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**DEVELOPMENT OF CHEMICAL PROFILES
FOR U.S. DEPARTMENT OF ENERGY
LOW-LEVEL MIXED WASTES***

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DEVELOPMENT OF CHEMICAL PROFILES FOR U.S. DEPARTMENT OF ENERGY LOW-LEVEL MIXED WASTES

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ABSTRACT

Chemical and radiological profiles of waste streams from U.S. Department of Energy (DOE) low-level mixed wastes (LLMWs) have been developed by Argonne National Laboratory (ANL) to provide technical support information for evaluating waste management alternatives in the Office of Environmental Management Programmatic Environmental Impact Statement (EM PEIS). The chemical profiles were developed for LLMW generated from both Waste Management (WM) operations and from Environmental Restoration (ER) activities at DOE facilities. Information summarized in the 1994 DOE Mixed Waste Inventory Report (MWIR-2), the Pacific Northwest Laboratory (PNL) Automated Remedial Assessment Methodology (ARAM), and associated PNL supporting data on ER secondary waste streams that will be treated in WM treatment facilities were used as the sources for developing chemical profiles. The methodology for developing the LLMW chemical profiles is discussed, and the chemical profiles developed from data for contact-handled (CH) non-alpha LLMW are presented in this paper. The hazardous chemical composition of remote-handled (RH) LLMW and alpha LLMW follow the chemical profiles developed for CH non-alpha LLMW.

INTRODUCTION

Chemical and radiological profiles of waste streams from U.S. Department of Energy (DOE) low-level mixed wastes (LLMWs) have been developed by Argonne National Laboratory (ANL) to provide technical support information for evaluating waste management alternatives in the Office of Environmental Management Programmatic Environmental Impact Statement (EM PEIS). LLMW is material that is both a Resource Conservation and Recovery Act (RCRA)-hazardous waste and a low-level radioactive waste. DOE LLMW contains RCRA-regulated chemicals or special waste types in a form or concentration sufficient to render the waste hazardous under the guidelines of Title 40, Part 261, of the *Code of Federal Regulations* (CFR). Two major sources of LLMW in the DOE system are (1) inventory and operations-generated wastes (i.e., Waste Management [WM] LLMWs) and (2) wastes generated from site restoration or decontamination and decommissioning (D&D) of DOE facilities (i.e., Environmental Restoration [ER] LLMWs). The WM LLMWs include the LLMW currently (1994 inventory) in storage and the LLMW projected to be generated through 2013 at 43 sites. The ER LLMWs include the secondary LLMW streams expected to be generated from the treatment of contaminated soils and from the D&D of facilities at 14 DOE sites through approximately 2030.

Handling of LLMW is classified as either contact-handled (CH) for waste with a dose-at-waste surface <200 mrem/h or remote handled (RH) for waste with a dose-at-waste surface >200 mrem/h. The handling category determines the level of protective shielding required

to safely store and process the material. LLMW is also classified as either alpha LLMW or non-alpha LLMW. The alpha LLMWs have combined activities from transuranic (TRU) radionuclides with half-lives greater than 20 years (between 10-100 nCi/g). The non-alpha LLMWs have TRU activities < 10 nCi/g. Radiological profiles for DOE LLMW have been developed and are described in a separate paper prepared by Wilkins et al. (1). Currently, the four radioactivity classifications — CH non-alpha LLMW, CH alpha LLMW, RH non-alpha LLMW, and RH alpha LLMW — determine the handling and routing for treatment and/or disposal of all LLMW.

WASTE STREAM CATEGORIES FOR LLMW

The most nearly complete information available on LLMW is contained in the recent update of the Mixed Waste Inventory Report database (2). This database is referred to as MWIR-2 in the EM PEIS and identifies the types of chemicals in over 2,000 waste streams of LLMW from major DOE installations. The LLMWs are grouped into nine major waste types: aqueous waste, organic liquids, solid process residues, soils, debris waste, special waste, inherently hazardous waste, unknown, and treated waste. In MWIR-2, these 2000+ waste streams within the nine major waste types are further condensed into 109 waste stream treatment codes on the basis of their physical-chemical characteristics. Many of these 109 waste stream treatment codes have similar physical-chemical compositions so that the waste streams can be treated with the same technologies to reduce or stabilize the toxic materials within the waste. For the EM PEIS, the 109 waste treatment codes have been further condensed into 32 treatment categories; the first 23 treatment categories constitute more than 90% of all LLMW. A baseline treatment flowchart for LLMW management has been developed by the Mixed Waste Treatment Project (3) to discuss the treatment technologies required for reducing or stabilizing toxic materials in these first 23 treatment categories. Descriptions of hazardous components in these 23 treatment categories are summarized in Table I.

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HAZARDOUS CHEMICAL CONSTITUENTS FOR LLMW

Detailed chemical analyses of the RCRA-hazardous constituents in LLMW are available for only a limited number of LLMW streams. In MWIR-2, only about 5-10% of the 2,000+ waste streams contain quantitative data on chemical composition. Much of the information on the hazardous chemical composition of LLMW is derived from site-specific (process) operational knowledge. The composition and concentration of RCRA-hazardous chemical constituents for the first 23 waste treatment categories of CH non-alpha WM LLMW were estimated from (1) compilation of the chemical data presented in MWIR-2 and (2) an engineering assessment of the industrial processes that generated the respective LLMW streams. In the EM PEIS, chemical profiles for alpha LLMW were not developed separately because of the relatively small volume compared with non-alpha LLMW.

Hazardous chemical constituents for ER-derived LLMW have been developed on the basis of chemical concentrations for specific secondary waste streams outlined in the Automated

Remedial Assessment Methodology (ARAM) database developed by Pacific Northwest Laboratory (4), as well as engineering estimates of the sources of LLMW generation. The ARAM was developed for the purpose of estimating the effects of different ER cleanup strategies on waste volumes, cost, labor, and reduction of public risk (4). In the ARAM database, the ER waste volumes are estimated on the basis of semirestricted ER alternatives. The chemical concentrations of secondary wastes are estimated from the measured concentrations of primary wastes; these secondary waste streams will be shipped to waste management facilities for treatment. It is assumed that ER wastes will be shipped to WM treatment facilities in two forms: pretreated, awaiting final treatment at WM facilities, and fully treated, awaiting final disposal. Two additional assumptions have been included in the ARAM LLMW estimates. First, radioactive, friable-asbestos-contaminated waste is included as an ER LLMW. Substantial amounts of ER friable-asbestos-contaminated radioactive waste are expected from ARAM results for the D&D of DOE facilities. Second, inadequate information exists for ARAM to distinguish between low-level waste (LLW) and LLMW during the D&D of DOE facilities. For the EM PEIS, it is estimated that 9% of the D&D waste listed as LLW in the ARAM results will be LLMW. The ARAM estimates are available for 14 major DOE sites for only 4 waste stream categories. The chemical profiles for ER-derived alpha LLMW and RH LLMW follow the profiles developed for the equivalent ER-derived CH non-alpha LLMW. Information about historical DOE site operations and industrial processes, as well as MWIR information, suggest that the waste streams of a given treatment category from different sites in the DOE complex are similar in chemical composition.

Currently, over 100 individual chemical species are identified in the MWIR-2 and ARAM databases; many of these species are either present in minute quantities, limited to only a few waste streams, or not regulated as RCRA-hazardous chemicals. To provide a consistent assessment of chemicals that is comparable across waste treatment categories, the chemical profiles developed are condensed into 16 distinct chemicals and/or grouped into classes of chemicals that are common to most waste streams. These include six toxic metals, three inorganic chemicals, and seven classes of organic chemicals that are grouped according to important treatment parameters such as density, solubility, volatility, and degree of chlorination.

Table II presents chemical profiles for WM LLMW. Chemical profiles for ER LLMW are provided in Table III.

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DISCUSSION

The WM LLMW database in MWIR-2 and the ER LLMW database in the ARAM do not provide sufficient quantitative chemical characterization of LLMW streams. Several assumptions have been made to utilize the information provided in these databases, and these assumptions introduce uncertainties into the LLMW chemical profiles. A 10%

reduction factor was used to convert gross waste volume to net LLMW volumes based on estimates from typical industrial waste filling practice. The estimated LLMW volumes and the ratio of specific waste stream volume to total waste volume estimated for each waste category were used to determine major waste streams and major contaminants under each waste category. The accuracy of the reduction factor used might result in uncertainty in the presence of contaminant in a particular waste category. The estimations of future waste generation volumes in these databases lead to uncertainties in developing the chemical profiles. At some DOE sites, the future waste generation rates are only projected to a single year, or to 5 or 10 years. The 20-year projection is estimated by assuming that the most recent generation rate will be continued for the remainder of the 20 years. Additional uncertainties might be introduced regarding the possible changes of future waste-generating operations. The assumption that chemical profiles are waste-stream-specific is made because insufficient data are available to develop site-specific chemical profiles. There is no justification for this assumption, and the true chemical profiles may vary from site to site. Limiting the chemical profiles to 16 chemicals may overlook an important chemical contaminant that appears only in minute quantities in the database but may be present in large quantities in a poorly characterized waste stream. Such an oversight can lead to significant errors when the developed chemical profiles are applied to estimate emissions generated from various treatment processes.

The chemical profiles developed for DOE LLMW are useful for the following tasks: (1) proposing appropriate treatment technologies for waste management and (2) estimating secondary wastes and emissions generated from various waste treatment processes. Currently, the lack of quantitative waste stream information makes the development of chemical profiles very difficult. Existing information is made useful on the basis of several assumptions; however, the uncertainties introduced by these assumptions cannot be accurately assessed with currently available data.

REFERENCES

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3. T.K. THOMPSON, "Mixed Waste Treatment Project: Functional and Operational Requirements for an Integrated Facility," prepared for Los Alamos National Laboratory, Albuquerque, N.M. (1992).
4. PACIFIC NORTHWEST LABORATORY, "Methodology for Selecting Technologies and Estimating Waste Volumes, Costs, and Labor Requirements for Environmental Restoration," Draft, Richland, Wash. (1994).

TABLE I Waste Matrices for DOE Mixed Low-Level Waste

Waste Matrix	EM PEIS Treatment Category	Waste Description
Aqueous liquids wastewater	1	Wastewaters containing less than 1% total solids (TS) and 1% organic material; acidic wastewaters with pH<2.0; basic wastewaters with pH>12.5; neutral wastewaters with 2.0<pH<12.5; and cyanide wastewaters.
Aqueous waste	2	Aqueous slurries containing dissolved and particulate material ~15%; acidic aqueous slurries with pH<2.0; basic aqueous slurries with pH>12.5; neutral aqueous slurries with 2.0<pH<12.5; and cyanide aqueous slurries.
Organic liquids	3	Aqueous halogenated organic liquids contain up to 50% water and at least 1,000 parts per million (ppm) halogenated compounds (HOCs).
	4	Aqueous nonhalogenated organic liquids contain up to 50% water and less than 1,000 ppm HOCs and a wide variety of organic solvents (acetone, methanol, etc).
	5	Halogenated organic liquids contain at least 1,000 ppm HOCs and less than 5% water.
	6	Nonhalogenated organic liquids contain less than 1,000 ppm HOCs and less than 5% water, dominated by organic solvents (toluene, benzene, etc.).
Solid process residues	7	Organic particulates, including residual or absorbed liquids, incinerator ash, dust, sand blasting residue, vermiculite, aluminum oxides, paint wastes, iron fines, and ion-exchange media.
	8	Inorganic sludges, including wastewater treatment sludges, pond sludges, off-gas treatment sludges, plating waste sludges, and reprocessing sludges.
	9	Salt wastes generated from evaporation bottoms, solids oxidizers, reactive salts, including chloride salts, sulfate salts, and nitrate salts.
	10	Solidified inorganic process residues that do not meet disposal criteria; e.g., cemented pond sludge, cemented fly ash.
	11	Nonhalogenated organic particulates and sludges contain less than 1,000 ppm HOCs; e.g., activated-carbon floor sweepings and oily sludges.
	12	Halogenated organic particulates and sludges contain at least 1,000 ppm HOCs; e.g., Freon sludge, grease cleaner sludges, and solids with absorbed solvents.
	13	Nonhalogenated solid organic chemicals contain less than 1,000 ppm HOCs, such as plastic or epoxy wastes. These wastes are packaged in bulk form and are either being excessed or have been expired.

TABLE I (Cont.)

Waste Matrix	EM PEIS Treatment Category	Waste Description
Solid process residues (cont.)	14	Halogenated solid organic chemicals contain at least 1,000 ppm HOCs. Treatment code 14 has been combined with treatment code 13 for this analysis.
	15	Contaminated soils without debris that is greater than approximately 95% by volume soil and rock, including contamination from spills, etc.
	16	Contaminated soils with debris that is at least 50% by volume soil and at least 5% by volume other debris, not including rock.
Debris waste	17	Metal debris includes metal debris without lead (Pb) or cadmium (Cd), lead-containing metal debris, and cadmium-containing metal debris; e.g., scrap metals, Cd-coated high efficiency particulate air (HEPA) filters, piping, and machine tools.
	18	Inorganic nonmetal debris includes concrete debris, glass debris, ceramic/brick debris, rock debris, and asbestos debris.
	19	Combustible debris includes materials constructed of plastic, rubber, wood, paper, cloth, and graphite and biological materials; e.g., rubber gloves, rags, plastic bags, and Teflon.
	20	Heterogeneous debris includes composite filters, metal debris, mercury-contaminated debris, inorganic nonmetal debris, combustible debris, asphalt debris, and laboratory equipment.
Special waste	21	Liquid organic lab packs and scintillation cocktails.
	22	Lab packs that contain aqueous liquids or aqueous scintillation fluids packaged in vials.
	23	Lab packs of only solid chemicals or other solid materials.

Source: Reference 2.

TABLE II. Chemical Profiles for WM LLMW (mg/kg)

Contaminant (mg/kg)	EM PEIS Waste Treatment Category										
	1	2	3	4	5	6	7	8	9	10	11
Arsenic	2.4	1.4	11	- ^a	-	7.7	8.3	25	3	-	-
Barium	220	1.0	75	-	-	33	260	2,000	1,650	-	-
Cadmium	8.9	17	-	4.9	1,100	1,100	120	40	-	22	60
Chromium	390	34	-	210	960	920	450	2,300	860	3,000	20
Lead	110	65	27	50	210	210	200	2,700	76	2	36
Mercury	0.2	0.23	220	280	6.3	6.0	135	790	-	7	39
Selenium	6	.5	37	40	-	-	36	340	-	-	1
Silver	10	1.6	44	44	-	-	10	70	8	-	11
Cyanides	50	45	-	180	-	-	-	150	-	-	-
Acetone, butanone, methanol	55,000	50	390	360,000	6,400	140,000	20,000	5,000	-	11	10,000
Toluene, xylene, benzene	.6	11	1,500	11,000	330	440,000	40,000	10,000	-	37	5,000
Trichloroethanes, etc.	21	63	13,800	800	121,000	7,500	12,000	2,200	120	97	160
Tetrachloroethane, etc.	60	59	780	45	27,000	1,600	2,200	20	-	150	1,200
Dichloroethanes, etc.	10	50	370	-	850	500	200	80	-	4	40
Methylene chloride	10	10	130	-	1,600	960	200	80	-	4	40
Chlorofluoro-hydrocarbons	5	5	300	-	50	-	90	90	-	63	20
EM PEIS Waste Treatment Category											
Contaminant (mg/kg)	12	(13,14)	15	16	17	18	19	20	21 ^b	22	23
Arsenic	-	-	5	5	1.7	-	-	10	-	-	-
Barium	-	-	15	15	-	1,000	400	2,000	-	-	-
Cadmium	60	2.7	3	3	300	1	2	5	-	1.6	5
Chromium	20	-	20	20	1,500	4	15	2,000	-	20	5
Lead	36	7.7	40	40	10,000	10	100	5,000	-	12	5
Mercury	39	-	5	5	250	200	2	100	-	-	5
Selenium	1	-	1.5	-	20	-	3	30	-	-	-
Silver	11	-	10	10	-	-	10	30	-	100	5
Cyanides	-	-	-	-	-	-	-	170	-	-	-
Acetone, butanone, methanol ^c	2,500	230	10	10	5	-	5	50	120,000	-	5
Toluene, xylene, benzene ^c	5,000	430	10	10	100	-	10,000	1,000	250,000	-	-
Trichloroethanes, etc. ^c	2,500	32	10	10	2,000	4	2,500	560	100,000	-	10
Tetrachloroethane, etc. ^c	19,000	15	7	7	1,200	-	1,200	350	80,000	-	-
Dichloroethanes, etc. ^c	600	51	-	-	400	-	700	200	10,000	-	-
Methylene chloride	600	-	-	-	1,200	-	600	200	20,000	10	-
Chlorofluoro-hydrocarbons ^c	300	-	-	-	500	-	1,000	100	-	-	-

^a A hyphen indicates no measured concentration.

^b Concentration in mg/kg within the organic liquid portion of the combined waste stream.

^c Concentration is the total for all organic compounds within the group.

TABLE III. Chemical Profiles for ER LLMW (mg/kg)

Contaminant (mg/kg)	Waste Stream Category			
	Aqueous Waste	Solid Process Residue	Debris Waste	Treated Waste
Arsenic	25	100	400	12
Barium	700	- ^a	1,000	75
Cadmium	60	-	50	3
Chromium	10	1,300	100	11
Lead	1,00	-	4,500	290
Mercury	450	150	225	1
Selenium	10	0.6	9	0.5
Silver	3	15	13	0.7
Cyanides	-	11	40	-
Acetone, butanone, methanol	0.1	10,000	20	-
Toluene, xylene, benzene	-	1,600	1,000	-
Trichloroethanes, etc.	1	5,700	1	0.1
Tetrachloroethane, etc.	0.1	800	3	-
Dichloroethanes, etc.	-	90	22	-
Chlorofluoro-hydrocarbons	-	2	0.2	-

^a A hyphen indicates no measured concentration.