

AN EVALUATION OF DESTRUCTIVE METHODS FOR MANAGING DECONTAMINATION WASTES*

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ABSTRACT

Results are discussed of a laboratory evaluation of destructive methods for processing chemical decontamination wastes. Incineration, acid digestion and wet-air oxidation are capable of degrading decontamination reagents and organic ion-exchange resins. The extent of destruction as a function of operating parameters was waste specific. The reagents used in the testing were: EDTA, oxalic acid, citric acid, picolinic acid and LND-101A.

INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) is concerned with evaluating the effectiveness and safety of chemical decontamination processes which are being proposed for light-water reactor 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 radwaste 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. In order to provide technical information to aid the NRC in making regulatory decisions on the disposal of chemical decontamination wastes, Brookhaven National Laboratory has provided a laboratory evaluation of processes for degrading chemical decontamination reagents. The three destructive methods tested using laboratory-scale equipment included: incineration, acid digestion, and wet-air oxidation.

SAMPLES TESTED

The simulated waste streams included in this study were limited to: decontamination reagents alone, anion exchange resins alone, and anion exchange resins equilibrated with the chemical reagents. The candidate reagents used in the testing were: ethylenediaminetetraacetic acid (EDTA), oxalic acid, citric acid, picolinic acid (PA), and LND-101A, a proprietary reagent used by London Nuclear Limited, Ontario, Canada. Samples identified as EOC, containing an equimolar mixture of EDTA, oxalic acid and citric acid, were included to simulate waste from a multi-reagent decontamination process.

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 (low-oxidation state metal ion) decontamination process reagent which uses picolinic acid.⁽¹⁾ Quantities of the strong base anion exchange resin, IRN-78 (Rohm & Haas), were equilibrated with an excess of 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.⁽²⁾

INCINERATION OF SIMULATED DECONTAMINATION WASTES

There are several different incinerator designs which range from a starved or controlled air incinerator, to molten glass and salts incinerators. (For a brief description, see Reference 1.) It was not the intent of this program to evaluate all different types of incinerators but to assess whether combustion of decontamination wastes is a viable means of destroying or degrading these wastes prior to final packaging for disposal. A second objective was to determine, where possible, how process parameters (e.g., temperature) may affect the overall applicability of the process.

A tube furnace was set up to study the degradation of simulated decontamination wastes by incineration. Details of the experimental apparatus and analytical procedures are described elsewhere.⁽²⁾ Several modifications were made on the laboratory-scale incinerator to increase the efficiency of the combustion process. A pure oxygen feed was used as the oxidizing gas. When compressed air was used, excessive amounts of ash and soot were observed. An afterburner was added to further oxidize the combustion gas and a CuO catalyst was used to insure the oxidation of reduced carbon species (e.g., CO) to CO₂. The length of the main chamber and the afterburner limit, to some extent, the amount of sample that can be combusted.

Destruction of the materials was monitored by a carbon mass balance. The off gas of the incinerator was passed through a sodium hydroxide gas scrubber to trap CO₂. The quantity of carbon from CO₂, determined by titration of carbonate-bicarbonate, was related to the initial carbon present in the sample. Organic acids, organic ion-exchange resins, and organic ion-exchange resins equilibrated with organic reagents were incinerated.

A summary of the incineration data is given in Table I. Following incineration of solid samples of organic reagents and the proprietary reagent LND-101A.

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80% and greater of the available carbon could be accounted for. The carbon recovered during incineration of the resin samples appears also to be in the range of 80% or greater. However, there is larger uncertainty in this value due to uncertainty in the carbon content and water content of the resins. Species other than CO_2 , CO , and CH_4 have been identified during the incineration of EDTA but in trace amounts.⁽²⁾ These include HCN and NO . Fourier Transform Infra-Red spectra of gas samples taken before the copper oxide catalyst indicate the presence of trace quantities of N_2O and HNO_3 during combustion of EOC_2 and N_2O , HNO_3 , NO_2 , and HCN during combustion of IRN-78 ion-exchange resins. However, the dominant species in all instances was CO_2 .

TABLE I
Summary of Incineration Tests

| Sample | Trapped Carbon (%) |
|----------------|--------------------|
| EDTA | 87-100 |
| Citric acid | 85-100 |
| Picolinic acid | 91-99 |
| EOC | 79-85 |
| LND-101A | 79-85 |
| IRN-78 | 85-95 |
| Ionac-365 | 86-96 |
| EDTA/IRN-78 | =97 |
| EOC/IRN-78 | 77-100 |
| PA/Ionac A-365 | 70-91 |

The results for the incinerations of resins equilibrated with decontamination reagents are comparable with those for the resins and acids alone. In most cases, greater than 90% of the available carbon was accounted for in the NaOH gas traps. If the estimates of available carbon in the acid/resin samples tested were low, then the reported percent carbon recovery for these samples may be high. However, the reproducibility of the tests demonstrates that the process was consistently effective at destroying the reagents and resins. There was no obvious explanation for the 77% and 70% carbon recovery observed for samples EOC/IRN-78 and PA/Ionac A-365, respectively.

Some parameters were waste specific. For example, the temperature of the main chamber normally had to be adjusted for the sample being combusted. While a temperature of 700°C was adequate for a solid sample of EDTA, citric acid burned too quickly at this temperature. This resulted in ash and char being deposited on the main chamber and into the afterburner. With damp resins (resins in the as-received form) in a pure O_2 stream, the oxidation could be more easily controlled. This may indicate that a change in combustion temperature is required for dried resins.

If an incinerator is broken down into three subsystems (feed system, the incinerator, and the off-gas system), the following comments may be applicable to large-scale processing. It was observed that combustion proceeded more completely if the sample was introduced into a hot combustion chamber. When samples were placed in a cold furnace and the temperature increased, char or soot formed. (Once the furnace is at temperature, these can be burned off within the hot zone.) Both compressed air and oxygen were tested as oxidizing mediums. When compressed air was used, particularly with resin samples, large amounts of soot

and smoke were formed. With compressed air or a depleted oxygen stream, pyrolysis can occur. The choice of oxidizing medium would then affect the rest of the incinerator design. Depending on the sample size, the soot and smoke can be transported as far as the gas trapping system. This is due, in part, to the larger gas flow rates required with a compressed air feed stream. Therefore, the size of the sample, the feed stream, and the length of the combustion zone are all important process parameters. These three factors all affect the residence time in the hot zones.

For the gas handling systems, an afterburner and a CuO catalyst were used to insure complete oxidation before trapping with caustic solution. An independent air feed to the afterburner may eliminate some of the soot and smoke evolved with a compressed air feed. It was found that the trapping efficiency of the scrub solutions depended on the sample size and the configuration of the traps. If all off-gases are to be trapped by this type of system, these solutions may require frequent replenishment since the trapping efficiency decreases rapidly as the solution pH drops. The combustion system we have used was all glass and no statement can be made about potential corrosion problems. Corrosion is known, however, to be a prime consideration with incinerators.⁽³⁾ In addition, a scrub solution such as the one used here (1 N NaOH) may cause corrosion in the off-gas system if the materials chosen are susceptible to attack by alkaline solutions.

No solid wastes remained in the incinerator as would be expected in processing actual radwaste. This is primarily because pure acids or acid/resin samples were combusted and conditions were optimized for complete combustion. However, the off-gas scrub solutions from actual radwaste incineration will contain large amounts of Na_2CO_3 and possibly NaOH or NaHCO_3 , depending on their pH. The acid scrubber may also contain nitrates, sulfates and chlorides, depending on the type of wastes. These may require further management prior to disposal.

CHEMICAL DIGESTION: SULFURIC ACID AND HYDROGEN PEROXIDE

While many chemical digestion systems have the potential to degrade or destroy chemical decontamination wastes, acid digestion as a process has been developed to a pilot plant scale for use with low-level radioactive wastes⁽¹⁾ and was therefore selected for study in the BNL program. After scoping studies with both HNO_3 and H_2O_2 as the secondary oxidant, H_2O_2 was selected for its ease of handling and its apparent better oxidation capabilities. No studies have been done of the effect of catalysts and only minor variations in process parameters have been studied. The primary goal was to determine if chemical digestion, specifically acid digestion, is effective for processing simulated chemical decontamination wastes.

The acid digestion unit has been described in detail elsewhere.⁽²⁾ The chemical system employed consisted of a hot sulfuric acid bath with hydrogen peroxide as the secondary oxidant and oxygen as a carrier gas. As for the incineration tests, the acid digestion off gas passed through a CuO catalyst and a CO_2 trap system and the fraction of destruction was determined by carbon mass balance.

The data listed in Table II indicate that more than 70% of the available carbon of the reagents or the resins can be accounted for if the acid digestion process conditions are optimized. Similar results are

achievable in the acid digestion of resin samples equilibrated with candidate decontamination reagents. The reproducibility of the carbon recovery values in general demonstrated that the acid digestion process was consistently effective at destroying the resins and reagents. However, the accuracy of the results is dependent on the accuracy of the calculation of carbon in the original acid/resin samples. For example, if the amount of carbon in the acid/resin samples was underestimated then the percent carbon recovery reported may be too high.

TABLE II
Summary of Acid Digestion Tests

| Sample | Trapped Carbon (%) |
|-----------------|--------------------|
| Citric acid | 70-88 |
| Picolinic acid | 77-97 |
| EOC | 62-83 |
| LND-101A | 92-98 |
| IRN-78 | 84-90 |
| Ionac-365 | 76-92 |
| EOC/IRN-78 | 79-99 |
| PA/Ionac A-365 | 70-87 |
| LND-101A/IRN-78 | 85-94 |

In general the sample size was limited such that between 0.5 g and 0.9 g of organic carbon was being processed. One test of an EOC/IRN-78 sample showed that the system could handle ≈ 2 g of organic carbon but it was necessary to prolong the reaction time. A larger percent carbon recovery may have been achieved had more than 52 mL of H_2O_2 been used. The result indicated that the amount of H_2O_2 used for the smaller samples was in excess. No effort was made to determine the minimum quantity of H_2O_2 needed for digestion of samples containing 0.5 g of carbon.

The results from the digestion of LND-101A indicated that a combination of smaller sample size, longer reaction time, large amounts of H_2O_2 , and the CuO catalyst all enhance the destruction of the reagent and reduce the amount of by-products (e.g., CO).

The optimum conditions for each reagent and for resins have not been determined although several tests have indicated those parameters that are most important to the process. These include amount and rate at which the secondary oxidant is added, sample size, temperature and for best efficiency, a secondary system for fully oxidizing other carbon containing gases (e.g., CO , CH_4) and volatiles (e.g., acetone). The process has been found to be more efficient if the secondary oxidant is added continuously and if the digestion is allowed to proceed beyond the time when the acid bath appears clear. This may, in part, be due to the greater difficulty in oxidizing lower molecular weight by-products. If the temperature of the digestion is decreased, longer reaction time and more peroxide may be required, but process control may be easier. (The reaction time in this instance could, in principle, be shortened by the use of a suitable catalyst.) In some initial tests with HNO_3 as the secondary oxidant, the process was more difficult to control than with hydrogen peroxide. However, in the work conducted in this program, no effort has been expended to investigate other oxidants or the potential usefulness of a catalyst. The tests conducted

focus primarily on the ability of the process to convert the wastes to more innocuous forms. No mechanistic studies have been done to elucidate those areas where changes in or additions of reactants would optimize the process.

WET-AIR OXIDATION OF DECONTAMINATION REAGENTS

Wet-air oxidation has been applied to the treatment of several industrial streams.⁽¹⁾ 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. A limited experimental program⁽⁴⁾ 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, 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.

The wet-air oxidation of decontamination reagents and ion-exchange resins was carried out in a batch mode using a 2-L autoclave. A quartz insert was used to isolate the solution from the steel body. Further details of the apparatus are given in Reference 5.

The samples processed consisted of either organic acids, organic ion-exchange resins, or acid/resin mixtures, in one liter of deionized water. Solutions contained either 0.5 or 1.0 percent by weight of material to be processed. Oxygen was used to pressurize the autoclave before heating the system. Typical ranges of operating conditions for processing the acid/resin mixtures were: initial oxygen pressure, 300 to 250 psi; maximum temperature, 210 to 225°C; maximum pressure, 550 to 720 psig; stirrer speed, 800 to 840 rpm; and run time, 5.5 to 6 h.

A summary of the process results is given in Table III. Values of percent organic carbon oxidized were used to monitor the efficiency of the process. These values were 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^(6,7) during the wet-oxidation process. The products formed (low molecular weight carboxylic acids such as formic, acetic, propionic, etc.) can resist^(7,8,9) further oxidation. Williams⁽⁷⁾ 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^(8,9) and by Bonnici⁽⁴⁾ 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 WAO samples were analyzed for the presence of the initial acid being processed. Based on the quantity of reagent remaining in

solution, the percent reagent degraded was calculated and the results are also listed in Table III.

TABLE III
Summary of Wet-Air Oxidation Tests

| Sample | Carbon Oxidized (%) | Reagent Degraded (%) |
|---------------------|---------------------|--------------------------|
| EDTA | 90 | >99 |
| Citric Acid | 82 | >99 |
| EOC | 56 | 99, 97, 65 ^a |
| Picolinic Acid (PA) | 34 | >99 |
| IRM-78 | 70 | ND |
| Ignac A-365 | 71 | ND |
| PA/Ionac A-365 | 58-62 | 95->99 |
| EOC/IRM-78 | 50-64 | >99, 99, 92 ^a |
| LND 101A/IRM-78 | 60-70 | ND |

^aValues are given for the percent of EDTA, oxalic acid, and citric acid degraded, respectively.

Based on the WAO 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 effect 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⁽⁴⁾ have reported that the products of oxidation of ion-exchange resins contained =15% low molecular weight carboxylic acid and that acetic acid

a major constituent, was somewhat resistant to further oxidation.

CONCLUSIONS

Resins, organic acids and acid/resin combinations can be successfully degraded by incineration, acid digestion and wet-air oxidation. For incineration, oxygen as a carrier gas and a high afterburner temperature both promoted a high degree of oxidation of these carbon containing materials to CO₂. Process temperature was important to minimize soot or maximize oxidation of the samples. The oxygen carrier gas and an excess of H₂O₂ helped to promote oxidation of the samples by the acid digestion process. However, a CuO catalyst was necessary to convert CO to CO₂. Complete oxidation of organic carbon was not achieved by wet-air oxidation under the process conditions used. Analyses of the process solutions for residual organic acid indicated that nearly all of the acid originally present was degraded. Further consideration should be given to processing the radioactive solutions remaining after wet-air oxidation.

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