

TREATMENT OF RADIOACTIVE MIXED WASTES IN COMMERCIAL LOW-LEVEL WASTES*

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ABSTRACT

Management options for three generic categories of radioactive mixed waste in commercial low-level wastes have been identified and evaluated. These wastes were characterized as part of a BNL study in which a large number of generators were surveyed for information on potentially hazardous low-level wastes. The general management targets adopted for mixed wastes are immobilization, destruction, and reclamation. It is possible that these targets may not be practical for some wastes, and for these, goals of stabilization or reduction of hazard are addressed. Solidification, absorption, incineration, acid digestion, segregation, and substitution have been considered for organic liquid wastes. Containment, segregation, and decontamination and re-use have been considered for lead metal wastes which have themselves been contaminated and are not used for purposes of waste disposal shielding, packaging, or containment. For chromium - containing wastes, solidification, incineration, containment, substitution, chemical reduction, and biological removal have been considered. For each of these wastes, the management option evaluation has necessarily included assessment/estimation of the effect of the treatment on both the radiological and potential chemical hazards present.

INTRODUCTION

MASTER

An evaluation of management options for potentially hazardous low-level radioactive wastes is being performed at Brookhaven National Laboratory (BNL) under contract to the Nuclear Regulatory Commission (NRC). This is part of a program in which BNL has been obtaining information on the amounts and characteristics of low-level wastes in order to identify those wastes which may be considered hazardous under the regulations of the Environmental Protection Agency. To establish a data base on such wastes, BNL has conducted a limited survey of fuel-cycle and non-fuel-cycle waste

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generators. Based on information obtained in this survey, three generic mixed low-level wastes have been identified as potentially significant contributions in terms of the volume represented. These are: organic liquid wastes, lead metal wastes and chromium-containing process wastes (these were generally ion-exchange resins or evaporator bottoms). The information obtained in the survey and the identification of these wastes will be summarized in the report, "An Analysis of Low-Level Waste: Review of Hazardous Waste Regulations and Identification of Radioactive Mixed Wastes," by B. S. Bowerman et al. The identification of these wastes and the evaluation of possible management options to be applied to them was not meant to be exhaustive.

Current management practices, administrative procedures, quality assurance and process controls exercised by the larger volume generators of these wastes have been investigated. Their consistency with NRC's guidance in 10 CFR Part 61 and the potential for the alleviation of concern pertaining to the potential hazard of waste as packaged for disposal have been considered. In some instances, the management options evaluated represent the current management practices. In particular, incineration, solidification, absorption, and containment in a high integrity container (HIC) are management methods that are already practiced for some low-level wastes.

The management options considered may be divided into three categories on the basis of ultimate effect. These are: destruction, immobilization, and reclamation/recovery. For each of the three main generic mixed low-level wastes, organic liquids, lead metal and chromium-containing process wastes, several specific treatments are being characterized and evaluated for their expected effect on the potential chemical hazard and, concurrently, on the radiological hazard. Finally, testing methods to allow determination of the effectiveness of a particular management option on a waste are being considered.

DISCUSSION

For the destruction, immobilization and reclamation/recovery categories, a brief descriptive summary is given of the specific management options, their expected process products or residues for a waste type, the effect on chemical and radiological hazards and the anticipated benefit (volume reduction, elimination of need for absorbent, etc.) of exercising the option.

Destruction Methods

Incineration

Incineration is a process of high-temperature oxidation (thermal decomposition/combustion) which can essentially completely destroy most wastes (99.99% efficiency). Oxidation products of hydrocarbon/organic incineration include CO_2 and H_2O , SO_x , NO_x , and hydrogen halides for sulfur-, nitrogen-, and halogen-containing wastes, and metal oxides for inorganic wastes. Inorganic constituents may form solid residues or they may vaporize (depending on their volatility) and recondense as an aerosol.⁽¹⁾ Organic materials leave minimum ash when efficiently incinerated. Attention must be paid to emission rates of C-14 and H-3 for organic wastes

containing labels of these radioisotopes, to ensure that regulated limits are not exceeded. Off-gas scrubbing may also be necessary. The possibility exists that some organic wastes may be burned in compliance with EPA guidance as secondary fuels, i.e., for recovery of their heat value, if their heat of combustion exceeds 18,600 KJ/kg.⁽²⁾ Several common laboratory solvents such as acetone, butyl alcohol, ethanol, methanol, hexane, and xylene are reusable for their heat recovery. Such activity is not considered "incineration" under EPA regulations.⁽³⁾

Incinerator design must lead to appropriate conditions of turbulence (i.e., mixing of waste and air/oxygen can occur), temperature (i.e., the thermal threshold for reaction must be reached), and time (i.e., sufficient exposure of the wastes to oxygen and high temperature must be ensured so that complete reaction can occur). The dependence of incineration efficiency on the specific nature of the wastes means that wastes must be well characterized.

Incineration can be disadvantageous from the point of view of set-up, installation, capital and testing costs. It can be conveniently used for large volume, low radioactivity, consistently known composition wastes. The process results in destruction of the original waste chemical hazard, emission of gases and, occasionally, aerosols which must be monitored for radioactivity. There is also production of, in most cases, ash which presents little or no chemical hazard and represents a significant volume reduction.

Acid Digestion

In the U.S., acid digestion was developed mainly at Hanford Engineering Development Laboratory (HEDL).⁽⁴⁾ It involves dehydrogenation and/or dehydration of organic compounds by concentrated H_2SO_4 at elevated temperature ($\approx 250^\circ C$), followed by oxidation of the resulting carbon to CO and CO_2 with HNO_3 or H_2O_2 . The severity of the acid digestion conditions, i.e., elevated temperature and highly corrosive reagents, requires special materials of construction for the equipment, so increased costs and operational hazards must be considered prior to its general application to low-level wastes.

This treatment has been applied to ion-exchange resins both in the U.S. and other countries, and to liquid organic waste streams. Results of work with the latter indicate that a certain amount of development would be required to make the process suitable for complete destruction of volatile organic liquids, including benzene. Volatile halogenated organics may be more easily treated than toluene. Toluene has been adequately handled by the HEDL digester, but benzene would probably require a change in design, because of its higher volatility and greater chemical stability.

The process may be applicable to a number of EPA-listed hazardous organics, but would have to be demonstrated for highly chlorinated compounds like PCBs (polychlorinated biphenyls) and dioxin. PCBs were tested in the digester used in the HEDL research program, and a considerable amount of organic material, more than half of which was unchanged PCB, appeared in the condensate.

Complete acid digestion of organic liquid wastes and ion-exchange resins (chromium-containing) would result in destruction of the organic chemical hazard with concurrent production of CO, CO₂, H₂O, and inorganic sulfates. A net volume reduction in the radioactive waste should be obtained.

Wet-Air Oxidation

Wet-air oxidation has been used for decades in treating a wide variety of aqueous industrial wastes containing dissolved or suspended organics. It is essentially a combustion process, i.e., organic compounds are converted (ideally) to CO₂ and H₂O. It is most economically applicable to aqueous wastes containing 2 to 20% by weight combustible material.⁽⁵⁾ In this process, aqueous waste is heated to 200-250°C and contacted with compressed air or oxygen at sufficient pressure (600-700 psi) to maintain the water in the liquid phase. These temperatures are generally required to achieve useful reaction rates for the "combustion" of organics. One recent advance in the state of the art is the use of homogeneous catalysts, bromide and nitrate ions, in an acidic medium. (Proprietary process based on a patent assigned to IT Enviroscience, Inc.⁽⁶⁾) This increases the rates of reaction, permitting either use of lower temperatures or treatment of wastes which may be relatively difficult to destroy.

The procedure is applicable to ion-exchange resin destruction and to certain liquid organic wastes, probably not including liquid scintillation wastes because of the limited solubility of toluene and xylene in water. In industry, the process has been found effective with several individual EPA-listed hazardous wastes, including copper and cadmium cyanide electroplating solutions, phenolic wastes, chlorinated hydrocarbon sludge and a number of other wastes from the refinery and petrochemical industries.⁽⁵⁾ This treatment should bring about destruction of waste chemical hazard, and possibility reduction in waste volume.

All Destructive Processes

Incineration, wet-air oxidation and acid digestion can all provide volume reduction, which may be considered an advantage. For mixed low-level waste of any class containing only C-14 and H-3 radioactivity, and no inorganic hazardous constituent such as chromium, the treatment converts all organic material to CO₂ and H₂O. No further treatment is required for disposal of whatever residue is formed in the process, so the volume of mixed waste is effectively reduced to zero. If the original waste contained inorganic constituent(s), the residue following treatment would no longer be radioactive, but it should contain inorganic material. In such a case, treatment, such as solidification or containment in a HIC, can be provided which is designed to permit the final waste to pass the EP toxicity test. This applies to all combustible mixed wastes containing inorganic hazardous constituents, i.e., their residues would most likely require further treatment in order to pass the EP toxicity tests.

Radioactive residues from destructive treatment of combustible waste containing no inorganic hazardous material can be disposed of by simply packaging in a suitable container, such as a polyethylene-lined 17H 55-gal drum, as long as it is Class A. If it is Class B or C, it will require

solidification or containment in a HIC according to the 10 CFR Part 61 regulations. Volume reduction is almost certain to be appreciable for the types of wastes considered, i.e., organic liquids and ion-exchange resins, even when solidification is required as a subsequent step.

Immobilization Methods

Solidification

As a process for application to the mixed wastes considered in this paper, solidification refers to fixation or immobilization of either liquids or dispersible solids in a solid monolithic waste form. The solidification agent or binder most commonly used for low-level waste is Portland cement. Other inorganic cements such as the proprietary Delaware Custom Material (DCM) and Envirostone are also used, as are bitumen or asphalt, and thermosetting polymers such as polyester resins and Dow Chemical Co.'s proprietary vinyl ester-styrene polymer (VES).

The literature on testing and use of these solidification agents is voluminous and no attempt will be made here to describe the various processes involved in their application to different wastes. Almost any waste can be solidified in any of the binders (with the exception that bitumen would generally not be applicable to organic liquids) as long as certain conditions are met. One of these conditions is that the waste loading must be kept low, frequently $\leq 10\%$ by weight. In some cases, this may be justifiable, but it must be remembered that it entails a large volume increase. Also, the suitability of the particular waste form would generally have to be demonstrated for each specific waste, especially liquid organic wastes. This applies particularly to release rates of organic constituents, since essentially all leach testing so far has been done to determine release rates of radioactive isotopes in inorganic chemical form. The applicability of solidification to liquid organic waste must address the immobilization of organic constituents.

Solidification of the inorganic residues from a destructive treatment of organic wastes appears, however, quite appropriate. The residues, if solidified in a straightforward manner and in a volume such that overall volume reduction of the original waste is achieved. There are several reasons why residues might require further treatment. They might, for example, be Class B or C low-level waste for which solidification or packaging in a HIC is mandated by 10 CFR Part 61, or they might contain an inorganic EPA-listed constituent such as chromium and be unable to pass the EP toxicity test as produced.

Solidification has been used for both ion-exchange resins and evaporator bottoms at nuclear power plants.⁽⁷⁾ The latter can be solidified readily in both inorganic cements and in the organic binders (bitumen and thermosetting polymers). Ion-exchange resins can be immobilized in Portland and other inorganic cements, but loadings must be kept low in order to ensure satisfactory waste form stability and performance. Higher loadings can be used with bitumen and thermosetting polymers, and extensive testing of resulting waste forms for radiation resistance, biodegradation, and leaching of radioactivity indicates good performance. It is not known

whether these forms would pass the EP toxicity test for chromium were chromate incorporated in the matrix.

Absorption

Absorption of wastes is a means of incorporating liquids in a solid matrix either through chemical affinity or by means of pore- or vacancy-filling mechanisms. To meet one of the current NRC requirements for packaging of low-level radioactive wastes for shallow land burial, generators must assure that contaminated free liquid does not exceed 1% for waste disposed of in a HIC or 0.5% by volume, for stabilized wastes. If absorbents are used for liquid wastes, they must be present in twice the necessary volume. In general, this requirement has been met through the use of a variety of absorbents including: vermiculite, zeolite, Speedi-Dri, Floor-Dry, diatomaceous earth, Superfine, Hi-Dri, Radlite, and Oil Dry.

The use of absorbents for immobilization of oils and organics has been documented in Lin and MacKenzie,⁽⁸⁾ Seidenberger and Barnard,⁽⁹⁾ Liskowitz⁽¹⁰⁾ et al., and many others have documented the use of absorbents for cleanup of hazardous organic materials.

Seidenberger and Barnard described the use of clay absorbents and Solusorb for clean-up of spilled organic solvents. The flash points of several solvents (ethyl alcohol, methyl iso-butyl, ketone, and toluene) were substantially increased when absorbed on Solusorb, but not on clay absorbent.

A number of patents have been awarded for the development of absorbents designed specifically for selective uptake of oils, organic liquids and/or liquid hazardous chemicals. Several of these have properties which make them useful for preferentially absorbing organic or hazardous chemicals over water.

It has been noted that for EPA-hazardous liquid wastes (especially laboratory wastes) planned to be landfilled, a common method of packaging is the EPA-specified lab pack (40 CFR Part 265 Section 316).⁽¹⁾ In short, this method consists in the use of a 55-gallon open-head steel drum being filled with small containers of chemicals packed in and separated by sufficient absorbent material to completely absorb all the liquid contents of the inside containers. NRC-licensed low-level waste generators (in compliance with requirements of 10 CFR Part 61) have been and are currently using a waste packaging method quite similar to this with the exception that twice the necessary volume of absorbent is required to be used.

Absorption of liquid organic wastes may be considered an immobilization method which results in a volume increase but, for effective absorbents, a reduced chemical hazard. The factors affecting retention for various absorbents are being evaluated.

Containment in a High Integrity Container

Containment in a specially-designed waste container is a management option that may be applicable to contaminated lead wastes and chromium-

containing waste ion-exchange resins and evaporator bottoms. A material being used for such containers is high density polyethylene (HDPE).⁽¹¹⁾

Current NRC requirements for performance of high integrity containers include that the HIC must have a 300-year design lifetime. This may be contrasted with the EPA monitored disposal site life of 30 years. Additionally, for NRC wastes, <1% free liquids may be disposed of in a HIC, while free liquids are expected at EPA sites. The understanding that a HIC must provide containment may be considered similar to the EPA liner performance objectives. NRC requirements for HICs containing radioactive wastes may be quite consistent with the use of this management option for wastes which may also have the potential to be EPA-hazardous.

Recovery/Reclamation

Distillation

Steam distillation can be used to remove water-immiscible, volatile compounds from a waste that is at least partially aqueous. It can also be used to recover heat-sensitive, high boiling-point water-soluble compounds. The process is based on the vapor pressure relationship of immiscible liquids, namely, that each immiscible component exerts its own vapor pressure independently, such that the pressure in the distillation system is the sum of the individual component vapor pressures for the conditions given. Conventional distillation may effectively be applied to liquid organic wastes in which the components are miscible.

Distillation is a method particularly suited for solvent recovery. Depending on the nature of the radioactive contamination, distillation may result in a (several) concentrated, labeled chemical fraction(s) which may or may not themselves be of concern with respect to potential hazards. Should the radioactive fraction(s) be potentially hazardous, they may suitably be subjected to any of several chemical destruction techniques.⁽¹²⁾ Should the radioactive fraction(s) be of no concern with regard to potential hazard, packaging for disposal can be performed according to 10 CFR Part 61.

For those organic wastes which consist of several solvents with at least one solvent species duplicated as radioactively-labeled material, e.g., C-14-labeled methanol in a methanol fraction, distillation could be effective in removing/separating the bulk radioactive fraction from other fractions (e.g., methanol separated from toluene). However, it is not effective in separating radioactive methanol from nonradioactive methanol. The net result of distillation for this type of system may be segregation of radioactive wastes such that some (those not of concern for potential hazardousness) may be directly packaged for burial while others (those of potential hazard concern) may be subjected to further treatment (e.g., specific chemical destruction, incineration) or reused (e.g., as part of an organic synthesis).

Liquid-Liquid Solvent Extraction

Liquid-liquid solvent extraction is a method of separating components of a liquid solution by bringing them into contact with another immiscible

liquid. The differential solubility of the original solution components in the second solvent can bring about a partitioning or redistribution of components from one solvent to the other. This management option is a step as opposed to a complete treatment in the preparation of a waste for disposal. It results essentially in the transfer of a waste component from one solvent to another. The situations in which this would be useful would likely involve quantities of radioisotope labeled chemicals in a solution of solvent(s) which would be of concern for its potential hazardousness. Additionally, the labeled chemicals themselves may be of concern for their potential hazard.

In short, liquid-liquid solvent extraction may be used to segregate radioisotope-labeled materials from a bulk solution. The final waste may thus be hazardous, but the volume of the radioactive fraction is reduced. Liquid-liquid solvent extraction cannot compete economically with biological oxidation or adsorption for treatment of large quantities of very dilute wastes.

Decontamination

The decontamination of lead metal wastes is currently being studied. Such a process may consist of melting of contaminated lead metal with the contamination fraction being removed as separated from the melt. The lead could be re-solidified and re-used while the contamination fraction would need evaluation to determine its potential hazardousness prior to disposal. Other processes, such as simple surface cleaning, may also be of value.

Segregation and Substitution

The possibilities of process changes at the waste generation site to bring about the segregation of potentially hazardous wastes from radioactive wastes should have already been considered by generators since this would be an obvious basis for volume reduction. Substitution of materials which are not of potential concern for EPA hazard may be effective for at least some of the three main wastes. Organic liquid wastes likely contain potentially hazardous solvents which may be substituted for by non-hazardous solvents. Chromium used as a corrosion inhibitor may be substituted for by a variety of other inhibitors.⁽¹³⁾ The feasibility of this management option may be based on economics and availability.

SUMMARY

The application of the management options discussed to mixed commercial low-level wastes can result in destruction of the chemical hazard with concurrent residue production, immobilization, and/or reclamation/recovery of the waste. Specific chemical destruction techniques may be used for residues or for small volume, specifically characterized radioactive wastes which are of concern for potential chemical hazards. The effectiveness of immobilization and containment methods is being investigated.

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