oxidized, more than 95% of the organic reagent was degraded. Results are given on the solidification test of NS-1 decontamination reagent in cement.

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