EVALUATION OF POTENTIAL MIXED WASTES CONTAINING LEAD, CHROMIUM, OR USED OIL*

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ABSTRACT

This paper presents the results of follow-on studies conducted by Brookhaven National Laboratory (BNL) for the Nuclear Regulatory Commission (NRC) on certain kinds of low-level waste (LLW) which could also be classified as hazardous waste subject to regulation by the Environmental Protection Agency (EPA). Such LLW is termed "mixed waste." Additional data have been collected and evaluated on two categories of potential mixed waste, namely LLW containing metallic lead and LLW containing chromium. Additionally, LLW with organic liquids, especially liquid scintillation wastes, are reviewed. In light of a proposed EPA rule to list used oil as hazardous waste, the potential mixed waste hazard of used oil contaminated with radionuclides is discussed.

It is concluded that the EPA test for determining whether a solid waste exhibits the hazardous characteristic of extraction procedure toxicity does not adequately simulate the burial environment at LLW disposal sites. and in particular, does not adequately assess the potential for dissolution and transport of buried metallic lead. Also, although chromates are, in general, not a normal or routine constituent in commercial LLW (with the possible exception of chemical decontamination wastes), light water reactors which do use chromates might find it beneficial to consider alternative corrosion inhibitors. In addition, it is noted that if used oil is listed by the EPA as hazardous waste, LLW oil may be managed by a scheme including one or more of the following processes: incineration, immobilization, sorption, aqueous extraction and glass furnace processing.

INTRODUCTION

The management and disposal of hazardous wastes are regulated by the EPA. Under the authority of the Resource Conservation and Recovery Act of 1976 (RCRA), the EPA promulgated requirements for the "Identification and Listing of Hazardous Waste" in 40 CFR Part 261. The disposal of LLW is regulated by the NRC under 10 CFR Part 61, or by NRC Agreement States under compatible State regulations. In addition to radiological properties, certain low-level wastes (e.g., scintillation cocktails) can exhibit characteristics which would classify the waste as hazardous under Part 261. These wastes are referred to as "mixed waste." Other LLW may contain substances which, while not necessarily hazardous under Part 261, can enhance radionuclide migration at waste disposal facilities (i.e., chelating agents). LLWs are either disposed of at commercial disposal facilities licensed under the authority of the Atomic Energy Act or by other means if radionuclide concentrations are sufficiently low. Concerns have emerged regarding the applicability of EPA regulations and permit requirements to the chemical constituents present in LLWs and the appropriate methods for managing mixed wastes.

As part of its technical assistance program for the NRC, BNL has conducted a series of studies on the identification and management of potential mixed wastes. This work was initiated with a literature and document review conducted in 1984; a recent report(1) summarizes the major findings. Another report(2) presents the results of a survey of LLW generators carried out for the purpose of identifying potential mixed wastes. BNL subsequently reviewed options available for the management of potential mixed wastes; the resulting report(3) has been published in draft form in order to allow a period for public comment. The present paper contains the results of follow-on studies which examine additional data on specific categories of potential mixed wastes.

The literature and document review(1) and survey of LLW generators(2) focused on establishing the types and volumes of potential mixed wastes shipped to commercial LLW sites for disposal. The literature review showed a lack of consistent quantitative data on the chemical components of LLWs, and the survey of LLW generators was conducted in order to fill this

gap. The survey was directed at those LLW generators identified in the early phases of BNL's studies, as well as at larger generators whose names were provided by NRC. The survey questionnaire was designed to obtain information on any potential mixed wastes and also on the presence and concentrations of various hazardous constituents such as phenols, hydrazine, cyanide, and chromates. Questionnaires were sent to 239 reactor and non-reactor generators of LLW. Of these, 97 responses were received, representing 22,000 m^3, or approximately 30% by volume, of all LLW sent to commercial disposal sites in 1984.(2)

The survey results indicated that the four types of LLW that are listed in the first column of Table 1 may be potential mixed wastes. Certain wastes, e.g., contaminated mercury amalgam, which are specific to particular generators, were also identified as potential mixed wastes.

The second column of Table 1 presents the reason -- i.e., ignitable, EP toxic, or listed -- that a particular type of LLW (from the first column) is tentatively classified as a hazardous waste under 40 CFR Part 261. The second column also contains the applicable EPA Hazardous Waste Numbers, which are used in 40 CFR Part 261 to designate the various kinds of hazardous waste. For example, a solid waste that exhibits the hazardous characteristic of ignitability but is not listed as a hazardous waste in Subpart D has the EPA Hazardous Waste Number of D001. Furthermore, a solid waste that exhibits the hazardous characteristic of EP toxicity but is not listed as a hazardous waste in Subpart D has an EPA Hazardous Waste Number corresponding to the toxic constituent causing it to be hazardous; for chromium and lead these are D007 and D008, respectively. Also, each hazardous waste listed in Subpart D is assigned an EPA Hazardous Waste Number. Five groups of spent solvents are listed as hazardous wastes from non-specific sources and are assigned EPA Hazardous Waste Numbers of F001 through F005.

The typical disposal practices and potential management options for organic liquid wastes, lead metal wastes, and chromium-containing process wastes were reviewed in a subsequent study.(3) The management options evaluated were categorized as destruction, immobilization and recovery and reclamation. Organic liquids may be effectively managed with destructive methods (e.g., incineration) whereas lead and chromium must be managed by immobilization or recovery and reclamation methods.

Metallic lead was identified as one of the constituents which could render radioactive wastes hazardous under 40 CFR Part 261 because, under certain circumstances, it can exhibit the hazardous characteristic of extraction procedure (EP) toxicity. Metallic lead may be the LLW itself, as in the case of discarded lead shielding which has been contaminated with radioactivity, or may be used in the packaging for other radioactive waste in order to control occupational exposures. In the former case, the lead might be disposed of either without any container or, if the radionuclide activities warrant it, inside a high-integrity container (HIC). In the latter case, the lead itself constitutes part or all of the container. Therefore, in order to assess the potential mixed waste hazard posed by metallic lead, more extensive evaluations were carried out of the interactions between metallic lead and the disposal environment as well as between metallic lead and materials likely to be encountered either as LLW constituents or as HIC materials. The following section of this paper discusses the results of these evaluations.

Low-level wastes containing chromates include process wastes from nuclear power plants where chromates are used as corrosion inhibitors. Of particular concern are evaporator concentrates, which are usually solidified prior to disposal, and ion-exchange resin wastes, which can be disposed of in solidified form or dewatered in a container. The resulting waste forms could, like metallic lead, exhibit the hazardous characteristic of EP toxicity. Existing information was insufficient to evaluate whether such wastes could be potential mixed wastes; therefore, a telephone survey was conducted to obtain more data on chromate use in nuclear power plants. A later section of this paper summarizes the results of this survey and the conclusions drawn from it. Although not identified in BNL's survey, LLW resulting from the chemical decontamination of light water reactors (LWRs) may contain chromates as a result of a preoxidation step common to several of these processes.

For the sake of completeness, this paper also includes a brief review of LLW consisting of organic liquids, especially scintillation fluids. This review is based on earlier work conducted by BNL. Organic solvents in LLW may be hazardous because they are listed hazardous wastes (e.g., toluene in scintillation liquids) or because they may exhibit the hazardous characteristic of ignitability.

On November 29, 1985, EPA published a proposed rule listing used oil as a hazardous waste (50 FR 49258-70). The rule would provide a definition of used oil and incorporate two modifications to the EPA hazardous waste mixture rule to exempt from regulation certain wastes containing oil. In the past, LLW consisting of or containing oil has been shipped for disposal. As a result, the proposed EPA rule, if finalized, would establish a new category of potential mixed waste. In its efforts to identify mixed wastes, BNL collected information on waste oil.(2) However, since such waste was not considered hazardous at that time, the category was not addressed in the study identifying potential mixed wastes, or in the draft report on mixed waste management options. Therefore, this paper also considers the sources and characteristics of and current management practices for waste oils shipped for disposal at commercial LLW burial sites. Such waste oils are generally referred to in this paper as LLW oils.

Definitions

The terms "waste," "waste form," and "waste package" are used in this paper in connection with LLW as follows:

● "Waste" means the as-generated LLW material itself, regardless of whether this material meets the stability requirements of 10 CFR Section 61.56[b].

DISCLAIMER

TABLE I

LLW Identified as Potential Mixed Waste

LLW Type	Reason for Tentative Classification as Hazardous Waste[a]	Volume Reported in Survey[b] (ft^3)	Percentage of Total Volume Reported in Survey[b]	Percentage of Potential Mixed Waste Volume Reported in Survey[b,c]	Source[d]
oil-containing wastes	listed (F030)[e]	32,678	4.2	50.2	R,I
solvent-containing wastes[f]	listed (F001 to F005) or ignitable (D001)	17,735	2.3	27.2	M,A,I,R
lead-containing wastes[g]	EP toxic (D008)	2,482	<0.1	3.8	M,A,I,R
chromium-containing wastes[h]	EP toxic (D007)	5,350	0.7[i]	8.2	R

[a]The EPA Hazardous Waste Numbers are given in parentheses. See text for explanation.
[b]Calculated using the as-shipped volumes reported in the survey. These volumes, depending on the waste category, may include absorbents, solidification agents, compactible or non-compactible trash or other packaging materials. Total volume reported in survey = 783,249 ft^3.
[c]Total potential mixed waste volume reported in survey = 65,144 ft^3. Percentages do not add up to 100% because potential mixed wastes specific to particular generators (9.4%) and chromium-containing waste from non-reactor sources (1.2%) are not included in the table.
[d]By facility type, I = industrial, R = reactor, M = medical, A = academic.
[e]Proposed rule. Federal Register FR 50 (230) pp. 49258-70.
[f]Scintillation fluids, lab solvents, cleaning and degreasing solvents and sludges.
[g]Shielding or containers.
[h]LWR process wastes or system decontamination wastes.
[i]Volume refers to light water reactor process wastes only.

- "Waste form" refers to LLW which has been processed (i.e., solidified) in order to meet the stability requirements of 10 CFR Section 61.56[b] or which, because of its inherent properties, is presumed to meet these requirements without processing.

- "Waste package" refers to an assembly consisting of the waste or waste form and a container. The container may be merely a convenience for processing, transportation, handling, and/or disposal -- e.g., a carbon steel drum containing Class A trash -- or may provide structural stability in order to meet the requirements of 10 CFR Section 61.56[b].

LEAD METAL BURIED AT LLW DISPOSAL SITES

LLW containing metallic lead can be divided into the following two broad categories: 1) nonradioactive lead used as part of a waste package to shield the LLW in the package (e.g., a lead "pig" containing a sealed radioactive source), and 2) lead used as shielding (but not as an integral part of a waste package) and discarded due to radioactive contamination (i.e., the lead itself is the waste). If the lead metal is an integral part of the waste package, then the interactions of the waste or waste form with the lead, which may result in degradation of the lead by the waste or waste form, are of concern before disposal because of the potential loss of

shielding and after disposal because of the potential for dissolution resulting in increased mobility of both the waste and the lead. Contaminated lead (i.e., lead itself as the LLW) may be disposed of in a high integrity container (HIC). The lead shielding disposed of by power plants and most of the container waste are apparently associated with dry waste, most of it Class A. One generator, however, described lead-lined 30-gal drums containing Class C waste.(2)

Interactions of Lead and LLW Package Components

Lead interactions with LLW constituents would be expected in the long term after water penetrates the waste containers. Specific examples include:

- Pigs containing sorbed aqueous waste and dry waste which includes glass.

- Large pigs containing irradiated cyclotron targets.

- Pigs which are encased in concrete and contain stainless steel sealed sources.

It appears that very little lead being shipped to LLW burial sites is in contact with actual waste forms. Although no waste of this kind was identified for any of the three usual waste form types -- cement, bitumen, and vinyl

ester-styrene polymer (VES)--it must be assumed that a certain amount is produced. Also, lead is in contact with concrete in pigs used by one broker to ship sealed sources. Interaction of lead with dry waste forms will be minimal, but after container breaching and subsequent penetration of water, significant reaction could occur.

In the case of bitumen, the lead should simply react with the trench water as though bitumen were not present. The bitumen would protect that part of the lead which it covered by reducing its contact with water.

Lead in contact with concrete is susceptible to corrosion by two mechanisms. In the alkaline medium in contact with wet concrete, and in the presence of oxygen, lead will react to form PbO unless sufficient CO_2 is present to form a protective carbonate layer. Even when a protective carbonate film has formed on the lead, galvanic cells can be set up between areas touching concrete and those not in contact, due to differential carbonation of the respective areas. Corrosion of the areas in contact with the concrete can then occur.

The known waste components which could be in contact with lead in burial site trenches are mostly dry solids which would undergo no significant reaction with lead. In some cases, damp sorbent or ion-exchange resins may contact the lead and cause a limited amount of corrosion. However, the only appreciable reaction will occur with trench water after breaching of containers. Several different components of LLW will undergo reaction with, or cause reaction of, lead in the presence of water.

- Glass in contact with lead has been found in underground tests to interact with the lead in such a way that a new glass surface $(x)PbO\cdot(y)SiO_2$ is formed.[6,7]

- The greatest interaction of lead in known waste packages is likely to be that in the pigs used to hold metals, specifically the irradiated copper cyclotron targets and the stainless steel sealed sources. Galvanic corrosion of the lead lead due to lead-copper and lead-steel galvanic couples could continue until all the lead was corroded, if not limited by build up of passivating layers (oxide and or carbonate) on the metals.[8]

- Organic acids such as formic, acetic, and higher molecular weight acids may be formed by radiolysis of cellulosics and certain plastics in lead-lined 30-gal drums containing Class C waste.[9] A worst case treatment (upper limit of Class C waste, breaching of the Nalgene waste holders, and penetration of the inner steel liners by the acids) indicates that several moles of lead could be dissolved in a 300-year period.[10] (This treatment applies to drums shipped prior to 1983. Since that time, the drums have been contained in Ferralium HICs which are expected to isolate their contents for several hundred years. For this type of containment, absence of water inside the lead-lined drums would reduce corrosion rates, and in any case, release of corrosion products to trenches would not occur until after breaching of the (HICs).

The container materials considered are high density polyethylene (HDPE) and special steel alloys (currently in general use for HICs), polyester resin (used for TMI-2 demineralizer waste), and concrete.

- No significant chemical interaction will occur between lead and HDPE or its radiolysis products, with or without water present.

- Physical damage to the HDPE is possible because of its creep properties. None of the others exhibit this type of behavior, and no physical damage to them should be caused by lead.

- Polyester radiolysis products could cause corrosion of lead, but no significant chemical reaction of lead or its corrosion products with polyester will take place.

- In the presence of water, galvanic corrosion of lead in stainless steel HICs would occur, but lead and its corrosion products would not affect the steel.

- Water can penetrate regular concrete and under some conditions might penetrate HICs made of polymer-impregnated concrete.

- In concrete HICs, lead would be susceptible to corrosion in the presence of water, but there would be no significant effect on the concrete.

The following conclusions and recommendations are presented regarding the interaction of lead metal with waste package components:

- Most identified lead waste will interact only slightly, if at all, with the LLW constituents with which it is buried until breach of containment permits water to come in contact with the waste. In order to minimize subsequent corrosion of lead, it should not be buried in direct contact with concrete, vinyl ester-styrene polymer, cellulosics and certain plastics in Class C waste, and metals which are cathodic to lead.

- Lead and its corrosion products will have no adverse chemical effect on HIC materials presently in use or under consideration. Deleterious physical effects could possibly occur with HDPE due to its creep properties. Because of this, if lead metal is to be buried in HDPE HICs, it is recommended that care be exercised in loading the lead so that edges and corners of lead sheets or structures are not allowed to come in contact with the container walls.

- Since significant corrosion of lead occurs only in the presence of water, it is recommended that free liquid water be kept out of all waste containers in which lead is to be buried.

Interactions of Metallic Lead and the Disposal Site Burial Environment

Lead metal has long been noted as being

resistant to corrosion; lead pipes with the insignia of the Roman emperors are said to still be in service.(11,12) Its chemical toxicity, however, has made consideration of its solubility in natural waters and in disposal facility waters a concern for both nonradioactive and radioactive waste disposal. In order to evaluate the potential for the dissolution of metallic lead buried at a near-surface disposal facility for LLW and for the subsequent migration of the dissolved lead species at the facility, the interaction between metallic lead and the disposal environment needs to be considered, assuming conservatively that there is no containment of lead within the waste packages.

From thermodynamic arguments, it is concluded that in the lead-water system, lead is relatively soluble (>1 M) as Pb^{2+} at pH values below 6.4 and redox potentials between -0.2 V and 1.7 V, depending on the pH. Additionally, it is concluded that lead metal is unstable with respect to its oxides, even under mildly reducing conditions. However, pure lead metal does not dissolve in distilled water free from dissolved oxygen, but is corroded by water with dissolved oxygen. In the presence of dissolved CO_2, the solubility of lead is limited by the low solubility of lead carbonate, $PbCO_3$, above pH 8. If the dissolution of atmospheric CO_2 into the water is facilitated (i.e., a well-aerated solution), the formation of a protective layer of $PbCO_3$ is favored and further dissolution of the lead metal is impeded.(13,14)

If other components are considered in addition to lead, water, and dissolved gases from the atmosphere, the solubility of lead will be controlled by various lead compounds, e.g., $Pb(OH)_2$, $Pb_3(PO_4)_2$, $Pb_4O(PO_4)_2$, and $Pb_5(PO_4)_3OH$, typical of noncalcareous soils, and $PbCO_3$, typical of calcareous soils. The predominant aqueous species are Pb^{2+} under acidic conditions of Pb^{2+}-carbonate complexes under basic conditions.(15) From the testing of buried lead samples for corrosion,(16) the following was concluded:

- Corrosion of lead increases in poorly aerated soils, probably because poorly aerated conditions are not conducive to the formation of a protective layer of lead carbonate.

- The presence of certain anions generally inhibits the corrosion of lead, e.g., bicarbonate and carbonate, chloride, silicate, and sulfate (probably by forming a protective layer of corrosion products on the metal).

- Organic soils are corrosive for lead. Certain organic salts of lead (e.g., acetate) are water-soluble and, in addition, may react with the protective layer of corrosion products if such a layer has formed.

- Organic compounds such as humic acids from decaying biomatter increase the dissolution and the mobility of lead compounds by the formation of complexes.(17)

Factors such as aeration, corrosion-inhibiting anions, and organic complexing agents, all of which affect the corrosion of lead, are not likely to be the same at the 30-ft burial depths typical of shallow land burial of LLW as at the 6-ft maximum depth of Romanoff's studies.(16) Therefore, at any given site, it will be necessary to determine these factors at the burial depth. In any case, the burial environment "seen" by the waste will depend upon the nature of the fill material surrounding the waste; this fill material may not necessarily have originated at the soil horizon at the burial depth of the waste. Extrapolations from corrosion data at the 6-ft horizon to corrosion behavior at the burial depth horizon must take account of the high probability of different environments at these two horizons. As an extremely simplified example, if the aeration at the 30-ft horizon is less than that at the 6-ft horizon, then (all other conditions being the same -- which is unlikely) the 30-ft-horizon environment will be more corrosive to lead. In short, it may be concluded that data such as Romanoff's taken at near-surface horizons (i.e., <6 ft deep) may be utilized to identify the environmental parameters significant for corrosion as well as to estimate how the rate and degree of corrosion depend on these parameters, but extrapolations from such near-surface data to corrosion behavior at greater depths must be made using data on the environmental conditions at the site under consideration at the expected burial depth.

Since the potential mixed waste hazard posed by metallic lead in LLW may depend on the burial conditions at the site being considered for LLW disposal, this study considered the burial environment for disposal of LLW by shallow land burial at sites falling into one of the following three categories, which were selected to span the range of conditions at actual disposal sites and are based on real-world archetypes:

- Poorly drained humid-area sites (e.g., Maxey Flats, KY)

    Poor aeration and high levels of dissolved organic carbon resulting from the "bathtub effect" could greatly enhance the dissolution and transport of lead buried at this kind of site.

- Well-drained humid-area sites (e.g., Barnwell, SC)

    The dissolved organic carbon at a well-drained humid area site may also enhance the dissolution and transport of buried lead.

- Well-drained arid-area sites (e.g., Richland, WA)

    There is little potential for the dissolution or transport of buried lead because of the short contact time between the waste and the water.

Since groundwater samples collected at several operating and closed humid-area LLW disposal sites have not contained dissolved lead attributable to buried lead,(18) the above assumptions regarding the enhanced dissolution and transport of lead at such sites may be conservative.

The effects of disposal conditions on lead metal have implications for the management of

lead mixed waste during disposal and for the management of the disposal facility after closure. At a poorly drained disposal facility, the chemical products of biodegradation, many of which have the potential for forming soluble complexes with lead, and the long contact time between the lead and the water tend to enhance the solubility and mobility of lead. The disposal of lead metal at poorly drained sites should be avoided, and, even at well-drained sites, lead metal should not be buried with biodegradable wastes, from which biodegradation products capable of forming soluble, mobile complexes with lead may arise. The use of an impermeable trench liner may result in the "bathtub" effect and, eventually, in conditions similar to those at a poorly drained site; water should not be allowed to accumulate in disposal trenches.

Water balance control strategies for arid-area shallow land burial sites like the one on the Hanford Reservation may require the use of fine-textured soil covers over the coarser material surrounding the waste in order to reduce drainage below the root zone, since it appears feasible to maintain dryness in a porous medium by utilizing such capillary barriers to divert infiltrating water from the emplaced waste.

Assessment of the Potential Mixed Waste Hazard of Lead Metal in LLW

The EP toxicity test protocol was devised by the EPA to assess the potential for the leaching of contaminants from potentially hazardous waste disposed of in an actively decomposing municipal landfill and the possible resulting contamination of an underlying aquifer. If the concentration of leached contaminants exceeds specified levels, the waste is considered to exhibit the hazardous characteristic of EP toxicity. More recently, the toxicity characteristic leaching procedure (TCLP) has been developed by the EPA and has been proposed for use in conjunction with an expanded toxicity characteristic.(19)

For the purpose of assessing the potential mixed waste hazard posed by metallic lead, the leaching conditions specified in the EP toxicity test may not be generally representative of the environment of the buried waste at a poorly drained humid-area disposal facility, particularly in the case of co-disposal of metallic lead and biodegradable wastes in the same or neighboring trenches, since the EP toxicity test is not carried out under poorly aerated conditions. (In the proposed TCLP, exposure of the waste to the air is to be minimized when volatiles are present.) Conditions favorable to the dissolution and transport of lead, i.e., poor aeration, and presence of complexing organics, may arise even in the absence of biodegradable waste as a result of biodegradation of the organic matter (e.g., decaying leaf litter) in many humid area soils. While lead metal has been found to have the characteristic of EP toxicity (based on test results from Idaho National Engineering Laboratory,(20)(as well as from the known solubility of lead acetate), the presence of air may reduce the rate of dissolution of the metallic lead if partial passivation of the lead by formation of a protective layer, e.g., lead carbonate $(PbCO_3)$,should occur. Such passivation of lead metal waste could even occur before disposal, depending on the prior history of the lead. (It is unclear how the opposite effects of

the protective layer and organic complexing agents balance out.) The EP toxicity test may provide a somewhat better representation of the burial conditions at a well-drained humid-area disposal site because of the presence of oxygen in such trench waters. For both types of humid-area sites, however, the pH of the trench waters is usually above 5, tending to neutral or slightly alkaline. In addition, the ability of the dissolved organic carbon to complex with aqueous lead has not been quantified and thus it cannot be compared with the ability of 0.5 N acetic acid to dissolve lead. Because of the episodic nature of the precipitation at an arid-area site, wet-dry cycling may need to be incorporated into a leaching test representative of burial conditions at such a site.

The following additional information would be needed in order to assess the potential mixed-waste hazard of buried metallic lead:

● The ability of biodegradation products to complex with lead in aqueous solution needs to be quantitatively assessed. It should be noted that a quantitative assessment of the effect of such complexing agents on lead is likely to be site-specific.

● The conditions need to be ascertained under which certain anions, e.g., sulfide (S^{2-}), carbonate $(CO_3{}^{2-})$ and sulfate $(SO_4{}^{2-})$, which form slightly soluble precipitates with lead, will passivate lead metal or immobilize dissolved lead. In addition, the competing effects of complexing agents that increase the solubility and mobility of lead and anions that decrease the solubility and mobility of lead need to be elucidated.(21)

● The effect of wet-dry cycling on the passivation of lead metal needs further investigation.

It should be noted that the assessment of the mixed waste hazard posed by metallic lead may have to be done on a site-specific basis for each shallow land burial site. A conservative mismanagement scenario for toxic waste may be justified for EPA's evaluation of the potential for ground water contamination by lead metal buried at the large number of municipal landfills and at the smaller but still relatively large number of hazardous waste disposal facilities because of the sheer magnitude of the problem in developing a sitespecific leaching test for each disposal facility. There are likely to be far fewer LLW disposal facilities, however. Initially, only one LLW disposal facility per state compact (or state, if it is not a member of a compact) would be expected. It would be much more feasible to tailor the parameters of a test protocol such as the toxicity characteristic leaching procedure to match those of a particular proposed or existing LLW disposal site for each of the relatively few such sites. Perhaps such a site-specific tailored test protocol could make use of soil and groundwater samples from the site in order to avoid the difficulty of simulating the array of naturally-occurring organic complexing agents. To some extent, such an approach is the laboratory analog of the field tests of corrosion of buried metals conducted under the auspices of the National Bureau of Standards. It would be

necessary, however, in accord with 40 CFR Section 260.21, to demonstrate that such a site-specific tailored toxicity test procedure is equivalent to the original testing method.

Since destruction of elemental lead in LLW by chemical processes is not possible, other management techniques, such as stabilization or segregation, must be employed for LLW packages containing metallic lead. Stabilization may be accomplished by completely encapsulating the lead in an inert binder material. (Incomplete encapsulation may enhance galvanic corrosion.) Further research and development work will be necessary since it is not clear from the preceding discussion that any of the binders in current use would be a suitable encapsulating material. Similar considerations would apply to the use of HICs. However, considering the small portion of LLW which contains lead -- less than 0.1 volume percent based on the 1985 BNL survey -- it is recommended that LLW containing metallic lead be segregated and disposed of at a facility reserved for such waste and located at a well-drained arid-area site with little potential for dissolution or transport of the metal.

CHROMIUM IN LLW

Three categories of LLW containing chromium were identified in BNL's survey; namely, 1) chromate-contaminated laboratory waste and trash from non-reactor facilities, 2) process wastes from LWRs, which use chromates as corrosion inhibitors, and 3) process wastes from reactors not using chromates as corrosion inhibitors. Of these, process wastes from LWRs which use chromates as corrosion inhibitors were considered most likely to exhibit EP toxicity and therefore to be potential mixed wastes. This was based on the solubility of chromate salts and on assumptions regarding the use of chromates in LWRs.

The information gathered in this study indicates that chromates are used in more plants than originally identified in the survey analysis. However, chromate usage is in non-radioactive systems, and management practices at the plants are directed at isolating coolant containing chromate from radwaste systems and at preventing radioactive contamination of systems containing chromate. Thus, chromates are, in general, not a normal or routine constituent in commercial LLW.

It is recommended that individual LWRs that use chromates should determine the extent to which chromates can contaminate LLW shipped for disposal, and whether this level of chromate contamination is sufficient for the wastes to exhibit EP toxicity. Because of the concerns and uncertainties regarding the management and disposal of mixed was es, LWRs which use chromates may find it beneficial to determine whether alternative corrosion inhibitors are available for their particular plant system. If they are not available, a review of the use of chromates at the plant should be conducted. This review should be directed at minimizing the potential for chromate contamination of radwaste systems. In addition, a method for identifying and tracking chromate losses should be devised which can be used to determine whether process wastes should be tested for EP toxicity.

Generators who determine that their process wastes are potentially EP toxic due to chromate contamination will have to test the wastes.

Confirmatory analytical testing is relatively straightforward. However, some difficulties may be expected in obtaining representative samples, particularly if the process wastes are ion-exchange resin wastes. For instance, if the resins are contained in portable demineralizer units which are intended to serve as disposal containers (after the resins are dewatered), then access to the resins may be impossible without damaging the container. In addition, resin beds in general do not absorb ions uniformly, and consequently a large number of samples may be required to adequately define the average chromate concentration in a resin bed.

In the case of evaporator concentrates, which are usually accumulated in holding tanks prior to solidification for shipment and disposal, sampling will be easier. The concentrates can be recirculated and mixed in the holding tank and samples obtained directly. Alternatively, extra solidification process control samples can be made and tested for EP toxicity.

Several disposal options are available for wastes that have been tested and found to be EP toxic due to chromate. These include immobilization in chemical matrices, and packaging in a high-integrity container. These have been discussed in detail in a related BNL study.[3]

One management option which is being considered and pursued by several generators contacted in this study involves replacing chromate with other, non-hazardous corrosion inhibitors. The advantage to this approach is that it eliminates the potential for mixed wastes.

LLW CONTAINING ORGANIC LIQUIDS

For the sake of completeness and because much of the discussion of LLW containing organic liquids is applicable to LLW oil, also discussed in this paper, the findings regarding this category of potential mixed waste which were presented in the earlier BNL studies in this series(1-3) are summarized here.

Wastes containing organic liquids are found to consitute 2.3% of the total volume reported in the responses to the 1985 BNL survey. From this survey, it may be concluded that the sources of organic liquid LLW from largest to smallest in terms of volume are academic generators (33.6 volume percent of the LLWs containing organic liquids), industrial generators (31.6%), medical generators (21.0%), and nuclear power plants (13.8%). Based on the results of the 1985 BNL survey, scintillation wastes (liquids and vials) constitute the largest portion (about 70 volume percent) of the LLWs containing organic liquids. Organic laboratory liquids ($\approx$21 volume percent) and miscellaneous solvents ($\approx$9 volume percent) constitute the balance of the LLWs containing organic liquids and reported in the 1985 BNL survey.

Some of these LLWs containing organic liquids, especially the spent solvents, may exhibit the hazardous characteristic of ignitability. In addition, LLWs may contain or consist of a variety of spent solvents which are likely to have been used in activities ranging from equipment degreasing to small-scale laboratory procedures to liquid scintillation counting and which are listed in 40 CFR Section 261.31, "Hazardous Wastes From Non-Specific

Sources," because of ignitability, toxicity, or both. Although the hazardous characteristic of ignitability may not be applicable to LLWs containing organic liquids in sorbed or solidified form, such wastes may still be radioactive mixed wastes if they may be considered listed wastes under EPA's spent solvent mixture rule.

Organic liquid wastes are generally amenable to management by destruction or immobilization. The destructive processes of incineration, acid digestion, and wet-air oxidation either chemically destroy the compounds of concern to EPA or accomplish relatively large volume reductions. Incineration has the widest applicability of any of the destructive processes. Any residues from the destructive processes may need further treatment, generally by immobilization processes such as solidification. Sorption may also be applicable to organic liquid LLWs instead of incineration. In addition, segregation of the organic component of LLWs containing organic liquids by processes such as distillation or solvent extraction may be part of an overall management scheme for such wastes.

LLW OIL

Some data are available regarding the quantities and radioactivity of LLW oil. The data from the 1985 BNL survey indicate that annual oil use at nuclear waste generators varies considerably, with reported quantities ranging from 1 to 10,000 gallons with one power plant reporting 200,000 gallons. The average annual use from the 1985 survey for 17 waste generators is about 13,800 gallons, but if the one generator reporting 200,000 gallons is excluded, the average oil use for the remaining 16 is about 2180 gallons. Note that the volume of oil used would be expected to be less than the volume of oil shipped for disposal, since the latter would include volumes of packaging and of solidification agents or sorbents. According to the supporting documentation for the Edison Electric Institute (EEI) petition on de minimis levels in oil wastes, the volume of oil wastes generated is highly variable (in agreement with the 1985 BNL survey data on oil use) and ranges up to 8,000 gal/yr (for a two-unit PWR). The EEI data also indicate that up to 17,000 gallons of waste oil may be stored on site and gross radioactivity levels are in the range of 10^{-7} to 10^{-5} µCi/mL for LLW oil. Respondents to the 1985 BNL survey reported activities from about 2×10^{-5} to 8×10^{-2} µCi/mL except for one power plant reporting 3.5×10^{-11} µCi/mL and one industrial generator reporting one gallon of vacuum pump oil with a much higher activity (3.53 µCi/mL). However, these values should be accepted with some caution since only one respondent explicitly gave the units of the activities. (Units of Ci/ft^3 were requested in the survey.) The radionuclides reported were generally those longer-lived fission and activation products normally occurring in nuclear power plant waste, namely, Cs-134, Cs-137, Co-58, Co-60, Zn-65, and Mn-54.

LLW oil does not seem to have been characterized chemically, but EPA studies of the chemical characteristics of used oil, in general, are likely to be applicable to LLW oil. The EPA has found that used oil typically contains a number of toxicants listed in Appendix VIII of 40 CFR Part 261 at levels ranging from 10^2 to 10^7 times higher than any health-based standard.[22]

Typical toxicants considered in the EPA study were lead, toluene, trichloroethylene, and naphthalene. As a result of the findings of its study, the EPA has proposed to list used oil (the definition of which would encompass LLW oil) as a hazardous waste. However, because of the exclusion of certain mixtures of wastes from full regulation as hazardous waste, incidental small amounts of used oil in waste-water and oil-contaminated wipers (e.g., oily rags) would be exempt from regulation as a hazardous waste. Some of the EPA's regulations already in force for treatment, storage and disposal facilities for hazardous waste would be applicable to used oil (including LLW oil) if the proposed listing of used oil as a hazardous waste were to be finalized. Particularly noteworthy, however, is the proposed 40 CFR Part 268, in which hazardous waste restricted from land disposal is identified. Among the criteria for allowing land disposal of hazardous waste are the concentrations of hazardous constituents in the leachate resulting from the proposed Toxicity Characteristic Leaching Procedure. Also noteworthy is the apparent use of generic test data to identify treatment technologies for particular kinds of hazardous wastes. The EPA Administrator is required by the proposed Part 268 to make a land disposal prohibition determination within six months after the date of identification or listing of hazardous waste. (The six-month period has not started for used oil since the listing has only been proposed.)

In November 1986, however, the EPA issued a final determination not to list used oil destined for recycling as a hazardous waste under 40CFR Part 261 because of concerns by the recycling industry that the "stigma" resulting from such a listing could seriously disrupt the recycling market.[23] Thus, the listing of used oil destined for disposal as a Part 261 hazardous waste remains unresolved and the development of management standards for used oil under RCRA Section 3014 is deferred. In response to this decision, the Hazardous Waste Treatment Council has announced a lawsuit against the EPA. The EEI, on the other hand, has reportedly intervened on behalf of the EPA.[24] At the time of this writing (at the end of January, 1987), the ultimate disposition of the proposal to list used oil as a hazardous waste is uncertain.

The site license for the Barnwell, SC, LLW disposal site permits disposal of only incidental or trace amounts of absorbed oil not exceeding 1% of the waste volume in a container. The site license for the Richland, WA, LLW disposal site currently permits receipt of LLW oil for disposal. It is likely that in the near future the license for the Richland facility will require stabilization of all wastes containing >10 weight percent oil. Sorption will be acceptable for disposal of LLW containing <10 weight percent oil.

Some waste generators mix LLW oil with other wastes, such as organic laboratory liquids, degreasing solvents, and aqueous wastes, before or during packaging for disposal. Management options for potential mixed wastes have been identified in a draft report[3] prepared by BNL for NRC and issued for comment. In particular, the management options identified in that document as applicable to organic liquid wastes may be applicable to LLW oil, as well. The

destructive methods (and their degree of applicability to LLW oil) considered are incineration (applicable), acid digestion (feasible, but needs development), and wet-air oxidation (probably not feasible without further development). It should be noted that inorganic hazardous contaminants such as lead which are likely to be found in LLW oils will not be destroyed by these methods and may render the residue a RCRA hazardous waste. The immobilization methods (and their degree of applicability to LLW oil) considered are sorption (applicable), solidification (feasible but needs development), and HICs (feasible in combination with sorption or solidification). Sorption and solidification appear to be the current management practices for LLW oil. A possible one-step management option which combines destruction of the bulk of the organic components of the LLW oil with immobilization of the residue is the glass furnace process. Recovery/reclamation and segregation are other applicable management options considered in Ref. 3.

In addition to the management options for organic LLW considered in Ref. 3, three additional processes, filtration, aqueous extraction, and ozonation, which have been utilized for used oil in general may have some applicability to LLW oil. Filtration is probably the most economically advantageous of the three processes, but its success or failure, as with any processing technique, varies greatly with the properties of the waste oil. Ozonation is the most esoteric of the three processes and will need the most development to be tailored to a specific LLW oil.

Because the results of a particular processing method depend on the properties of the particular LLW oil, any proposed management scheme will have to be generic in nature, but such a scheme will likely include one or more of the following processes: filtration, immobilization, sorption, and aqueous extraction.

CONCLUSIONS

Although most LLW has only a slight potential, if any, for interaction with lead metal unless water contacts the waste, corrosion of lead could be enhanced by contact with waste forms of either vinyl ester-styrene or cement. In addition, radiolysis of cellulosics and plastics may produce organic acids corrosive to lead. Galvanic corrosion of lead pigs containing copper cyclotron targets or sealed sources may also be possible.

The EP toxicity test protocol does not adequately simulate burial conditions at any of three generic categories of disposal sites, namely, poorly drained humid-area sites (e.g., Maxey Flats, KY), well-drained humid-area sites (Barnwell, SC), and well-drained arid-area sites (Richland, WA). The use of acetic acid or acetate buffers as the leachant may not adequately simulate the ability of the dissolved organic carbon in the humid-area trench waters to dissolve or complex with lead. The conditions of the EP toxicity test do not adequately simulate the anaerobic conditions which develop at a poorly drained humid-area site nor do they simulate the intermittent wetting at a well-drained arid-area site. It is recommended that site-specific leaching test protocols

tailored to the conditions at particular LLW disposal sites be devised which would make use of soil and water samples from the site.

The use of chromates in LWRs is limited to cooling systems which are normally nonradioactive, and therefore the liquid is not processed through radwaste cleanup systems routinely. Thus chromates are, in general, not a normal or routine constituent in commercial LLW (with the possible exception of chemical decontamination wastes). It is however, recommended that individual LWRs that use chromates should determine the extent to which chromates can contaminate LLW shipped for disposal and whether this level of contamination is sufficient for the wastes to exhibit EP toxicity.

Used oil typically contains toxicants such as lead, toluene, trichloroethylene and naphthalene at levels 10^2 to 10^7 times greater than health-based standards, and therefore, has been proposed for listing as a hazardous waste by the EPA. Activities for LLW oil have been reported to range from about 10^{-7} to 10^{-5} μCi/mL in two surveys and up to 8×10^{-2} μCi/mL (with one anomalous value for one gallon of LLW oil--3.52 μCi/mL) in a third survey. The radionuclides reported in LLW oil are generally the longer-lived fission and activation products, i.e., Cs-134, Cs-137, Co-58, Co-60, Zn-65, and Mn-54. Sorption and solidification seem to be the current prevalent management practices for LLW oil, but a management scheme for LLW oil can include one or more of the following processes: incineration, filtration, immobilization, sorption, aqueous extraction, and glass furnace processing.

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